Contents

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Double exchange model and the unique properties of the manganites

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1. Introduction		109
		107
1.1 Basic physical p	properties of the manganites; 1.2 Electron models	
2. Effective Hamilt	tonian of the DE model	112
2.1 Derivation of th	ne Hamiltonian for a system of classical spins; 2.2 Quantum spin	
3. Properties of the DE model in the dynamical mean field approximation		114
3.1 Dynamical mea	n field approximation in the classical spin model; 3.2 Analysis of Furukawa's numerical solutions;	
3.3 Relation betwe	en $T_{\rm C}$ and the average kinetic energy; 3.4 A simplified double exchange model; 3.5 The coherent	
potential method; 3	3.6 Variational approach in the mean field approximation	
4. Phase diagram of the model		123
4.1 Monte Carlo ca	alculations; 4.2 Inclusion of direct antiferromagnetic exchange; 4.3 Experimental studies of phase	
separation in mang	anites	
5. Orbital degenera	acy in the double exchange model	126
5.1 Electronic spect	trum and the phase diagram; 5.2 Comparison with experiment	
6. Effects of electro	on – lattice interaction	128
6.1 Interaction of e	g electrons with lattice vibrations; 6.2 The dynamical mean field approximation to the DE model	
with lattice interact	ion; 6.3 Comparison of the theory and experiment	
7. Open problems i	n the physics of manganites	131
7.1 Metal-insulate	or transition; 7.2 Charge ordering	
8. Conclusions		132
References		133

Abstract. In this review the double exchange (DE) model forming a basis for the description of the physics of colossal magnetoresistance manganites is discussed. For a limiting case of exchange interaction which is large compared with the band width, the effective Hamiltonian of the DE model is derived from that of the sd-exchange model. Since this Hamiltonian is very complicated, the dynamical mean field approximation, successful for other strongly correlated systems, is found to be more suitable for describing the model of interest. Two simplified versions of the DE model, both capable of accounting for a wide range of physical properties, are proposed - one using classical localized spins and the other involving quantum spins but no transverse spin fluctuations. A temperature-electron concentration phase diagram for a system with consideration for the domain of phase separation is constructed, whose basic features are shown to be in qualitative agreement with experimental data for the manganites, as also are the temperature and electron concentration dependences of their electrical resistiv-

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Received 7 August 2000 Uspekhi Fizicheskikh Nauk **171** (2) 121–148 (2001) Translated by E G Strel'chenko; edited by A Radzig ity, magnetization, and spectral characteristics. At the quantitative level, introducing additional electron – lattice interaction yields a good agreement. A number of yet unresolved problems in the physics of manganites, including the mechanism of temperature- or doping-induced metal – insulator phase transition and the nature of charge ordering, are also discussed. By comparing predictions made by computing approach with the experimental data, the adequacy of the DE model is assessed and its drawbacks are analyzed. Numerous recent theoretical studies of the unique properties of this broad class of strongly correlated systems are summarized in this review.

1. Introduction

1.1 Basic physical properties of the manganites

Following the high- T_c copper oxide superconductors, another class of transition metal oxides, the manganites, have prompted an explosion of research activity in the last decade. Of most interest among these are compounds of the type La_{1-x}A_xMnO₃, where *A* denotes a bivalent atom in the sequence Ca, Sr, Ba, etc., and *x* is its concentration varying over a wide range $0 \le x \le 1$. Changing *x* affects the properties of the manganites dramatically, causing a chain of phase transitions and producing various types of ordering in the system, such as magnetic, structural, and electronic ordering.

Among the unique properties discovered in the manganites about 50 years ago (see Ref. [1] for a review), the colossal magnetoresistance (CMR) is particularly noteworthy. This



Figure 1. Typical resistivity and magnetoresistance curves for manganites. The data are taken from Ref. [1].

effect is seen within the x range where the metal ferromagnetic phase exists, and manifests itself in that the resistivity ρ of the material changes (decreases) when a magnetic field is applied. The size of the effect, $\Delta \rho / \rho$, may be as high as tens of percent in fields of order 1 T and has a maximum around the Curie temperature T_C (Fig. 1). It is just this effect which — because of its potential for engineering applications — attracted the attention of investigators in the early 1990s, but on the other hand the physical properties exhibited by the manganites are so rich and diverse that this fact alone is attracting intense experimental and theoretical interest.

Another remarkable property of the manganites is the appearance of a metal ferromagnetic phase in a certain concentration range around $x \approx 0.3$. (Fig. 2) The parent compound LaMnO₃ constitutes an antiferromagnetic insulator with a magnetic structure of type A (Fig. 3). Substituting calcium for lanthanum turns the system into a ferromagnetic metal and for x > 0.5 it again becomes an antiferromagnetic insulator with a magnetic structure of type G in the final compound CaMnO₃, and of type C in the intermediate concentration region. The magnetic structures of the A, C, and G types make up two-sublattice antiferromagnets. From Fig. 3 it is seen that the A, C, and G structures are arrays of ferromagnetic {100}, {110}, and {111} planes alternating in their mutual spin orientations in neighboring planes. Note, though, that this magnetic scheme is a simplified one which will be revised and improved later in this paper.



Figure 2. Magnetic phase diagram of $La_{1-x}Ca_xMnO_3$ [2]. Vertical axes show: magnetization *M* (left) and the logarithm of the conductivity σ at T = 80 K (right). F is a ferromagnetic phase, A, C, and G are antiferromagnetic phases.



Figure 3. (a) The crystal structure of the manganites: filled circles at the cube corners, La; the circle at the center, Mn, and open circles, O. (b) The magnetic structure of the manganites: filled and open circles denote oppositely directed spins.



Figure 4. Temperature dependence of the resistivity of $La_{1-x}Sr_xMnO_3$ for various Sr concentrations [3].

As the temperature increases, the ferromagnetic phase is replaced by the paramagnetic phase, with the conductivity of the latter being sharply decreased. The temperature behavior of electrical resistivity depends strongly on the concentration of the dopant (Fig. 4). A characteristic feature of these curves is the point T_0 , where CMR has a maximum (point T_0 lies in the neighborhood of T_C). As the temperature decreases from T_0 , $d\rho/dT > 0$ is observed, corresponding to the metal phase, whereas above T_0 we have $d\rho/dT < 0$. This behavior of $\rho(T)$ is typical of the manganites, indicating that the appearance of a metallic state due to the transition through the Curie point is closely related to the CMR effect.

A comprehensive recent review of the experimental work on manganites is presented in Ref. [1], which acquaints the reader with all the physical properties of these compounds and how they depend on the chemical composition. As to the theoretical studies, although their number is growing at an ever increasing rate, no exhaustive review of the existing approaches has yet been attempted. In the next section, the available theories and results are briefly surveyed, and in the remaining sections a detailed discussion is given.

1.2 Electron models

The La_{1-x}Ca_xMnO₃ type oxides can be considered as mixedvalence solid-solution compounds formed by LaMnO₃ and CaMnO₃ with La³⁺Mn³⁺O₃²⁻ and Ca²⁺Mn⁴⁺O₃²⁻ ion valence states, respectively. The intermediate state has a valence structure (La_{1-x}³⁺Ca_x²⁺)(Mn_{1-x}³⁺Mn_x⁴⁺)O₃ containing trivalent (3d⁴) and tetravalent (3d³) manganese ions. Thus, doping a parent compound LaMnO₃ with a bivalent element at concentration x produces an equal amount of holes in the 3d band of the material (for x < 0.5). For x > 0.5, the compound can be treated as the parent compound CaMnO₃ doped with electrons of concentration 1 - x. Thus we see that 3d-band holes or electrons compose charge carriers in mixed valence manganites.

The occurrence of the metal ferromagnetic phase in manganites was explained back in 1951 by Zener [4] based on the assumption of a strong intraatomic exchange interaction between a localized spin and a delocalized electron. Because of this coupling, the electron spin always aligns parallel to that of the ion. If ion spins are all aligned in a single direction, an electron can move freely from one lattice site to another, thus reducing the total energy of the system. By this means the ferromagnetic state in this case does not result from the usual ion-ion exchange interaction but rather is due to a kinetic effect. This mechanism of ferromagnetic ordering was called the double exchange — a well established, if not entirely satisfactory term reflecting the fact that the ferromagnetic coupling between the spins of two neighboring Mn ions has its origin in the double transition $Mn \mathop{\rightarrow} O \mathop{\rightarrow} Mn$ an electron performs via an intermediate O ion. Double exchange is a correlation type effect, and the manganites therefore belong to the class of highly correlated electron systems. We will mainly rely on the double exchange concept in briefly outlining the theory of the manganites below.

The double exchange (DE) model is characterized by the Hamiltonian

$$H = -\sum_{ij\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} - J_{\rm H} \sum_{i} \mathbf{S}_{i} \cdot \mathbf{s}_{i} , \qquad (1.1)$$

where the first term describes the motion of an electron over the lattice sites *i*, *j* with spin σ , and the second term accounts for the Hund exchange coupling, it being assumed that $J_{\rm H} \ge zt$, where *z* is the number of the nearest neighbors. Here, S_i is the localized ion spin, and s_i is the conduction electron spin which, in terms of the electron creation and annihilation operators, can be written in the following way

$$\mathbf{s}_{i} = \frac{1}{2} \sum_{\sigma\sigma'} a_{i\sigma}^{\dagger} \mathbf{\sigma}_{\sigma\sigma'} a_{i\sigma'} , \qquad (1.2)$$

where the vector $\boldsymbol{\sigma}$ is composed of Pauli matrices.

Thus, the DE model constitutes an sd-exchange model valid under the strong coupling condition: $J_{\rm H} \ge zt$. In this situation one should employ the small parameter $zt/J_{\rm H}$ and go over to an effective Hamiltonian. In the limit $J_{\rm H} \rightarrow \infty$, the low-energy physics of the system is described by the

Hamiltonian [5, 6]

$$H = -\sum_{ij\sigma} t_{ij}(\theta_{ij})\tilde{c}_i^{\dagger}\tilde{c}_j.$$
(1.3)

Here, \tilde{c}_i and \tilde{c}_i^{\dagger} are spinless fermion operators (see below), and $t_{ij}(\theta_{ij})$ is the effective matrix element for the electron hopping (jump) between nearest-neighbor lattice sites, whose value depends on the angle θ_{ij} between ion spins at the two sites involved. As Anderson and Hasegawa [5] have shown for the problem of two classical spins, the following relation holds:

$$t(\theta) = t\cos\frac{\theta}{2}.$$
 (1.4)

An extension of this result to a spin lattice was given by de Gennes [6].

To describe real manganites, a term must be added to the Hamiltonian (1.3) accounting for the indirect — via oxygen ions — antiferromagnetic exchange interaction between the localized spins of the Mn ions. The Hamiltonian then describes the competition between the ferromagnetic and antiferromagnetic trends in the system. De Gennes [6], using the mean field approximation, charted a magnetic phase diagram for the model at (T, n) surface (*n* being the electron concentration) and showed that in different parts of the pattern there exist four phases — the paramagnetic, ferromagnetic, antiferromagnetic, and canted — of which the latter is a two-sublattice magnetic structure with an uncompensated spontaneous moment.

The above result came under criticism long ago [7, 8], however. Essentially, it was realized that de Gennes spatially homogeneous phases can, under certain conditions, be less favorable energetically than inhomogeneous phases presenting, for example, an antiferromagnetic matrix containing finely divided antiferromagnetic domains. The energy gain in this case results from the redistribution of charge carriers: antiferromagnetic regions are depleted of charges which instead move to ferromagnetic regions and serve to reduce the kinetic energy of the carriers there. This 'phase separation' phenomenon appears to be inherent in the theory of strongly correlated systems: it has already been studied within the Hubbard and tJ models and, experimentally, in cuprates. It should be noted that in structural experiments the inhomogeneous phase we have described above (i.e. the antiferromagnetic structure with ferromagnetic inclusions) may behave as a canted structure, so that interpreting experimental data requires a detailed knowledge of the phase separation phenomenon, which is a key problem in the theory of manganites.

Since one of the possible varieties of the inhomogeneous phase in a manganite presents an antiferromagnetic dielectric matrix with ferromagnetic inclusions containing charge carriers, it follows that increasing the carrier concentration enhances the density of these inclusions, and the system may transform into a metal state in the percolation limit. Thus, the insulator-metal phase transition and the phase separation phenomenon are closely related effects in the manganites [9].

The DE model became the key operative model for studying the properties of the manganites. To be able to compare in quantitative terms the theory and experiment, methods for working with the Hamiltonian (1.1) not only under strong coupling, but also under intermediate, $J_{\rm H} \simeq zt$, conditions had to be developed. Because in the latter case no small parameter is available, the dynamical mean field (DMF) approximation, which is effective in the theory of strongly correlated systems [10], had to be employed. Furukawa [11] developed this approach for the Hamiltonian (1.1) in the classical spin approximation for ions. The variation of the Curie temperature with the electron concentration and the dependence of electrical resistivity and magnetoresistivity on temperature and other model parameters were computed numerically and found to compare well with the observed properties of the manganites [12].

Millis et al. [13] argued against the DE model as the basic theory for the manganites, having shown, in particular, that its predictions for $T_{\rm C}$ and resistivity are an order of magnitude too high and too low, respectively. To explain the physical properties of the manganites it was proposed to include the lattice degrees of freedom and, in particular, to allow for the possibility that the cubic lattice may be distorted locally due to the Jahn-Teller effect on manganese ions. Paper [13] stimulated intense research activity along these lines. The shortcoming of the DE model has also been recently pointed out in Ref. [14]. On the other hand, Narimanov and Varma [15], combining the mean field approximation with a variational approach developed by themselves, argue that the DE model alone can quantitatively account for the observed properties of the manganites. Considering the controversy over what the DE model can and cannot do, Monte Carlo studies of the Hamiltonian (1.1) using the exact small cluster diagonalization procedure have become critical. The temperature – concentration phase diagram obtained in this way for the DE model agrees reasonably well with the experimental data [16].

There is, however, one important aspect which is left out of account in the Hamiltonian (1.1) as a tool for describing the manganites — the degeneracy of electronic states. In the cubically symmetric field of its oxygen environment, the fivefold degenerate 3d-level of the Mn ion splits into two levels: the three-fold degenerate t_g level and the two-fold degenerate e_g level. Owing to the Hund coupling, the three electrons at the t_g level form a localized ion spin S = 3/2, whereas the e_g electron is itinerant. It is these e_g states which should be treated as itinerant in the model (1.1). A new approach to the theory of the manganites, one allowing for the orbital degeneracy, was pioneered in Refs [17, 19].

While experimental data on the manganites have been reviewed in considerable detail in Ref. [1] (and earlier in Ref. [18]), no monograph has yet been devoted to theoretical work on these materials. To the authors' knowledge, only four theoretical reviews are currently available, each of which briefly discusses only one particular aspect of the theory of the manganites: the semiconductor aspect [8], the dynamical mean field approximation [12], the transport properties and the metal–insulator phase transition from the percolation theory viewpoint [9], and charge ordering and the structure of inhomogeneous phases [20].

The purpose of the present paper is to discuss as fully as possible the theory of the physical properties concerning manganites. The basic aspect of this theory is the double exchange model, and because its Hamiltonian is very complicated, it is essential that all possible approaches to its treatment be tried and the results of their application compared.

2. Effective Hamiltonian of the DE model

2.1 Derivation of the Hamiltonian for a system of classical spins

As indicated above, the DE model presents a limiting case of the sd-exchange model subject to the conditions of strong Hund coupling, $J_{\rm H} \ge zt$. To obtain an effective Hamiltonian of the DE model, the initial Hamiltonian (1.1) must be projected onto the lower eigenvalue subspace of the exchange Hamiltonian

$$H_{\rm ex} = -J_{\rm H} \sum_{i} \mathbf{S}_i \cdot \mathbf{s}_i \,. \tag{2.1}$$

It is readily seen that this Hamiltonian has two eigenvalues

$$-J_{\rm H}N\left[S_T(S_T+1) - S(S+1) - \frac{3}{4}\right]$$

= $-J_{\rm H}N\left\{\begin{array}{cc} S, & S_T = S + \frac{1}{2}, \\ -S - 1, & S_T = S - \frac{1}{2}. \end{array}\right.$ (2.2)

Here, *N* is the number of lattice sites and S_T is the total spin at a site, formed by the localized ion spin plus the spin of the collective electron. Clearly, for $J_H > 0$ each electron in the ground state has its spin aligned parallel to the localized one.

We carry out the projection procedure for classical spins first. Let θ_i and ϕ_i be the polar and azimuth angles of the classical spin vector **S** defined for each lattice site; then one obtains

$$\begin{cases} S_i^x = S \sin \theta_i \cos \phi_i , \\ S_i^y = S \sin \theta_i \sin \phi_i , \\ S_i^z = S \cos \theta_i . \end{cases}$$
(2.3)

The scalar product $S_i \cdot \sigma$ can now be rewritten in the form of a two-row matrix defined in electron spin space:

$$\mathbf{S}_i \cdot \mathbf{\sigma} = \begin{pmatrix} S_i^z & S_i^- \\ S_i^+ & -S_i^z \end{pmatrix},\tag{2.4}$$

where $S_i^{\pm} = S_i^x \pm i S_i^y$.

The matrix (2.4) has the eigenvalues $\lambda_{1,2} = \pm S$ and the eigenvectors

$$\mathbf{e}_{1} = \begin{pmatrix} \cos\frac{\theta_{i}}{2} \\ \sin\frac{\theta_{i}}{2}\exp(\mathrm{i}\phi_{i}) \end{pmatrix}, \quad \mathbf{e}_{2} = \begin{pmatrix} -\sin\frac{\theta_{i}}{2}\exp(-\mathrm{i}\phi_{i}) \\ \cos\frac{\theta_{i}}{2} \end{pmatrix}.$$
(2.5)

From these we can construct the matrix

$$R_{i} = \begin{pmatrix} \cos \frac{\theta_{i}}{2} & -\sin \frac{\theta_{i}}{2} \exp(-i\phi_{i}) \\ \sin \frac{\theta_{i}}{2} \exp(i\phi_{i}) & \cos \frac{\theta_{i}}{2} \end{pmatrix}$$
(2.6)

determining a rotation in the spin space. In a similar fashion we define the matrix R_i^+ ($R_i^+R_i = \hat{I}$, where \hat{I} is the identity matrix). Notice that the matrix (2.4) is diagonalized by letting the matrices R_i^+ and R_i act on it from the left and from the right, respectively.

Let us apply the matrices R_i and R_i^+ to transform the initial Hamiltonian (1.1). For this purpose we first introduce the new Fermi operators

$$\begin{pmatrix} d_{i\uparrow} \\ d_{i\downarrow} \end{pmatrix} = R_i^+ \begin{pmatrix} a_{i\uparrow} \\ a_{i\downarrow} \end{pmatrix}$$

$$= \begin{pmatrix} \cos\frac{\theta_i}{2} a_{i\uparrow} + \sin\frac{\theta_i}{2} \exp(-i\phi_i) a_{i\downarrow} \\ -\sin\frac{\theta_i}{2} \exp(i\phi_i) a_{i\uparrow} + \cos\frac{\theta_i}{2} a_{i\downarrow} \end{pmatrix},$$
(2.7)

$$\begin{pmatrix} d_{i\uparrow}^{\dagger} d_{i\downarrow}^{\dagger} \end{pmatrix} = \begin{pmatrix} a_{i\uparrow}^{\dagger} a_{i\downarrow}^{\dagger} \end{pmatrix} R_{i} = \begin{pmatrix} a_{i\uparrow}^{\dagger} \cos \frac{\theta_{i}}{2} + a_{i\downarrow}^{\dagger} \sin \frac{\theta_{i}}{2} \exp(i\phi_{i}), \\ -a_{i\uparrow}^{\dagger} \sin \frac{\theta_{i}}{2} \exp(-i\phi_{i}) + a_{i\downarrow}^{\dagger} \cos \frac{\theta_{i}}{2} \end{pmatrix}.$$
(2.8)

The exchange Hamiltonian (2.1) then takes the diagonal form

$$H_0 = J_{\rm H} S \sum_{i\sigma} \sigma d_{i\sigma}^{\dagger} d_{i\sigma} \qquad (\sigma = \pm 1) \,. \tag{2.9}$$

In terms of the new operators, the hopping part of the Hamiltonian may be rewritten as

$$H_t = -\sum_{ij\sigma} t_{ij} a_{i\sigma}^{\dagger} a_{j\sigma} = -\sum_{ij\sigma\sigma'} t_{ij} d_{i\sigma}^{\dagger} (R_i^+ R_j)_{\sigma\sigma'} d_{j\sigma'} .$$
(2.10)

Now since we are concerned with the case $J_{\rm H} \rightarrow \infty$, the spin of the electron must be parallel to the localized spin, implying that the only term to be retained in H_i is the $\uparrow\uparrow$ matrix element of the operator $(R_i^+R_i)$:

$$(R_i^+ R_j)_{\uparrow\uparrow} = \cos\frac{\theta_i}{2}\cos\frac{\theta_j}{2} + \sin\frac{\theta_i}{2}\sin\frac{\theta_j}{2}\exp\left[-\mathrm{i}(\phi_i - \phi_j)\right].$$
(2.11)

It is convenient at this point to introduce the 'zero-spin' operators

$$c_i \equiv d_{i\uparrow} = \cos\frac{\theta_i}{2} a_{i\uparrow} + \sin\frac{\theta_i}{2} \exp(-\mathrm{i}\phi_i) a_{i\downarrow}, \qquad (2.12)$$

in terms of which the hopping part of the Hamiltonian can be written as

$$H_t = -\sum_{ij} \tilde{t}_{ij} c_i^{\dagger} c_j \,, \tag{2.13}$$

where

$$t_{ij} = t_{ij} (\mathbf{R}_i^+ \mathbf{R}_j)_{\uparrow\uparrow}$$

$$\equiv t_{ij} \left(\cos \frac{\theta_i}{2} \cos \frac{\theta_j}{2} + \sin \frac{\theta_i}{2} \sin \frac{\theta_j}{2} \exp\left[-i(\phi_i - \phi_j)\right] \right) (2.14)$$

is the effective matrix element for electron hopping from one site to another. Separating the real from the imaginary part in Eqn (2.14) yields the following two equivalent expressions for the matrix element of interest:

$$\tilde{t}_{ij} = t_{ij} \sqrt{\frac{1}{2} \left\{ 1 + \frac{\mathbf{S}_i \cdot \mathbf{S}_j}{S^2} \right\}} \exp\left(-\frac{\mathrm{i}\omega_{ij}}{2}\right)$$
$$\equiv t_{ij} \cos\frac{\theta_{ij}}{2} \exp\left(-\frac{\mathrm{i}\omega_{ij}}{2}\right). \tag{2.15}$$

Here, the angle θ_{ij} is formed by two spins localized at sites *i* and *j*, and the function ω_{ij} is known as the Berry phase [21, 22].

The Berry phase is usually ignored, giving

$$\tilde{t}_{ij} = t_{ij} \cos \frac{\theta_{ij}}{2} , \qquad (2.16)$$

which is equivalent to Eqn (1.4). A recently elaborated theory [23] of the anomalous Hall effect in the manganites showed that carriers moving in a *topologically nontrivial* spin environment acquire a Berry phase which ultimately provides a qualitative explanation for the observed temperature dependence of the anomalous Hall coefficient.

2.2 Quantum spin

The matrix element for effective hopping between two neighboring sites was calculated by Anderson and Hasegawa [5] for both classical and quantum spins. The classical result has been mentioned earlier. For quantum spins, the exchange Hamiltonian is diagonalized using the eigenfunctions of the spin operators and the technique of Clebsch–Gordan coefficients, with the eigenvalues of the exchange Hamiltonian being of course given by Eqn (2.2). The hopping matrix element for quantum spins is identical to that for classical spins if one assumes that the following equality holds:

$$\cos\frac{\theta}{2} = \frac{S_0 + 1/2}{2S + 1} , \qquad (2.17)$$

where $S_0 = |\mathbf{S}_1 + \mathbf{S}_2| \pm 1/2$ is the total spin of the system consisting of two localized spins and an electron spin. Thus, in the quantum case the Hamiltonian of the DE model is again given by Eqn (2.13), but the effective hopping matrix element is now determined by the eigenvalues of the total spin for a system of two sites between which electron hopping takes place.

At this point mention should be made of the original approach taken in Ref. [24], in which the effective quantum Hamiltonian was obtained as a sum of polynomials evolved from the scalar product of localized spins located at two sites and which yielded the same — up to a sign — eigenvalues (2.17) of the hopping matrix element.

An alternative approach to the derivation of an effective Hamiltonian for quantum spins, one involving the use of the projection operator technique, was proposed for the DE model by Kubo and Ohata [25] and then extended in Ref. [26]. Essentially, what was proposed is to apply the canonical transformation — in order, first, to exclude the doubly occupied electron states at the site, and second, by considering a strong Hund coupling, to retain only those electron states which have their spins parallel to the localized spin. The idea, in other words, was to create an electron hopping friendly situation at a site. Such a canonical transformation is carried out conveniently by the use of projection operators.

Employing the projection operators P and Q = 1 - P, the space of the eigenstates $|\psi\rangle$ of the initial Hamiltonian H can be divided into two subspaces, $P|\psi\rangle$ and $Q|\psi\rangle$, the former containing empty and singly occupied states with spin parallel to the localized one, and the latter containing doubly or singly occupied states with spin antiparallel to the localized one. Then in either subspace the Schrödinger equation $H|\psi\rangle = E_g|\psi\rangle$ for the degenerate ground state can be written as the following pair of equations:

$$PHP|\psi\rangle + PHQ|\psi\rangle = E_{g}P|\psi\rangle,$$

$$QHP|\psi\rangle + QHQ|\psi\rangle = E_{g}Q|\psi\rangle.$$
 (2.18)

Because here we are concerned with the subspace of $P|\psi\rangle$, it is necessary to eliminate states belonging to the other subspace, $Q|\psi\rangle$. Using the definition of the projection operator $(P^2 = P, Q^2 = Q)$ and eliminating $Q|\psi\rangle$ by application of the second of Eqns (2.18), we arrive at

$$(H_{\rm eff} - E_{\rm g})P|\psi\rangle = 0, \qquad (2.19)$$

where

$$H_{\rm eff} = PHP - PHQ \frac{1}{QHQ - E_{\rm g}} QHP \qquad (2.20)$$

is the effective Hamiltonian for the lowest eigenvalue subspace. Taking the limit $J_{\rm H} \rightarrow \infty$ leaves us with only one term in the Hamiltonian (2.20). It follows then that in order to obtain an explicit form of the quantum Hamiltonian for the DE model, the form of the projection operator P must be specified. Since, as already pointed out, the subspace $P|\psi\rangle$ must only contain empty or singly occupied states with spin parallel to the localized spin, it is easily verified that the following projection operator possesses such properties [26]:

$$P = \prod_{i} P_{i} = \prod_{i} (P_{hi} + P_{si}^{+}), \qquad (2.21)$$

where the operator

$$P_{hi} = (1 - n_{i\uparrow})(1 - n_{i\downarrow}) \tag{2.22}$$

removes doubly occupied states, and the operator

$$P_{si}^{+} = \sum_{\sigma\sigma'} \left(\frac{\mathbf{S}_{i} \cdot \mathbf{\sigma} + (S+1)\hat{I}}{2S+1} \right)_{\sigma\sigma'} \tilde{c}_{i\sigma}^{\dagger} \tilde{c}_{i\sigma'}$$
(2.23)

ensures that the electron spin is parallel to that of the ion. Here, the operator $\tilde{c}_{i\sigma}^{\dagger} = (1 - n_{i,-\sigma})c_{i\sigma}^{\dagger}$ accounts for the absence of doubly occupied states at a given site.

Now, using the explicit form of the projection operator given by Eqns (2.21)-(2.23), the effective quantum Hamiltonian of the DE model is

$$H_{\text{eff}} = PHP$$
$$= -\sum_{ii\sigma\sigma'} t_{ij}(1 - n_{i,-\sigma})c^{\dagger}_{i\sigma}(P^+_i P^+_j)_{\sigma\sigma'}(1 - n_{j,-\sigma'})c_{j\sigma'}, \quad (2.24)$$

where

$$P_i^+ = \frac{\mathbf{S}_i \cdot \mathbf{\sigma} + (S+1)\hat{I}}{2S+1} \,. \tag{2.25}$$

The Hamiltonian (2.24) has been first proposed in Ref. [25] and since that time it was the subject of intense studies. It should be remembered that this Hamiltonian corresponds to the limiting case of strong Hund coupling. If this condition needs to be relaxed and the parameters zt and $J_{\rm H}$ need to be considered as comparable in magnitude, one should use the original sd-model Hamiltonian (1.1) and employ nonperturbative methods of analysis. One such approach is the dynamical mean field method.

3. Properties of the DE model in the dynamical mean field approximation

3.1 Dynamical mean field approximation

in the classical spin model

A method that is widely used in the theory of strongly correlated systems is that of considering systems in spaces of

high dimensionality d. The limit $d = \infty$ corresponds to the true mean field approximation for such systems [10, 27]. Because mean field type approximations do not require that the interactions be weak, the behavior of the systems can be studied over a wide range of the values taken by the Hamiltonian parameters. Unlike the conventional mean field approximation, in which the field is always static, the approximation based on the limit $d = \infty$ involves a dynamical mean field, so that analyzing systems in the $d = \infty$ limit corresponds to the dynamical mean field (DMF) approximation. In the past decade, the DMF method has been applied quite successfully to a number of basic models in the manybody theory, including the Hubbard model [28, 29], the tJ model [30, 31], and the Falicov-Kimball model [32-34], so that the quasi-particle spectra, phase transitions, and quite a few transport properties exhibited by these models have been studied in considerable detail. Importantly, small-cluster numerical calculations using exact diagonalization or Monte Carlo methods lend support to the DMF results.

The DE model has been studied in a series of papers by Furukawa [11, 12, 35–40]. Central to DMF approach is the fact that at $d = \infty$ in any lattice model the electron self-energy Σ is a local quantity, i.e. it does not depend on the quasimomentum and is a function of the frequency alone [41, 42]. The **k** dependence of the electron Green's function on the lattice appears only through the bare spectrum $\varepsilon_{\mathbf{k}}$:

$$G(\mathbf{k}, \mathrm{i}\omega_n) = \frac{1}{\mathrm{i}\omega_n - \varepsilon_{\mathbf{k}} + \mu - \Sigma(\mathrm{i}\omega_n)} \,. \tag{3.1}$$

Let us introduce the local (single-site) Green's function

$$G_{\rm L}(i\omega_n) = \frac{1}{N} \sum_{\mathbf{k}} G(\mathbf{k}, i\omega_n)$$
$$= \int d\varepsilon N_0(\varepsilon) \frac{1}{i\omega_n - \varepsilon + \mu - \Sigma(i\omega_n)} . \tag{3.2}$$

In the last expression in Eqn (3.2) we have introduced the quantity $N_0(\varepsilon)$, the density of states in the bare spectrum of the original (finite *d*) lattice, so that information about the real lattice is contained in this function only. Now the local Green's function $G_L(i\omega_n)$ can be considered as the Green function of a single-site problem with a certain effective bare Green's function $G_0(i\omega_n)$ and with the same self-energy $\Sigma(i\omega_n)$, so that we can write

$$G_{\rm L}({\rm i}\omega_n) = \frac{1}{G_0^{-1}({\rm i}\omega_n) - \Sigma({\rm i}\omega_n)} \,. \tag{3.3}$$

On the other hand, $G_L(i\omega_n)$ may be treated as the Green function of a single-site problem in which the influence of all the rest of the lattice on a given site reduces to an effective mean field of the quantity $G_0^{-1}(i\omega_n)$, which defines the action [11, 35–37]

$$S = -\int_{0}^{\beta} \mathrm{d}\tau_{1} \int_{0}^{\beta} \mathrm{d}\tau_{2} \,\Psi^{\dagger}(\tau_{1}) G_{0}^{-1}(\tau_{1}-\tau_{2}) \Psi(\tau_{2})$$
$$-J_{\mathrm{H}} \int_{0}^{\beta} \mathrm{d}\tau \,\mathbf{m} \cdot \Psi^{\dagger}(\tau) \,\boldsymbol{\sigma} \,\Psi(\tau) \,.$$
(3.4)

Here, $G_0(\tau_1 - \tau_2)$ is the function $G_0(i\omega_n)$ in the time representation, and $\Psi^{\dagger} = (a_{\uparrow}^{\dagger}, a_{\downarrow}^{\dagger})$ is the two-component spinor. The single-site Green's function G_L is defined as a path integral over the Grassmann variables ψ^* and ψ , both the spinors:

$$G_{\rm L}(\tau_1 - \tau_2) = \frac{1}{Z} \int \delta \Omega_{\rm m} \delta \psi^* \delta \psi \exp\left(-S[\psi^*, \psi]\right) \psi(\tau_1) \psi^*(\tau_2) ,$$
(3.5)

$$Z = \int \delta \Omega_{\mathbf{m}} \delta \psi^* \delta \psi \exp\left(-S[\psi^*, \psi]\right).$$
(3.6)

The symbol $\int \delta\Omega_{\mathbf{m}}$ stands for path integration over the directions of the classical spin vector \mathbf{m} . The integrals with respect to the Grassmann variables are easily evaluated, and Eqns (3.5) and (3.6) can be written in the following form

$$G_{\rm L}(i\omega_n) = \frac{1}{Z} \int \delta\Omega_{\mathbf{m}} \exp\left[-S_{\rm eff}(\mathbf{m})\right] \frac{1}{G_0^{-1}(i\omega_n) + J_{\rm H}\mathbf{m}\sigma}, \quad (3.7)$$
$$Z = \int \delta\Omega_{\mathbf{m}} \exp\left[-S_{\rm eff}(\mathbf{m})\right],$$

where the effective action $S_{\rm eff}(\mathbf{m})$ is defined by

$$\int \delta \psi^* \delta \psi \exp\left(-S[\psi^*, \psi]\right) = \exp\left[-S_{\text{eff}}(\mathbf{m})\right],$$
$$S_{\text{eff}}(\mathbf{m}) = -\sum_n \ln \det\left[\frac{1}{i\omega_n} \left(G_0^{-1}(i\omega_n) + J_{\text{H}}\mathbf{m}\mathbf{\sigma}\right)\right]. \quad (3.8)$$

Numerical evaluation of the integral in Eqn (3.7) yields the explicit form of $G_{\rm L}(i\omega_n, G_0^{-1})$, whereas Eqns (3.2) and (3.3) jointly determine the relationship between G_0^{-1} and Σ . Thus, the set of equations (3.2), (3.3), and (3.7) yield the quantities $G_0^{-1}(i\omega_n)$ and $\Sigma(i\omega_n)$ and the Green function $G(\mathbf{k}, i\omega_n)$. The average value of the local spin is given by the integration over the directions of the vector **m**:

$$\langle \mathbf{m} \rangle = \int \delta \Omega_{\mathbf{m}} \exp\left[-S_{\text{eff}}(\mathbf{m})\right] \mathbf{m} \,. \tag{3.9}$$

Let us first consider several special cases which allow analytical solutions to the above equations [12]. For the paramagnetic phase, the rotational invariance gives $G_0(i\omega_n) = g_0(i\omega_n)I$, where *I* is the unitary two-row matrix, and g_0 is a scalar. Noting further that $\langle \mathbf{m} \rangle = 0$ and $\langle \mathbf{m}^2 \rangle = 1$, Eqn (3.7) yields the following expressions for the local Green's function G_L and the self-energy Σ :

$$G_{\rm L}(\mathrm{i}\omega_n) = \frac{1}{2} \left(\frac{1}{g_0^{-1}(\mathrm{i}\omega_n) + J_{\rm H}} + \frac{1}{g_0^{-1}(\mathrm{i}\omega_n) - J_{\rm H}} \right) I, \quad (3.10)$$

$$\Sigma(i\omega_n) = G_0^{-1}(i\omega_n) - G_L^{-1}(i\omega_n) = J_H^2 G_0(i\omega_n).$$
 (3.11)

The spectral density of single-particles states

$$A(\omega) = -\frac{1}{\pi} \operatorname{Im} G_{L}(i\omega_{n} \to \omega + i\delta)$$
(3.12)

has two peaks in this case, each centered at energy $\omega = \pm J_{\rm H}$ and having width $\text{Im } g_0^{-1}(\omega) \sim t$, where t is the hopping matrix element. The peak intensities are the same for either spin projection.

In the case of the ferromagnetic state with a spontaneous moment $M = \langle m_z \rangle$, a redistribution of intensity over electrons with different spin orientations takes place. In the limit $J_{\rm H} \rightarrow \infty$, for the bare density $N_0(\omega)$ of Lorentzian shape with the width W, the following analytical expressions for the propagator Green's function (3.1) are obtained following the analytical continuation $i\omega_n \rightarrow \omega + i\delta$:

$$G_{\sigma}(\mathbf{k},\omega) = \frac{P_{\sigma}^{+}}{\omega + J_{\mathrm{H}} + \mu - P_{\sigma}^{+}\varepsilon_{\mathbf{k}} + \mathrm{i}P_{\sigma}^{-}W} + \frac{P_{\sigma}^{-}}{\omega - J_{\mathrm{H}} + \mu - P_{\sigma}^{-}\varepsilon_{\mathbf{k}} + \mathrm{i}P_{\sigma}^{+}W}.$$
 (3.13)

Here, the P_{σ}^{\pm} are the statistical weights of the electron states for various values of the spin projection onto the spontaneous moment vector:

$$P_{\sigma}^{\pm} = \frac{1 \pm M_{\sigma}}{2} \,. \tag{3.14}$$

Thus, there are two bands of single-particle states, which are centered at the energies $\omega + \mu = \pm J_{\rm H}$ and have the width W. The intensities of the upper and lower band interchange as spin orientations are varied. In the ground (M = 1) state, electrons with spin $\sigma = \uparrow$ fill the lower band, and those with $\sigma = \downarrow$ fill the upper band. Electron systems with such properties are usually called ferromagnetic semimetals. As the temperature increases, opposite spin states appear in either band. In the paramagnetic phase, states with opposite spins are of the same intensity in both bands, consistent with expression (3.10) for the local Green's function.

3.2 Analysis of Furukawa's numerical solutions

For finite $J_{\rm H}$, Eqns (3.2), (3.3), and (3.7) are solved numerically. An important result which was established in the numerical computation of the density of states $A_{\sigma}(\omega)$ for a cubic lattice is that the band gap decreases with increasing temperature [12].

Qualitatively, this can be understood by considering the form of the Anderson–Hasegawa hopping matrix element. This is proportional to $\cos(\theta/2)$, where θ is the angle between two spins at the sites between which the hopping takes place. As the temperature increases, θ deviates from 0 due to spin fluctuations, and the average of $\cos(\theta/2)$, and hence the average of the hopping matrix element, decreases in magnitude. The single-particle states decay due to spin fluctuations as can be seen from Eqn (3.13). For spin $\sigma = \uparrow$ at T = 0, the factor $P_{\sigma}^- = 0$, so that such electrons behave like free particles. The opposite spin electrons, on the contrary, offer a maximum attenuation of $\sim W$ (bare band width) and correspond to incoherent states. This behavior is also characteristic of other models of collectivized ferromagnets with strong correlation [43, 44].

The DE model thus describes a semimetallic ground state, i.e. the Fermi surface exists only for electrons with the majority spin orientation, the state of the system corresponding to a saturated ferromagnet. Experiments on spin resolution photoemission show that doped manganites constitute semimetals [45, 46].

The Curie temperature $T_{\rm C}$ can be found by solving the simplified equations (3.2), (3.3), and (3.7) numerically under the condition M < 1. In the limit $J_{\rm H} \gg W$, the curve $T_{\rm C}(x)$ so obtained turns out to be close in form to the curve $T_{\rm C}(x) \sim x(1-x)$. For $x \to 0$ and $x \to 1$, $T_{\rm C} \to 0$ because of the fact that the ferromagnetism in the system is due to the kinetic energy of the carriers. The particle–hole symmetry also remains to be valid for finite $J_{\rm H}$ [12]. Also, the tendency towards $T_{\rm C}$ increasing with W continues in this case. Experimental data on $T_{\rm C}$ for the La_{1-x}Sr_xMnO₃ system [47] are fitted accurately by the curves calculated for $W \approx 1$ eV,

 $J_{\rm H} \approx 4$, values which are typical of 3d-metal oxides and consistent with manganite band calculations [12].

The transport properties of the model are calculated from the Kubo formula. The conductivity in the limit $d = \infty$ is given by [48]

$$\sigma(\omega) = \sigma_0 \sum_{\sigma} \int d\omega' I_{\sigma}(\omega', \omega' + \omega) \frac{f(\omega') - f(\omega' + \omega)}{\omega},$$
(3.15)

where

$$I_{\sigma}(\omega_1,\omega_2) = \int N_0(\varepsilon) \,\mathrm{d}\varepsilon \, W^2 A_{\sigma}(\varepsilon,\omega_1) A_{\sigma}(\varepsilon,\omega_2) \,,$$

and $A_{\sigma}(\varepsilon, \omega)$ is the spectral density of states of the propagator Green's function:

$$A_{\sigma}(\varepsilon,\omega) = -\frac{1}{\pi} \operatorname{Im} G_{\sigma}(\varepsilon,\omega+\mathrm{i}\delta).$$

In Eqn (3.15), $f(\omega)$ is the Fermi distribution function, and the constant σ_0 has the dimension of conductivity. Figure 5 shows the temperature dependences of electrical resistivity and magnetization calculated from $\sigma(\omega)$ with $\omega = 0$ and from Eqn (3.9), respectively. Here ρ_0 is a constant corresponding to Mott's minimum conductivity value at d = 3. Above T_C , the resistivity has a value of the order of Mott's limit $\rho_0 = 1/\sigma_0$ with a very weak temperature dependence. Below T_C , it falls off rapidly as the magnetization increases. Detailed DMF calculations show [11, 35–37] that the resistivity varies with magnetization as

$$\frac{\rho(M)}{\rho(M=0)} = 1 - CM^2, \qquad (3.16)$$

where *C* is a numerical constant independent of the temperature and magnetic field. Thus, the dependence of ρ on *T* and *H* enters through the magnetization M = M(T, H). This means that the electrical resistivity in the DE model is entirely due to the scattering of carriers by magnetic order fluctuations. In the weak coupling limit $J_{\rm H} \ll W$ (in the Born approximation) one finds C = 1 [49], however in the strong coupling limit $J_{\rm H} \gg W$ DMF calculations yield C > 1. From the experiments on the La_{1-x}Sr_xMnO₃ system with x = 0.175 it follows that $C \approx 4$ [47], and the relation (3.16) is found to be



Figure 5. Resistivity ρ and magnetization *M* as functions of temperature, calculated using the DMF method [12].

followed closely by theoretical results for the same electron concentration and $J_{\rm H}/W = 4$ [12]. Measurements show that the resistivity of La_{1-x}Sr_xMnO₃ varies from about 10² $\mu\Omega$ cm at low temperatures to $\rho(T_{\rm C}) \approx 2 \,\mu\Omega$ cm, which is of order of the Mott limit. We thus see that La_{1-x}Sr_xMnO₃ constitutes a good metal for $T \ll T_{\rm C}$, and a poor one for $T \ge T_{\rm C}$. The theoretical DE-model results of Fig. 5 cover the full range of the property variation.

A comparison of calculated and experimental findings on optical conductivity in $La_{1-x}Sr_xMnO_3$ also supports the DE model (Fig. 6). The conductivity peak is due to interband transitions, at which the electron energy changes by about $2J_H \approx 3 \text{ eV}$ — consistent with the observed peak's position near $\omega = 3 \text{ eV}$. The temperature dependence of the peak intensity is also in good agreement with theory.

We now treat collective excitations in a ferromagnetic semimetal. In the discussion above we used the classical spin model, corresponding to the limiting case where quantum spin $S \ge 1$. A linear spin wave theory is now constructible by using a small parameter 1/S and assuming an arbitrarily strong interaction. For this purpose, the spin operators in the DE-model Hamiltonian should be replaced by the Bose operators of spin deflections by means of the Holstein– Primakoff formulas $S_i^+ = \sqrt{2S} b_i$, $S_i^z = S - b_i^{\dagger} b_i$. Then to lowest order in 1/S the spin wave energy $\omega_{\mathbf{q}}$ is given by [38,51]

$$\omega_{\mathbf{q}} = \frac{1}{SN} \sum_{\mathbf{k}} f_{\mathbf{k}\uparrow} \left[J_{\mathrm{H}} - \frac{2J_{\mathrm{H}}^2}{2J_{\mathrm{H}} - \varepsilon_{\mathbf{k}} + \varepsilon_{\mathbf{k}+\mathbf{q}}} \right], \qquad (3.17)$$

where $f_{\mathbf{k}\uparrow}$ is the Fermi function for the electrons with the dominant spin orientation.



Figure 6. Optical conductivity: (a) experimental data for $La_{1-x}Sr_xMnO_3$ [50]; (b) calculated DMF results [12].

In the limit of large $J_{\rm H}$, the $t/J_{\rm H}$ expansion in Eqn (3.17) yields an expression that does not depend on $J_{\rm H}$. For a simple cubic lattice, restricting electron hoppings to nearest neighbors only, the bare energy spectrum takes the form

$$\varepsilon_{\mathbf{k}} = -2t(\cos k_x + \cos k_y + \cos k_z) \,.$$

Equation (3.17) in this case leads to the following expression for the spin wave energy:

$$\omega_{\mathbf{q}} \approx \frac{1}{z} E_{\mathrm{SW}} (3 - \cos q_x - \cos q_y - \cos q_z) , \qquad (3.18)$$

where

$$E_{\rm SW} = \frac{zt}{SN} \sum_{\mathbf{k}} f_{\mathbf{k}\uparrow} \cos k_x \,. \tag{3.19}$$

Result (3.18) agrees with that of Kubo and Ohata [25]. In the limit $J_{\rm H} \rightarrow \infty$, the spin wave spectrum of the DE model is identical in form to that of a Heisenberg ferromagnet. This implies that the effective spin – spin interaction is short-range, the reason being that the electron level is spin-split by $2J_{\rm H}$ as seen from the denominator in Eqn (3.17). For intermediate values of $J_{\rm H}$, the spin wave dispersion departs from law (3.18) [51]. From Eqn (3.19) it follows that to an order of magnitude $E_{\rm SW} \sim xzt/S$. Assuming that the scale of the Curie temperature is the width of the spin wave spectrum, we obtain that $T_{\rm C} \sim xzt/S$, which for the manganites gives about 2000 K — an order of magnitude higher than the observed values.

The question which remains to be answered is the role of the vertex corrections for the electron – magnon interaction. A spin wave spectrum was examined numerically for S = 1/2in the limit $J_{\rm H} \rightarrow \infty$ [52] and exhibited a dispersion relation of the type (3.18) which, however, departed from this behavior in the limits $n \rightarrow 0$ and $n \rightarrow 1$ — presumably due to the vertex renormalization. These renormalizations are important where the electron kinetic energy is less than the characteristic spin wave frequencies ($E_{\rm kin} \leq \langle \omega_{\bf q} \rangle$). In the opposite limiting case they are weak. In the manganites, where ferromagnetism occurs for $0.2 \leq x \leq 0.4$, these renormalizations may apparently be considered small. This brings the theoretical predictions for the spin wave spectrum we have discussed above into agreement with experiment (Fig. 7), but why $T_{\rm C}$ is that high still remains unclear.



Figure 7. Spin wave dispersion in $La_{0.7}Pb_{0.3}MnO_3$ [53] compared with DMF calculations for x = 0.3 [38].

The DMF approximation has also been used to construct the phase diagram of the DE model [54]. It should be noted here that, along with the ferromagnetic phase existing over the entire range of concentrations *n* for infinite $J_{\rm H}/W$, in the case of finite $J_{\rm H}/W$ an indirect antiferromagnetic exchange interaction of magnitude $t^2/J_{\rm H}$ arises in the system, producing an antiferromagnetic phase near half-filled band (n = 1). On the other hand, the DE model yields an inhomogeneous phase — an electron-rich finely divided phase embedded in an antiferromagnetic matrix. The islands of the electron-rich phase are either ferro- or parasinglet regions (phase separation). The occurrence of phase separation in the DMF approximation has been demonstrated in Ref. [54]. A manifestation of phase separation are the jumps in $n(\mu)$, the electron concentration as a function of the chemical potential. An example is demonstrated in Fig. 8b, where the electron concentration jumps from n = 0.88 to n = 1. This shows that the homogeneous state is unstable within this interval. Were such a state realized in one way or another, it would inevitably break up into two phases with electron concentrations corresponding to the ends of this interval, i.e. a ferro- or para-phase with n = 0.88, and an antiferromagnetic insulating phase with n = 1. The phase diagram for the DE model in the limit $d = \infty$ is displayed in Fig. 8a [54].

Here, unlike Furukawa's earlier papers which we cited above, a more realistic expression for the bare electron density of states, viz.

$$N(\varepsilon) = \frac{2}{\pi W} \sqrt{1 - \left(\frac{\varepsilon}{W}\right)^2}, \quad -W < \varepsilon < W, \quad (3.20)$$



Figure 8. DE model behavior in the DMF approximation [54]: (a) T-n phase diagram; (b) electron concentration as a function of the chemical potential; $J_H/t = 4$.

0.08

0.06

0.04

 $T_{\rm C}/t$

3.3 Relation between $T_{\rm C}$ and the average kinetic energy

The authors of Ref. [55] undertook the task of revising the DMF approximation to DE model in terms of fitting the experimental data on manganites with high $T_{\rm C}$, for which double exchange is believed to be the dominant mechanism. To approach real materials as closely as possible, the DE model was extended somewhat by including the orbital states of the charge carriers. The Hamiltonian used was the generalized Hamiltonian of the sd-model:

$$H = -\sum_{ij\alpha\beta\sigma} t_{ij}^{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{j\beta\sigma} - J_{\rm H} \sum_{i\alpha\sigma\sigma'} \mathbf{S}_i \cdot a_{i\alpha\sigma}^{\dagger} \mathbf{\sigma}_{\sigma\sigma'} a_{i\alpha\sigma'}.$$
 (3.21)

Here, the α , β label the orbital-moment-degenerate states (i.e. two-fold degenerate e_g states in the case of the manganites), so that the parameter $t_{ij}^{\alpha\beta}$ is a matrix in orbital indices in this case.

The key physical characteristic discussed in the analysis is K, the average kinetic energy of an electron:

$$K = -\frac{2}{zN} \sum_{ij\alpha\beta\sigma} \langle t_{ij}^{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{j\beta\sigma} \rangle .$$
(3.22)

In the simplest case of no orbital degeneracy, this quantity is expressed in terms of the electron Green's function:

$$K = \int d\varepsilon \,\varepsilon N_0(\varepsilon) \frac{1}{\pi} \int d\omega \, f(\omega) \,\mathrm{Im} \, G(\varepsilon, \omega) \,. \tag{3.23}$$

Although the ferromagnetic ordering temperature $T_{\rm C}$ depends strongly on the system's major parameters such as the electron concentration *n* and the exchange parameter $J_{\rm H}$, in fact it is determined by *K*, a quantity which itself is strongly dependent on *n* and $J_{\rm H}$. Indeed, referring to Fig. 9 [55] which shows the classical-spin DMF calculated results of the preceding section, the proportionality between ΔK and $T_{\rm C}$ indicates the average total energy of electrons as a fundamental energy parameter of the system and one which determines its ferromagnetic ordering temperature. This conclusion drawn from numerical work is fully consistent with Zener's early idea that electron motion through the lattice causes ferromagnetism in the framework of the DE model.

An important observation in Ref. [55] is that the value of K can be extracted by measuring the frequency dependence of conductivity, because K appears as a measure of spectral weight in this dependence. The DMF electron self-energy is independent of \mathbf{k} so that the vertex corrections may be neglected giving a conductivity of the form

$$\sigma_{\alpha\beta}(\mathbf{i}\omega_n) = \frac{e^2}{\mathbf{i}\omega_n} \left\{ S(\infty) - \sum_{\mathbf{k}\sigma} T \sum_m \mathrm{Tr} \left[\gamma_{\mathbf{k}}^{\alpha} G_{\sigma}(\mathbf{k}, \mathbf{i}\omega_m) \gamma_{\mathbf{k}}^{\beta} G_{\sigma}(\mathbf{k}, \mathbf{i}\omega_n + \mathbf{i}\omega_m) \right] \right\}.$$
(3.24)

Here $\gamma_{\mathbf{k}}^{\alpha}$ is a current component. Since we are concerned with materials of cubic symmetry, one has $\sigma_{\alpha\beta} = \sigma \delta_{\alpha\beta}$. From Eqn (3.24), the conductivity expression can be reproduced.

Since the conductivity obeys the sum rule [56, 57], we can write down that

$$S(\infty) = \frac{a^{d-2}}{e^2} \int_0^\infty \frac{2}{\pi} \,\mathrm{d}\omega \,\sigma(\omega) = \sum_{i\delta\alpha\beta\sigma} t_{\delta}^{\alpha\beta} \delta^2 \langle a_{i\alpha\sigma}^{\dagger} a_{i+\delta\alpha\sigma} + \mathrm{H.c.} \rangle.$$
(3.25)





Figure 9. Relation between the Curie temperature and the electron kinetic energy for the DE model with two degenerate e_g orbitals [55]. (a) T_C as a function of J_H/t . Solid circles correspond to n = 0.70, stars and open squares correspond to n = 0.25. Portion of the curve for n = 0.25 is obtained analytically over the region $J_H/t \ll 1$ (stars). (b) Variation of the electron kinetic energy over the interval $(0, T_C)$ versus T_C for n = 0.7 [$K_{J_H=0}(T = 0) = 1.01t$] [55].

Here δ is the vector connecting the two sites between which hopping takes place. If electron hopping between nearest neighbors is dominant, it follows from Eqn (3.25) that

$$\int_0^\infty \frac{2}{\pi} \,\mathrm{d}\omega \,\sigma(\omega) = \frac{e^2}{a^{d-2}} \,K,\tag{3.26}$$

i.e. $S(\infty) = K$.

Now from Eqn (3.24) there follows an operative formula for calculating the optical conductivity in the framework of the DE model:

$$\sigma(\omega) = e^{2} \sum_{\sigma} \int d\varepsilon N_{0}(\varepsilon) \varphi(\varepsilon) \times \int \frac{d\omega'}{\pi} \frac{f(\omega') - f(\omega' + \omega)}{\omega'} A_{\sigma}(\varepsilon, \omega') A_{\sigma}(\varepsilon, \omega' + \omega), \quad (3.27)$$

which is in fact identical to Eqn (3.15) given earlier. The only difference is in the matrix elements for the vertex parts of the currents. In Eqn (3.27), $\varphi(\varepsilon) = (1/3)(4t^2 - \varepsilon^2)$ corresponds to the Bethe lattice, whereas in Eqn (3.15) we have the quantity W^2 , which corresponds to a cubic lattice.

Thus, there are two ways in which the average kinetic energy K can be evaluated: from Eqn (3.23) using the electron

Green's function or from the experimentally found conductivity, by integrating it with respect to frequencies. By comparing these quantities, the adequacy of the DE model in describing real manganites can be checked.

Numerical calculations of $T_{\rm C}$ and K were done for La_{0.7}Sr_{0.3}MnO₃, a compound whose ground state is ferromagnetic and which is believed to be described adequately by the DE model (see Fig. 9). It was found that K(T = 0)depends only weakly on $J_{\rm H}$ over an extended region of $J_{\rm H}$ and that $K(T = 0) \approx 0.84$ eV for this compound. In the limit $J_{\rm H} \rightarrow 0$, the calculations yield $T_{\rm C}/K(T = 0) \approx 0.16$ that is almost independent of the model details. For finite $J_{\rm H}$ (for electron concentrations *n* corresponding to the ferromagnetic ground state) it was found that $T_{\rm C} \sim \Delta K$ (the difference in *K* at T = 0 and $T > T_{\rm C}$) (Fig. 9b). It turned out also that for $J_{\rm H} \rightarrow 0$, $\Delta K/K \rightarrow 1/3$ but as $J_{\rm H}$ decreases, so does ΔK . At a certain critical value of $J_{\rm H}$, $\Delta K = 0$, and below this value of $J_{\rm H}$ the ferromagnetic ground state is not possible.

3.4 A simplified double exchange model

Abandoning the idea of a quantized localized spin in Furukawa's approach makes the theory highly questionable in terms of the physical adequacy of the approximation employed. A series of papers on the subject [58-61] produced a theory of double exchange in the $z \rightarrow \infty$ limit, in which the localized spin was viewed as a quantum one with S = 1/2. To make the problem practically solvable, however, the double exchange model itself was simplified by ignoring the transverse-spin-fluctuation contribution, thus replacing the initial Hamiltonian for the sd interaction by an Ising-type Hamiltonian of the form

$$H_{\rm int} \to -\frac{1}{2} J_{\rm H} \sum_{i} S_i^z (a_{i\uparrow}^{\dagger} a_{i\uparrow} - a_{i\downarrow}^{\dagger} a_{i\downarrow}) , \qquad (3.28)$$

where S_i^z is the operator for the *z* component of the localized spin at the site *i*, and $S_i^z S_i^z = 1$.

In second-order perturbation theory in the parameter $W/J_{\rm H}$ one can go over from the initial Hamiltonian $H = H_{\rm kin} + H_{\rm int}$ with the simplification (3.28) to an effective Hamiltonian H which is conveniently written down as

$$H = -t \sum_{ij\sigma} c^{\dagger}_{i\sigma} c_{j\sigma} - \sum_{ij} J_{ij} n_{i\uparrow} n_{j\downarrow} . \qquad (3.29)$$

Here the $c_{i\sigma}(c_{i\sigma}^{\dagger})$ are annihilation (creation) Fermi-like operators of the complex consisting of a localized spin at the site *i* and an electron with a parallel spin residing at the same site, so that

$$c_{i\sigma} = \frac{1}{2} (1 + \sigma S_i^z) a_{i\sigma} , \qquad (3.30)$$

and in addition $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$. Site states with antiparallel spins in the complexes are described by the operators $(1/2)(1 - \sigma S_i^z)a_{i\sigma}$ and are omitted as lying higher by an amount of order $J_{\rm H}$. The finite values of $W/J_{\rm H}$ give rise to an additional intersite term in the Hamiltonian (3.29), accounting for the exchange antiferromagnetic interaction between electrons, of order $J \sim t^2/J_{\rm H}$ for nearest neighbors.

In the limit $z \to \infty$, the quantities t and J scale in the usual way like $t \to t^*/\sqrt{z}$, $J \to J^*/z$, where t^* and J^* are the constants of the theory. The Hartree–Fock approximation of intersite interaction becomes exact in this limit, so that the exchange term in Eqn (3.29) can be linearized, and the Hamiltonian of the simplified DE model finally becomes

$$H = -\frac{1}{2} \sum_{i} h_i S_i^z + \sum_{i\sigma} \varepsilon_{\sigma} c_{i\sigma}^{\dagger} c_{i\sigma} - t \sum_{ij\sigma} c_{i\sigma}^{\dagger} c_{j\sigma} . \qquad (3.31)$$

Here we have included the local magnetic field h_i acting on the localized spin, and introduced the chemical potential μ such that

$$arepsilon_{\sigma} = -\mu - \sum_{j} J_{ij} \langle n_{j-\sigma}
angle \, .$$

Let us consider now the single-particle Green's function for correlated electrons, viz.

$$\mathcal{G}_{\sigma}^{ii'}(\tau - \tau') = - \left\langle T_{\tau} \tilde{c}_{i\sigma}(\tau) \tilde{c}_{i'\sigma}^{\dagger}(\tau') \right\rangle.$$
(3.32)

Since the operators $c_{i\sigma}$ and $c_{i\sigma}^{\dagger}$ obey rather complicated permutation relations between themselves and with S_i^z , treating them perturbationally requires a special diagram technique [58] of the kind used for the Hubbard operators [62]. Using the technique of Ref. [58] one obtains the Dyson equation which, when Fourier transformed with respect to the time variable $\tau - \tau'$, takes the form

$$\sum_{i_{1}} \{ G_{\sigma}^{0^{-1}}(i\omega_{s})\delta_{ii_{1}} - \Sigma_{\sigma}^{ii_{1}}(i\omega_{s}) - t_{ii_{1}} \} \mathcal{G}_{\sigma}^{i_{1}i'}(i\omega_{s}) = \delta_{ii'}, \quad (3.33)$$

where $G^0_{\sigma}(i\omega_s) = (i\omega_s - \varepsilon_{\sigma})^{-1}$ is the bare Green's function. Since in the limit $d \to \infty$ the electron self-energy is momentum independent and depends only on the frequency, as mentioned before, it is diagonal in site indices, $\Sigma^{ii'}_{\sigma} = \Sigma^{ii}_{\sigma} \delta_{ii'}$, and its form for the Hamiltonian (3.31) is given by [59]

$$\Sigma_{\sigma}^{ii}(\mathrm{i}\omega_s) = -\frac{1-\sigma m_i^d}{2\mathcal{G}_{\sigma}^{ii}(\mathrm{i}\omega_s)}\,,\tag{3.34}$$

where $m_i^d = \langle S_i^z \rangle$ is the average value of the localized spin. The derivation of Eqns (3.33) and (3.34) is not simple and yet is analogous to the one Brandt and Mielsch [63] carried out for the Falicov–Kimball model.

From Eqn (3.33) the one-site Green's function is followed immediately:

$$\mathcal{G}_{\sigma}^{ii}(\mathrm{i}\omega_s) = \int N_0(\varepsilon) \left[\mathrm{i}\omega_s - \varepsilon_{\sigma} - \Sigma^{ii}(\mathrm{i}\omega_s) - \varepsilon\right]^{-1}, \qquad (3.35)$$

where $N_0(\varepsilon)$ is the density of states for the bare electron spectrum ε_k .

Equations (3.34) and (3.35) exhibit a closed system of equations for determining the self-energy part of the function and the one-site Green's function proper. The equations for $\langle S_i^z \rangle$ can also be obtained by a diagram technique of the type used for *c*-operators and can be written as [60, 61]

$$\begin{split} m_i^d &= \tanh \frac{1}{2} \lambda_i \,, \end{split} \tag{3.36} \\ \lambda_i &= \lambda_i^0 + \eta_i \,, \qquad \lambda_i^0 = y_i + \ln \frac{1 + \exp(\beta \mu_r - y_i^s)}{1 + \exp(\beta \mu_r + y_i^s)} \,, \\ \eta_i &= \sum_{\omega_s} \left\{ \ln \frac{(1 + m_i^d) G_{\uparrow}^0(\mathrm{i}\omega_s)}{2\mathcal{G}_{\uparrow}^{ii}(\mathrm{i}\omega_s)} - \ln \frac{(1 - m_i^d) G_{\downarrow}^0(\mathrm{i}\omega_s)}{2\mathcal{G}_{\downarrow}^{ii}(\mathrm{i}\omega_s)} \right\}. \end{split}$$

Here we introduced the notion

$$y_i = \beta h_i, \qquad y_i^s = \frac{1}{2} \beta \sum_j J_{ij} m_j^s,$$
$$\mu_r = \mu + J^* \frac{n}{2}, \qquad \beta = \frac{1}{T},$$

and m_i^s is the magnetization the itinerant electrons create at a given site. The quantities m_i^s and μ are determined from the equations

$$m_i^s = \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle, \quad n = \langle n_{i\uparrow} \rangle + \langle n_{i\downarrow} \rangle.$$
 (3.37)

The proper averages $\langle n_{i\sigma} \rangle$ are expressed in terms of the diagonal Green's function $\mathcal{G}_{\sigma}^{ii}(i\omega_s)$ via summation with respect to frequency.

Since the quantities $\langle n_{i\sigma} \rangle$ are functions of m_i^d , so m_i^s are the functions of m_i^d , and Eqn (3.36) written in a very nearly meanfield form is a closed equation for m_i^d . In the general case, the system of equations (3.34), (3.35) for the electron Green's function and Eqn (3.36) for m_i^d can only be solved numerically. There is one special case, however, the Bethe lattice, which admits an analytical solution for the electron Green's function, thus significantly simplifying the study of the magnetic properties of the system.

In the limit $z \to \infty$, the itinerant-electron density of states on the Bethe lattice has the form of Eqn (3.20), with W = 4tbeing the width of the bare band. From Eqns (3.34) and (3.35), with $h_i = m_i = m_i^s = 0$ (paramagnetic phase), the onesite Green's function $\mathcal{G}_{\sigma}^{ii} \equiv \mathcal{G}_{\sigma}$ is found as

$$\mathcal{G}_{\sigma}(\mathrm{i}\omega_s) = \frac{8}{W^2} \left\{ \Omega_s - \sqrt{\Omega_s^2 - \frac{W^2}{8}} \right\},\tag{3.38}$$

where $\Omega_s = i\omega_s + \mu_r$. It is seen that the correlation narrowing of the band is determined by the quantity $W/\sqrt{2}$.

Differentiating Eqn (3.36) with respect to the field h_i yields the equation for the static susceptibility

$$\chi(i,i') = \frac{\mathrm{d}m_i}{\mathrm{d}h_{i'}} \,.$$

The divergences of $\chi(\mathbf{q})$ at $\mathbf{q} = 0$ and $\mathbf{q} = (\pi, \pi, \pi)$ determine the regions of instability of the paramagnetic phase against ferro- and antiferromagnetic ordering. Variation of $T_{\rm C}$ and $T_{\rm N}$ with the electron number density *n* is shown in Fig. 10. In the region where the $T_{\rm C}$ and $T_{\rm N}$ curves intersect, one needs to compare the energies of the ferromagnetic and antiferromagnetic phases to resolve the phase issue.

Let us consider the state of the system within the ferromagnetic phase. In this case local characteristics are independent of the site index, while retaining their dependence on the spin. The one-electron Green's function is given then by

$$\mathcal{G}_{\sigma}(\mathrm{i}\omega_s) = \frac{8}{W^2} \left\{ \Omega_s - \sigma v - \sqrt{\Omega_s^2 - \sigma v^2 - a_{\sigma}^2} \right\}, \qquad (3.39)$$

where

$$a_{\sigma}^2 = \frac{1}{8} W^2 (1 + \sigma m^d), \quad v = \frac{1}{2} J^* m^s$$

The magnetizations m^d and m^s and the chemical potential μ are obtained from Eqns (3.35)–(3.37) after the summation



Figure 10. Curie and Néel temperatures versus electron number density in the simplified DE model [60]: I, $J^* = 0.1$; 2, $J^* = 0.2$; 3, $J^* = 0.3$; 4, $J^* = 0.4$.

with respect to the discrete frequency ω_s . The equations then take the form

$$m^{d} = \tanh \frac{1}{2} \lambda_{\mathrm{F}}, \qquad (3.40)$$
$$\lambda_{\mathrm{F}} = \frac{1}{\pi} \int_{0}^{\infty} \mathrm{d}t \ln \frac{1 + \exp \beta \left(\mu_{r} - \nu - a_{\uparrow} \cos t\right)}{1 + \exp \beta \left(\mu_{r} + \nu - a_{\downarrow} \cos t\right)},$$

$$m^{s} = nm + (1 - m^{2}) \sum_{\sigma} \frac{1}{\pi} \int_{0}^{\pi} dt \, \sin^{2} t f(a_{\sigma} \cos t + \sigma v) \,, \ (3.41)$$

$$n = \sum_{\sigma} (1 + \sigma m) \frac{1}{\pi} \int_0^{\pi} \mathrm{d}t \, \sin^2 t f(a_\sigma \cos t + \sigma v) \,, \tag{3.42}$$

where the integration with respect to t arises from the summation of frequencies.

As seen from Eqn (3.39), the band structure of the system is determined by the parameter a_{σ} , the half-width of the correlated band for spin σ . The dependence of a_{σ} on spin is responsible for a number of phenomena in the ferromagnetic phase, in particular, for the negative shift of the chemical potential. Analysis of Eqns (3.40)–(3.42) shows that $d\mu/dT$ changes sign at the Curie point.

Figure 11 depicts the temperature dependence of m^d . It is seen that as the electron concentration decreases from n = 0.5to n = 1, the curves gradually change their shape, acquiring two points of inflection near n = 1. The dashed curve in the figure demonstrates the temperature dependence of a Heisenberg ferromagnet in the mean-field approximation, when the magnetization m is given by

$$m = \tanh \frac{T_{\rm C}}{T} m$$
.

Near n = 1, the $m^d(T)$ curves are reminiscent of the behavior of the magnetization for a Heisenberg ferromagnet with a low concentration of paramagnetic impurities. Due to the strong sd exchange interaction, the localized spin is bound to — and forms a complex with — a conduction electron residing at a given site. Consequently, the spin of the complex is S + 1/2, and that of a free site is S, so that these sites behave as impurity spins with concentration $1 - n \ll 1$.



Figure 11. Temperature dependence of the averaged localized spin for various electron number densities [60]: 1, n = 0.50; 2, n = 0.70; 3, n = 0.80; 4, n = 0.90; 5, n = 0.95; 6, n = 0.99.

At this stage we present the expression for the total internal energy of the ferromagnetic phase as obtained by averaging the Hamiltonian (3.31):

$$\frac{E_{\rm F}(T)}{N} = -\frac{1}{4} J^* [n^2 - (m^s)^2] + W \sum_{\sigma} \left(\frac{1+\sigma m}{2}\right)^{3/2} \\ \times \frac{1}{\pi} \int_0^{\pi} {\rm d}t \, \sin^2 t \cos t f(a_{\sigma} \cos t + \sigma v). \tag{3.43}$$

In the case of a two-sublattice antiferromagnetic structure with wave vector $Q = (\pi, \pi, \pi)$ we have $m_i = p_i m, m_i^s = p_i m^s$, where $p_i = \exp(i\mathbf{Q}\mathbf{R}_i) = \pm 1$ (for sites in the first and second sublattices). In this situation we look for a solution of Eqn (3.33) in the form

$$\mathcal{G}_{\sigma}^{ii}(\mathrm{i}\omega_s) = \mathcal{G}_{\sigma}^{(1)}(\mathrm{i}\omega_s) + p_i \mathcal{G}_{\sigma}^{(2)}(\mathrm{i}\omega_s)$$

For the Bethe lattice, this yields separate equations for $\mathcal{G}_{\sigma}^{(1)}$ and $\mathcal{G}_{\sigma}^{(2)}$, and for the quantities m^d , m^s and μ equations similar to Eqns (3.40)–(3.42) result. The internal energy of the antiferromagnetic phase is given then by

$$\frac{E_{\rm A}(T)}{N} = -\frac{1}{4} J^*[n^2 + m^2] + \frac{1}{4} W^2 (1 - m^2) \frac{1}{\pi} \int_0^{\pi/2} {\rm d}t \, \sin^2 t \cos^2 t \, \frac{f[E(t)] - f[-E(t)]}{E(t)}$$
(3.44)

where

$$E(t) = \sqrt{\frac{1}{8} W^2(\alpha_1^2 \sin^2 t + \alpha_2^2 \cos^2 t) + v^2},$$

$$\alpha_1^2 = \frac{1}{2} - \frac{1}{2} \sqrt{1 - m^2}, \qquad \alpha_2^2 = \frac{1}{2} + \frac{1}{2} \sqrt{1 - m^2}.$$

The quantities $\pm E(t)$ determine two energy bands for correlated electrons residing in an antiferromagnetic phase, the parameter t replacing the unperturbed electron spectrum ε_k of the usual periodic lattice. By comparing the energies, the lines of the first-order transitions between the ferro- and antiferromagnetic phases can be determined. It is easy to see, however, that the simplified DE model shows signs of phase separation in that the compressibility $dn/d\mu$ becomes negative in a certain range of electron concentrations. An analysis of the negative compressibility results suggests that the phase separation between the ferromagnetic and the paramagnetic phases is only possible for $J^* > J_c^* = 0.318$. Of practical interest in this context are lower values of J^* , for which separation between the ferro- and antiferromagnetic phases should be sought. At a fixed J^* there is a number density point n^* , obtained from the relation $E_{\rm F}(n^*) = E_{\rm A}(n^*)$, such that in the interval $0 < n < n^*$ the ground state is ferromagnetic, whereas in the interval $n^* < n < 1$ it is antiferromagnetic. In this situation the ground state energy viewed as a function of *n* is not convex throughout the entire range of its argument, 0 < n < 1, thus necessitating the use of the Maxwell procedure; this gives us two electron concentration points, $n = n_{PS}$ and n = 1. For values in-between, the system exists as a combination of ferromagnetic regions with electron concentration $n = n_{PS}$ and antiferromagnetic regions with n = 1.

In the T-n phase diagram for $J^* = 0.1$ shown in Fig. 12, the phase separation region is bounded by the horizontal axis and by the dashed lines emanating from the point of intersection of the $T_{\rm C}(n)$ and $T_{\rm N}(n)$ curves. The points a and b are calculated from the equations of the theory, whereas the dashed lines are drawn schematically in order to obtain the phase separation sector qualitatively in the diagram. The phase diagram for the simplified DE model is generally consistent with that obtained from the Furukawa model with $J_{\rm H}/W = 4$ (see Fig. 8). The difference is that the latter model exhibits a region of separation between the para- and antiferromagnetic phases, so that a purely antiferromagnetic phase exists only on the n = 1 axis (at any temperatures). It should be noted, though, that the authors of Ref. [55] did not study the region of large $J_{\rm H}/W$ corresponding to the value $J^* = 0.1$ in Fig. 10, which excludes a detailed comparison of the phase diagrams under study.

Efforts have also been made to study other properties of the simplified DE model [59–61]. In particular, the inverse static magnetic susceptibility of the paramagnetic phase was found to be linear — and thus to obey the Curie–Weiss law



Figure 12. Phase diagram for the simplified DE model [60]. PS stands for the phase separation.

122

— over a wide temperature range up to the close vicinity of $T_{\rm C}$; in that latter area deviations appear in the opposite direction to those seen in the Heisenberg model. Calculations of the temperature dependence of electrical resistivity showed a dramatic increase of ρ on approaching $T_{\rm C}$.

Thus, despite different approximations underlying the Furukawa and simplified DE models, both yield very much the same physics. The simplified DE model, however, has the advantage of being more powerful analytically, providing reasonably simple transcendent equations for such local quantities as the magnetization of an individual site. The model does not require much computer work and provides a number of analytical results.

3.5 The coherent potential method

Since the inclusion of the quantum dynamics of localized spins (i.e. of the finite values of the atomic spin S) is quite problematic within the DMF approach, alternative approaches are being applied to the DE model in the tightbinding regime. Among them is the CPA (coherent potential approximation). As is well known, the CPA (in the absence of the electron – electron interaction) is exact in the limit $d = \infty$ and is widely used to describe electronic states in binary alloys with chaotically distributed components [64]. An extension of the standard CPA of Ref. [64] to systems with localized spins (such as the DE model) was given by Kubo [65]. Kubo succeeded in calculating the electron Green's function and density of states in the framework of the DE model in the limit of low electron concentration $n \rightarrow 0$ (i.e. in the case of a ferromagnetic semiconductor). He found that in the tightbinding case the electron band splits into two subbands centered on the atomic levels $-SJ_{\rm H}$ and $(S+1)J_{\rm H}$, corresponding to the electron spin being aligned parallel and antiparallel to the localized spin.

An extension of the Kubo method to metals with electron number densities covering the broad range 0 < n < 1 has been given recently by Edwards et al. [14, 66] using the approach which Hubbard [67] applied to the model now carrying his name. The approach is based on an alloy analogy and assumes the electrons with a given spin projection to be frozen in calculating Green's function for the opposite spin electron. For the DE model with a finite spin the situation is complicated by the presence of an additional scattering mechanism which involves the interchange of the electron spin with the localized atomic spin. In the limit $n \rightarrow 0$, the computed Green's functions go over into Kubo's ones [65]. A method developed in Refs [14, 16] accounts for uncoupling of the Green's function equations of motion in the spirit of Hubbard's approximation [67], which considers only the 'correction for scattering' while neglecting the 'resonant term'.

An elegant Green's function uncoupling technique developed in Ref. [66] for finite S extends the original Hubbard approach to the DE system and corresponds to the CPA for a DE model with an arbitrary electron concentration. Using Green's functions so obtained, the electrical resistivity owing to spin fluctuation scattering in the paramagnetic phase is calculated for two models, elliptical and Lorentzian, of the electron-band density of states. Calculations are performed for the entire electron concentration range 0 < n < 1, at the ends of which the resistivity goes to infinity and somewhere in the middle of which it has a minimum. For the case of an elliptical density of states, ρ_{min} is of order 1 m Ω cm, more than an order of magnitude below the values observed in the manganites. For the Lorentzian density of states, on the other hand, the resistivity is an order of magnitude higher. It is with this density of states that Furukawa's numerical calculations yielded ρ values of the same order as in experiment. It turns out that the paramagnetic Lorentzian density of states strongly overpredicts ρ — whence Furukawa's claim that the DE model in its pure form is adequate in describing the physics of the manganites.

Also calculated in Ref. [66] was the magnetic susceptibility of the paramagnetic phase for $J_{\rm H} \rightarrow \infty$ within the same CPA framework. The physical results are discouraging however, because whatever the finite values of *S* and *n*, the DE model in this approximation does not show the paramagnetic phase to be unstable against ferromagnetism. At the same time, for $S \rightarrow \infty$ the CPA equations for Green's function are consistent with DMF equations for the classical spin. An attempt is made to see exactly where in the analysis the authors' uncoupling procedure [66] makes the magnetic properties of the DE model unphysical.

3.6 Variational approach in the mean field approximation

We consider now another possible way of introducing the mean field concept into the DE model which, even though different from the DMF approach, represents an attempt to take account of the local disorder present in the system. Substituting a bivalent atom for a lanthanum atom in a manganite creates a random local potential v_i which may exert considerable influence on the behavior of charge carriers and, ultimately, on virtually all the physical properties of these materials. Together with spin disorder, this atomic disorder may lead to the localization of carriers in the paramagnetic phase. The simplest model which includes both these disorder types in the presence of a magnetic field is described by the Hamiltonian

$$H = -\sum_{ij} t \cos \frac{\theta_{ij}}{2} a_i^{\dagger} a_j + \sum_i [v_i a_i^{\dagger} a_i - \mu_B SH \cos \theta_i]. \quad (3.45)$$

An original way of including a variational mean field acting on a local spin was proposed by Varma [68]. Let $P(\theta)$ be the distribution function of the mean field acting on the spin. Assuming that the spin makes an angle θ with the magnetic field, and neglecting the orientational correlation of neighboring spins, the entropy of the spin system can be written in the form

$$S = -\int d\theta \,\sin\theta P(\theta) \ln P(\theta) + S^0_{\rm spin}(S) \,, \qquad (3.46)$$

where the term $S_{\text{spin}}^0(S)$ is independent of $P(\theta)$. In a similar way we write down the electron energy E_e and the spin energy E_s in the presence of a magnetic field, and in addition the total free energy $F = E_e + E_s - TS$. Denoting the polar and azimuth angle of the local spin vector by θ_i and ϕ_i , respectively, we have

$$E_{\rm e} = \int_0^{2\pi} \frac{\mathrm{d}\phi_1}{2\pi} \int_0^{2\pi} \frac{\mathrm{d}\phi_2}{2\pi} \int_0^{\pi} \mathrm{d}\theta_1 \sin\theta_1 \int_0^{\pi} \mathrm{d}\theta_2 \sin\theta_2 P(\theta_1) P(\theta_2)$$

$$\times \int_{-\infty}^{\infty} d\varepsilon \, \varepsilon \rho \left(t \cos \frac{\theta}{2}, \, \varepsilon \right), \qquad (3.47)$$

$$E_{\rm s} = -H \int_0^{2\pi} \frac{\mathrm{d}\phi_1}{2\pi} \int_0^{\pi} \mathrm{d}\theta_1 \sin\theta_1 \cos\theta_1 P(\theta_1) \,. \tag{3.48}$$

Here the electron density of states $\rho(t, \varepsilon)$ corresponds to the Hamiltonian (3.45) with diagonal disorder and is expressed in terms of the density of states in the absence of disorder by averaging it over the random potential v_i :

$$\rho(t,\varepsilon) = \left\langle \rho_0(t,\varepsilon-v) \right\rangle_v. \tag{3.49}$$

Minimizing further the free energy functional F with respect to the distribution $P(\theta)$ we obtain the equilibrium value of this function, viz.

$$P(\theta) = \exp\left\{-\left[Z(\theta) + \xi - H\cos\theta\right]\frac{1}{T}\right\},\qquad(3.50)$$

where

$$Z(\theta) = 2 \int_{0}^{2\pi} \frac{\mathrm{d}\phi_{1}}{2\pi} \int_{0}^{2\pi} \frac{\mathrm{d}\phi_{2}}{2\pi} \int_{0}^{\pi} \mathrm{d}\theta_{1} \sin\theta_{1} P(\theta_{1})$$
$$\times \int_{-\infty}^{\mu} \mathrm{d}\varepsilon \left(\varepsilon - \mu\right) \rho\left(t\cos\frac{\theta}{2}, \varepsilon\right). \tag{3.51}$$

This expression depends on the angle θ through the angle $\theta(\phi_1; \theta_1; \phi; \theta)$ between two oriented spins. The quantity ξ in the exponential is a Lagrangian multiplier and is determined by normalizing the distribution function $P(\theta)$, Eqn (3.50), to unity.

Thus, minimization of the free energy functional leads to an expression for $P(\theta)$ of the form (3.50), in which the exponential is again a functional of the same function, thus implying that Eqn (3.50) sets up a nonlinear integral equation for the distribution function $P(\theta)$. The kernel of this equation is determined by the density of states in the bare spectrum, and this is the only characteristic of the model.

Equation (3.50) has to be solved numerically, although for the paramagnetic phase, when $P(\theta)$ is a very nearly uniform function in a weak magnetic field, one can apply an iteration procedure and obtain an expression for the static magnetic susceptibility, with the Curie temperature defined by the relation

$$T_{\rm C} = \int_0^{\pi} \mathrm{d}\theta \sin\theta \cos\theta \int_{-\infty}^{\mu} \mathrm{d}\varepsilon \,(\mu - \varepsilon)\rho\left(t\cos\frac{\theta}{2}, \,\varepsilon\right). \quad (3.52)$$

Calculations show that $T_{\rm C}$ is rather insensitive to the form of the density of states in the bare spectrum for a fixed width ρ_0 of the distribution. The $T_{\rm C}(x)$ curve calculated for the case of no local disorder is fitted well by the function x(1 - x), while the quantity $T_{\rm C}$ lies in the range 100–300 K and is consistent with the experimental data [47]. The band width used in the calculation of $T_{\rm C}$ was W = 1.8 eV.

The influence of disorder on $T_{\rm C}$ has been examined by means of Eqn (3.52) for a Gaussian random potential v_i . In this case $t \cos(\theta/2)$ is replaced by the quantity $t_{\rm eff}$ which can be found from the relation

$$\frac{1}{t_{\rm eff}^2} = \frac{1}{t^2 \cos^2(\theta/2)} + \frac{3}{V_0^2} ,$$

where V_0 is the width of the Gaussian distribution used. From Eqn (3.52) it follows that T_C decreases with increasing V_0 .

Paper [15] also presents the temperature dependences of the magnetization and electrical resistivity and calculates the magnetoresistance as a function of the temperature and magnetic field, all for the DE model with no disorder. The sum total of the theoretical results are in good agreement with the experimental data for manganites with high $T_{\rm C}$. At the same time, the inclusion of diagonal disorder effects in the model (3.45) makes it possible, in principle, to obtain results which may be compared with data on low- $T_{\rm C}$ manganites, in which the role of atomic ordering is *a priori* large.

4. Phase diagram of the model

4.1 Monte Carlo calculations

Because the DE model works properly for large and intermediate values of the parameter $J_{\rm H}/W$, any approximate scheme aimed at calculating physical properties must be checked by numerical computations, which are exact in a sense. For calculating the phase diagram of the DE model, the Monte Carlo method has been found to be very effective [16, 54, 69, 70].

We have to calculate the partition function Z. For the DE model with classical spins we can write that

$$Z = \prod_{i} \left(\int_{0}^{\pi} \mathrm{d}\theta_{i} \sin \theta_{i} \int_{0}^{2\pi} \mathrm{d}\varphi_{i} \right) \operatorname{Tr}_{c} \left[\exp \left(-\frac{H}{T} \right) \right], \quad (4.1)$$

where the integration goes over the two angles specifying the spin orientation at each site *i*, and Tr_c denotes the trace over the electronic degrees of freedom. The Hamiltonian *H* describes electron motion in the field of fixed classical spins. If the concentration of electrons is low, their interaction can be neglected, and *H* is then a quadratic form in Fermi operators, which can always be diagonalized. Let its eigenvalues be ε_{λ} (note that they are the functionals of the set of specified angles $\{\theta_i, \varphi_i\}$). If the ε_{λ} 's are found numerically for a certain cluster of lattice atoms, then *Z* for this cluster can be calculated with the formula

$$Z = \prod_{i} \left(\int_{0}^{\pi} \mathrm{d}\theta_{i} \sin \theta_{i} \int_{0}^{2\pi} \mathrm{d}\varphi_{i} \right) \prod_{\lambda} \left[1 + \exp\left(-\frac{\varepsilon_{\lambda}}{T}\right) \right].$$
(4.2)

Thus, Z should be calculated in two stages: firstly, one diagonalizes the Hamiltonian of the cluster for a given spin configuration, and then integrates the result over all the possible spin configurations. The difficult problem of 'accounting for sign' is avoided here, unlike in the quantum Monte Carlo method.

In Refs [16, 54, 69, 70], Z and spin pair correlation functions were calculated for clusters of various dimensionality. In the case d = 1, numerical work was done for chains of up to 40 atoms for $J_{\rm H}/t = 1, 2, 3, 4, 8, 12$, and 18. In the case d = 2, calculations were carried out for a 6×6 cluster and occasionally for a larger, 10×10 , one. Finally, for d = 3, clusters of 4^3 and 6^3 atoms were used. For each set of parameters $J_{\rm H}/t$, n, and T, spin pair correlation functions were calculated, from which the thermodynamic state of the system — i.e. the presence or absence of a long-range magnetic order — was determined. The results of these computer studies are summarized in Fig. 13.

There are three phases in the $(J_H/t, n)$ plane in the figure: the ferromagnetic (F) phase, the modulated phase (IC stands for incommensurate), and the phase separation region (PS). In the case d = 2, PS and IC have no clearly defined boundary between them — but rather a crossover region (shown as shaded area). The phase separation region was determined from the behavior of the compressibility κ defined as the



Figure 13. Phase diagrams for the classical spin DE model obtained by the Monte Carlo method (a) in one dimension, and (b) in two dimensions.

second derivative of energy:

$$\frac{1}{\kappa} = \frac{\partial^2 E}{\partial n^2} = \left(\frac{\partial n}{\partial \mu}\right)^{-1}.$$
(4.3)

Those values of electron number density, where $n(\mu)$ has a jump (the compressibility goes to infinity), determine the stability boundary for the homogeneous phase (see Fig. 8).

Reference to Fig. 13a, b shows that the main features of the phase diagram are retained with any dimensionality: a vast region of ferromagnetic state and a phase separation region near half-filled band. Both phases are inalienable features of the DE model. The situation with saturated ferromagnetism in this model is reminiscent of Nagaoka's theorem [71], according to which a hole in a half-filled Hubbard model with a large on-site Coulomb repulsion produces ferromagnetic ordering in the system. Thus, saturated ferromagnetism has the same origin in the Hubbard and DE models. As for the phase separation effect, it appears to be quite general for strongly correlated systems. At any rate, it has been well established theoretically in the halffilled Hubbard model and experimentally in HTSC cuprates.

The PS phase that appears in the phase diagrams of Fig. 13 represents an antiferromagnetic matrix which has no

conduction electrons and contains inclusions in the form of ferromagnetic phase islands with elevated electron concentration. Electrons in these regions make gain in kinetic energy owing to the ferromagnetic ordering, but this gain is accompanied by a rise in Coulomb repulsion energy. This energy can be minimized by the spatial expansion of the electron-rich regions, in which case a stripe structure with alternating regions of insulating and metallic phases may arise.

Calculations for 3d clusters are rather difficult but, this being an intermediate case between 1d and 2d on the one hand and $d = \infty$ on the other, the general properties of the phase diagram for the 3-dimensional system should remain unchanged. Direct 3d-cluster calculations showed the ferromagnetic phase to be stable over a wide range of n (Fig. 14). These data are extracted from the analysis of the calculated spin pair correlations, which have a positive sign in the ferromagnetic region. To obtain $T_{\rm C}$ in the units of degrees, an estimate of t is needed. For the manganites, the band width lies in the range 1-4 eV. Given the band width of 12t from tight-binding calculations of the energy spectrum for a cubic crystal, one finds that t lies in the range 0.08-0.33 eV. A rough estimate based on the results in Fig. 14 puts the maximum $T_{\rm C}$ within the interval 100–400 K. This range is consistent with experiment, suggesting that ferromagnetic states in manganites can be described adequately only by means of the electron DE model [54].



Figure 14. Upper limit for the Curie temperature in a 3d model in the limit $J_{\rm H} \rightarrow \infty$ (after Ref. [54]).

Another question is whether it is adequate to use classical spins in describing manganites with the localized spin S = 3/2. Specialized quantum calculations for cluster chains of atoms with S = 3/2 were performed in Ref. [54] using a Lanczos scheme to numerically diagonalize the cluster Hamiltonian and to calculate the energy of the ground state for a specific total spin. The boundary of the ferromagnetic phase obtained in this way changed only slightly from the classical spin results shown in Fig. 13a. Near half-filled band $(n \approx 0.85)$, negative values of compressibility, indicating the onset of phase separation, were observed. In the quantum case, the F, IC, and PS phases are, all three of them, present in the phase diagrams of 1d systems - exactly as they are in the classical spin case. The distinction lies in the fact that the transition from the PS to F phase proceeds smoothly. Calculations for S = 1/2 retain the essential features of the phase diagram for a 1d system. We can therefore be more or less confident that in the 3d case replacing the atomic spin by

the classical one also does not alter the phase diagram of the DE model qualitatively.

4.2 Inclusion of direct antiferromagnetic exchange

In the DE model, the indirect antiferromagnetic exchange interaction arises near the half-filled band. For n = 1 and $J_{\rm H}/W \ge 1$, the effective Hamiltonian goes over into that of the Heisenberg model with a nearest-neighbor exchange interaction $I \sim W^2/J_{\rm H}$. In the manganites, there can also be direct exchange between localized manganese spins, via oxygen ions. Thus, in the general case we have to introduce an additional term $J' \sum_{ij} \mathbf{S}_i \mathbf{S}_j$ into the Hamiltonian (1. 1). The presence of such an electron-concentration-independent exchange will dramatically reconstruct the phase diagram of the system.

The role of direct exchange interaction has been analyzed in a Monte Carlo study [70] of spin correlations in cluster chains based on the previous result [16] indicating that the DE-model phase diagram weakly depends on the dimensionality of the system and therefore the behavior of a threedimensional system can be understood from one-dimensional results. The resulting J'-n phase diagram is shown in Fig. 15. For intermediate values of *n* and J'/t < 0.11, the ferromagnetic metal phase (FM) is seen to exist. When J'/tincreases above 0.11, a phase transition occurs to an insulating phase with a modulated magnetic structure (IC). In particular, at n = 1/4 a spiral phase with a wave vector $q = \pi/2$ appears. For J'/t = 0.25, this is the only phase stable at this value of electron number density, whereas in the range 0.35 < n < 0.6 the antiferromagnetic phase becomes stable. Also, antiferromagnetic phases occur for the half-filled band (n = 1) and for an empty band (n = 0)(in the latter case, due to the direct exchange being switched on). In the vast regions between the ferro- and antiferromagnetic phases, phase separation takes place. The occurrence of such states is signaled by jumps in $dn/d\mu$. Unlike the pure DE model results discussed above, the inclusion of direct exchange causes phase separation to occur even in the small-n region. A similar result was obtained analytically in Ref. [73]. At the same time, the authors of Ref. [70] argue that their scenario of an antiferromagnet undergoing phase separation into ferromagnetic regions is more accurate physically than that of a magnetic polaron moving in an antiferromagnetic matrix [74]. We note for completeness that paper [70] also provides a detailed discussion, within the framework of the present model, of the total and spectral densities of states for electrons as well as of the optical conductivity in various regions of the phase diagram.

The phase diagram depicted in Fig. 15a is in a sense consistent with that of Fig. 15b obtained by the energy comparison of various phases calculated analytically for the DE model with added antiferromagnetic exchange between localized spins. Analytical calculations, which are possible for the limiting case of low electron number density, $n \ll 1$, have yielded [72] energies for four homogeneous phases with two sublattices which need not be antiferromagnetic but whose spins form a certain angle θ different from π (the canted AF structure of de Gennes [6]). It turned out that there are four electron concentration values that separate the regions of realization of the magnetic phases as follows: AF, an antiferromagnetic phase $(n < n_1)$; QC, a quantum canted structure with two bands $(n_1 < n < n_2)$ and one band $(n_2 < n < n_3)$ filled; CC, a classical canted structure $(n_3 < n < n_4)$, and FR, a ferromagnetic structure $(n > n_4)$.



Figure 15. Phase diagrams for the DE model with direct antiferromagnetic exchange J': (a) Monte Carlo classical spin results [70], (b) analytical calculations for a finite spin S [72]. CC denotes the canted phase (see text), κ is the electron gas compressibility.

The energies of the phases indicated are

$$E_{AF} = -\frac{ztn}{\sqrt{2S+1}} - \frac{1}{2} zJ'S^{2},$$

$$E_{QC} = E_{AF} - \frac{3}{8} \frac{zt^{2}}{J'(2S+1)^{2}} (n-n_{1})^{2},$$

$$E_{CC} = -\frac{zt^{2}n^{2}}{4J'S^{2}} - \frac{1}{2} zJ'S^{2},$$

$$E_{F} = -ztn + \frac{1}{2} zJ'S^{2},$$
(4.4)

respectively. The critical electron concentrations are given by

$$n_{1} = \frac{8\pi^{4}}{3} \left[\frac{J'(2S+1)^{3/2}}{zt} \right]^{3}, \quad n_{2} = \frac{27}{z} n_{1},$$
$$n_{3} = \frac{8J'S^{3/2}}{t}, \quad n_{4} = \frac{2J'S^{2}}{t}.$$

From expressions (4.4) it follows that the compressibility κ for the phases QC and CC is negative, indicating that they are unstable to phase separation. For not small values of *n*, the numerical calculations of Ref. [72] lead to the phase diagram shown in Fig. 15b. For intermediate electron concentrations, the stable phases are F and CC. At low concentrations, the CC phase becomes unstable (even in regions where the compressibility is positive).

The DE model Hamiltonian with additional antiferromagnetic exchange is electron – hole symmetric, therefore the phase diagram for 0.5 < n < 1 should be similar to that for 0 < n < 0.5. It turns out, however, that the manganites behave very differently for electron number densities in these two intervals. This breaking of the electron – hole symmetry is due to the orbital degeneracy of electron states in real manganites (see Section 5).

Thus, numerical [16, 54, 69, 70] and analytical [72, 75–77] DE-model studies reveal the presence of phase separation similar to that arising in the Hubbard [78] and tJ [79] models. Over a wide range of electron number densities and Hamiltonian parameters, the homogeneous states of these models are unstable towards a phase separation. These inhomogeneous states come in a number of varieties: ferromagnetic (or paramagnetic) islands with elevated electron concentration in an dielectric antiferromagnetic matrix; islands of canted ferro- or antiferromagnetic phase, and magnetic polarons. The latter (if they are low-mobile ones due to a large effective mass or disorder-induced localization) exhibit a limiting — with one electron per microvolume — case of phase separation with local ferromagnetic order [8, 49].

The observation of phase separation in the DE model suggests that many experimental data on the manganites should be reinterpreted in the light of the existence of magnetically and electronically nonuniform states in these materials. In particular, transport properties and the metal – insulator transition should perhaps be analyzed using percolation theory rather than in terms of the properties of uniform states. The importance of percolation for the manganites has been emphasized by Gor'kov and Kresin [9, 19], and there is some experimental evidence to support this idea [80, 81]. In particular, the percolation concept provides a natural way to explain the existence of a critical hole concentration $x_c \sim 0.16$ above which a ferromagnetic metal state occurs in La_{1-x}A_x²⁺MnO₃ [19].

4.3 Experimental studies of phase separation in manganites

Along with the theoretical results on phase separation in the DE model, there is much experimental evidence for its existence in the manganites, coming from neutron scattering, NMR, and from photoconductivity and other transport properties. The bulk of the data show that along the (electron concentration or temperature) boundary of the ferromagnetic region, there exist in actual manganites inhomogeneous phases in which ferromagnetic clusters with an elevated electron number density coexist with another phase, possibly an antiferromagnetic insulator. Experimental evidence for phase separation in various manganites has been reviewed in detail elsewhere (see, e.g., Ref. [54]), so that only a few examples will be given here.

In Ref. [82], the spin dynamics in $La_{1-x}Ca_xMnO_3$ were examined in the ferromagnetic range of electron concentrations (0 < x < 0.5) using inelastic neutron scattering. For x = 1/3 (corresponding to a Curie temperature of 250 K), it is found that spin wave dispersion curves at low *T* are gapless, characteristic of an isotropic ferromagnet. At large *T*, however, a diffusion scattering component was observed at the center, whose intensity increased toward T_C due to the decreased spin wave scattering intensity. Such a three-peak spectrum is absent at x = 0.15 and x = 0.175, where a usual two-peak spin-wave-scattering structure is observed. The three-peak structure is explained by assuming that the system constitutes an inhomogeneous phase in which a ferromagnetic metallic matrix (producing two side peaks) contains inclusions of a paramagnetic phase (producing the central diffusive peak).

Small-angle neutron scattering studies on the same (La, Ca) system showed the existence of metallic ferromagnetic drops in the dielectric antiferromagnetic matrix at sufficiently small x = 0.05 and 0.08 [83]. The density of the drops was 60 times smaller than that of the holes x, and their diameter was below 10 Å. Magnetically, drops are far from a saturated ferromagnet. The average spin deflection from the quantization axis is about 70°.

5. Orbital degeneracy in the double exchange model

5.1 Electronic spectrum and the phase diagram

The DE model was from the very first aimed at explaining the physical properties of the manganites, despite the neglect of the orbital degeneracy of the itinerant electrons in e_{g} symmetric states. At the same time, the orbital degeneracy of Jahn-Teller ions has long been recognized as an important factor for transition metal compounds behaving as magnetic insulators [84-86]. Anderson [86] was the first to show that the kinetic exchange between magnetic ions in an insulator depends on the symmetry of degenerate trivalent orbitals and the geometry of the crystal lattice. A complete theory of kinetic exchange in dielectric crystals with Jahn-Teller ions was developed by Kugel' and Khomskii [84, 85] based on the Hubbard model with additional intraatomic exchange interaction. It turned out that spin and orbital degrees of freedom are strongly coupled in such crystals (even in the absence of the spin-orbit interaction in ions) and that this manifests itself primarily in orbital ordering. Both types of ordering strongly affect each other, so that given one type of ordering the theory is capable of predicting the other.

Because insulators of this type are raw materials for metallic (doped) manganites, the above ideas were carried over to the double exchange model applicable (in the general case) to metallic systems [17, 19, 87]. Orbital degeneracy radically changes the picture of double exchange and leads to the formation of anisotropic magnetic structures. We follow the approach of van den Brink and Khomskii [17] in the discussion below.

The DE model Hamiltonian in the presence of orbitally degenerate states can be written as

$$H = -\sum_{ij\sigma\alpha\beta} t_{ij}^{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{j\beta\sigma} - J_{\rm H} \sum_{i\sigma\sigma'\alpha} \mathbf{S}_i \cdot a_{i\alpha\sigma}^{\dagger} \sigma_{\sigma\sigma'} a_{i\alpha\sigma'} + J' \sum_{ij} \mathbf{S}_i \mathbf{S}_j \,.$$
(5.1)

Here α and β indices label the components of the degenerate electron state. For the manganites, these are the orbitals $d_{x^2-y^2}$ and d_{z^2} belonging to the two-fold degenerate level of e_g symmetry; they are labeled by the indices $\alpha = 1$ and 2, respectively. Note the term of magnitude $J' \ll t \ll J_H$, added to the Hamiltonian to account for the direct (antiferromagnetic) ion – ion exchange.

The hopping matrix elements $t_{ij}^{\alpha\beta}$ depend on the orbital number and are related to each other by certain relationships depending on the overlap of the functions $d_{x^2-y^2}$ and d_{z^2} [84, 86]. Using these relationships, one obtains expressions for the Fourier components of the quantities $t_{ij}^{\alpha\beta}$. In the nearestneighbor approximation, we have

$$t^{11}(\mathbf{k}) = -2t_{xy}(\cos k_x + \cos k_y),$$

$$t^{12}(\mathbf{k}) = t^{21}(\mathbf{k}) = -\frac{2}{\sqrt{3}}t_{xy}(\cos k_x - \cos k_y),$$

$$t^{22}(\mathbf{k}) = -\frac{2}{3}t_{xy}(\cos k_x + \cos k_y) + \frac{8}{3}t_z \cos k_z.$$
 (5.2)

In the absence of a magnetic ordering in a cubic crystal, we find $t_{xy} = t_z = t$, but in the presence of such ordering the hopping matrix elements depend on the mutual orientation of the spins at the sites between which the hopping occurs. In writing the expression for $t^{\alpha\beta}(\mathbf{k})$ above it is assumed that the magnetic ordered crystal possesses a tetragonal symmetry.

Consider now the simplest three antiferromagnetic structures possible in a two-sublattice cubic crystal: the types A, C, and G (see Fig. 3). These structures are characterized by the values of angles θ_{xy} between the neighboring spins in the *xy*plane and the angle θ_z made with the *z* axis:

$$\begin{split} \mathbf{A}(\theta_{xy} = \mathbf{0}, \theta_z = \pi) \,, \qquad \mathbf{C}(\theta_{xy} = \pi, \theta_z = \mathbf{0}) \,, \\ \mathbf{G}(\theta_{xy} = \theta_z = \pi) \,. \end{split}$$

We will consider localized spins as classical vectors. Then, following Ref. [17], we define the quantities t_{xy} and t_z by the equations

$$t_{xy} = t \cos \frac{\theta_{xy}}{2}, \quad t_z = t \cos \frac{\theta_z}{2}.$$
 (5.3)

These expressions suggest that instead of the Hamiltonian (5.1) we have to deal with an effective Hamiltonian which does not contain the Hund (sd-exchange) term whose contribution has already been accounted for in Eqns (5.3). The average energy of the effective Hamiltonian can be written in the following form

$$\langle H_{\text{eff}} \rangle = \frac{J'}{2} \left(\cos \theta_z + \cos \theta_{xy} \right)$$

$$+ \sum_{\mathbf{k}\sigma} \left[\varepsilon_+(\mathbf{k}) f\left(\varepsilon_+(\mathbf{k}) \right) + \varepsilon_-(\mathbf{k}) f\left(\varepsilon_-(\mathbf{k}) \right) \right], \quad (5.4)$$

where $\varepsilon_{\pm}(\mathbf{k})$ is the electron bare spectrum obtained through the equation

$$\det \|t^{\alpha\beta}(\mathbf{k}) - \varepsilon \delta_{\alpha\beta}\| = 0, \qquad (5.5)$$

and $f(\varepsilon)$ is the Fermi distribution function. From Eqn (5.5), one finds

$$\varepsilon_{\pm}(\mathbf{k}) = -\frac{4}{3} t_{xy}(\cos k_x + \cos k_y) - \frac{4}{3} t_z \cos k_z$$

$$\pm \left\{ \left[\frac{2}{3} t_{xy}(\cos k_x + \cos k_y) - \frac{4}{3} t_z \cos k_z \right]^2 + \frac{4}{3} t_{xy}^2 (\cos k_x - \cos k_y)^2 \right\}^{1/2}.$$
 (5.6)

The first term in Eqn (5.4) supplies the direct exchange energy, and the second is the contribution to the energy from the itinerant electrons renormalized by the interaction with the magnetic structure.

For a fixed electron concentration one calculates the average energy (5.4) at T = 0 for each pair of angles θ_{xy} and



Figure 16. Magnetic phase diagram for the average exchange model with degenerate e_g electrons [17].

 θ_z corresponding to the magnetic structures A, C, and G and then picks up the minimum value of this average. This yields a magnetic phase diagram in the (t/J', n) plane (Fig. 16). At very low electron number density *n*, the A structure is stable at all t/J'. As *n* increases, the figure indicates that phase C appears firstly, followed again by A (at high and low t/J'), and finally by ferromagnetic phase F. This particular phase succession is determined by the density of states in the electronic spectrum for these magnetic structures.

5.2 Comparison with experiment

Let us consider lanthanum manganite, $La_{1-x}M_xMnO_3$ (M = Ca, Sr), the best studied manganite of all. Two limiting cases of this system, LaMnO₃ and CaMnO₃, are both insulators, but their electronic structures differ in having the e_g states filled and empty, respectively. Thus, doping LaMnO₃ with calcium gives rise to collectivized hole states for x < 0.5, and to electronic states for x > 0.5. According to the standard DE model, the behavior of the manganites at low x should be similar to that for $x \sim 1$ (electron – hole symmetry). Experiments show, however, that hole and electron compounds behave very differently. For x < 0.5 we usually have metal ferromagnetic states, whereas for manganites with x > 0.5 a striped insulating phase with a dopingdependent period is typical.

This difference can be understood in terms of degenerate e_g states. In undoped LaMnO₃, e_g electrons are localized, the degeneracy being removed by orbital ordering. If we start doping this system, we may ignore the orbital degeneracy and apply the standard DE model. At the opposite extreme — if we are dealing with CaMnO₃, for example — a different situation obtains. Here the e_g states are empty, forcing us to take into account the two-fold degeneracy of the e_g states when putting an electron at an e_g level — hence the theoretical problem we have discussed above. From Fig. 16 we see that anisotropic magnetic structures dependent on the concentration of doped electrons must occur. Thus, for $t/J' \approx 4$ the phases

$$F(x \le 0.5), \quad A(0.5 \le x \le 0.6), \quad C(x \ge 0.6)$$
(5.7)

must be stable. Experimental data [88] show that the system $Nd_{1-x}Sr_xMnO_3$ (which is ferromagnetic for 0.25 < x < 0.5) exhibits type A antiferromagnetic ordering in the range 0.5 < x < 0.6 and that type C occurs for 0.6 < x < 0.8. In

 $Pr_{1-x}Sr_xMnO_3$ [89], the type A structure exists for 0.5 < x < 0.7. These data agree with the phase diagram and, in particular, with the section (5.7) of it. Furthermore, there is evidence that the unsaturated metal ferromagnetic state observed in Ca_{1-y}R_yMnO₃ [90, 91] constitutes also a canted antiferromagnetic state of type C [17].

One further manifestation of the degeneracy of the e_g state deserves mention. The calculation of the spectrum (5.6) shows that dispersion curves for the C phase are very nearly onedimensional. As is well known, disorder in 1d structures leads to localization. This explains why the C phase is insulating for electron doping y = 0.15. By the same token, since spectra in the A and ferromagnetic phases are of 2d and 3d nature, respectively, these structures are less sensitive to disorder and are therefore expected to be more metallic — which is indeed the fact ascertained in experiment.

6. Effects of electron-lattice interaction

6.1 Interaction of $e_{\rm g}$ electrons with lattice vibrations

The assumption that electrons interact only with localized spins set limits on the application of the DE model to the study of real materials. One possible extension of the model is to introduce an additional interaction between the electrons and the lattice — an approach necessitated, in particular, by the lattice distortion studies of Ref. [92], which indicated strong electron-lattice coupling to be present in the manganites. The behavior of the electron-lattice system is determined by the dimensionless coupling constant, namely, the ratio of the interaction energy to the kinetic energy of the electrons. The presence of a strong coupling may create a situation [13] in which the paramagnetic phase of the system has its electrons localized in the form of polarons, whereas lowering the temperature makes them delocalized in the ferromagnetic phase, where the long-range ferromagnetic order increases the kinetic energy, thus decreasing the effective electron-lattice coupling. This latter coupling explains the fact that the resistivity of CMR materials above $T_{\rm C}$ typically exceeds the characteristic Mott limit and indeed rapidly increases as the temperature is lowered.

The modeling of the interaction of electrons with localized spins and with phonons has been discussed in detail in Ref. [93] under the assumption that the properties of doped manganites depend to a great extent on the Jahn-Teller effect, in which the two-fold degenerate e_g -orbital electronic states are split via the coupling of the electrons to the lattice degrees of freedom.

For simplicity, the phonons in Ref. [93] are treated as localized classical oscillators. We will describe by vector **r** the displacement of the oscillator from its equilibrium position. Let us assume that as the oscillator is displaced from its equilibrium position r = 0, a restoring force appears, characterized by a coefficient k, which is independent of the site number. The Hamiltonian for the lattice degrees of freedom then can be written as

$$H_{\rm ph} = \sum_{i} \frac{1}{2} k \mathbf{r}_{i}^{2} \,. \tag{6.1}$$

The two-fold orbitally degenerate e_g electronic level can be split by interaction with an appropriate phonon mode. In the manganites, such a mode is characterized by a two-component vector $\mathbf{r} = (r_z, r_x)$, which is conveniently parameterized by the magnitude *r* and angle ϕ by writing $\mathbf{r} = r(\cos \phi, \sin \phi)$. The interaction in this case can be approximated by

$$H_{\rm el-ph} = g \sum_{i\alpha\beta\sigma} a^{\dagger}_{i\alpha\sigma} \tau^{\alpha\beta} a_{i\beta\sigma} \cdot \mathbf{r}_i \,. \tag{6.2}$$

Here, g is the electron-phonon coupling constant, and the vector $\mathbf{\tau} = (\tau_z, \tau_x)$ is composed of the Pauli matrices and operates in the space of orbital states.

Thus, we have to add to the DE-model Hamiltonian (3.21) the energy of interaction between the electrons and phonons and the energy of the phonons, giving

$$H = -\sum_{ij\alpha\beta\sigma} t_{ij}^{\alpha\beta} a_{i\alpha\sigma}^{\dagger} a_{j\beta\sigma} - \mu \sum_{i\alpha\sigma} a_{i\alpha\sigma}^{\dagger} a_{i\sigma\sigma}$$
$$- J_{\rm H} \sum_{i\sigma\sigma'} \mathbf{S}_{i} \cdot a_{i\alpha\sigma}^{\dagger} \mathbf{\sigma}_{\sigma\sigma'} a_{i\alpha\sigma'} + H_{\rm el-ph} + H_{\rm ph} , \qquad (6.3)$$

where a term with the chemical potential μ has also been added.

We next consider this model in the dynamical mean field approximation in the same manner as was done for the DE model with no electron – phonon coupling.

6.2 The dynamical mean field approximation to the DE model with lattice interaction

Again, we have to calculate the electron Green's function

$$\hat{G}(\mathbf{k}, \mathrm{i}\omega_n) = \frac{1}{\mathrm{i}\omega_n - \hat{\varepsilon}_{\mathbf{k}}^{\alpha\beta} + \mu - \hat{\Sigma}(\mathrm{i}\omega_n)}, \qquad (6.4)$$

which is now a tensor, $G_{\sigma\sigma'}^{\alpha\beta}$, in the orbital and spin spaces. In Eqn (6.4), $\hat{z}_{\mathbf{k}}$ is the bare spectrum corresponding to the transition matrix $t_{ij}^{\alpha\beta}$. Recall that in the DMF approximation the momentum dependence of the electron self-energy Σ is ignored, and all the physical properties are determined by the local Green's function $\hat{G}_{\mathrm{L}}(i\omega_n)$, defined as in Eqn (3.2).

We assume that the orbital space exhibits no long-range order and that the quantities $G_{L\sigma\sigma}^{\alpha\beta}$, and $\Sigma_{\sigma\sigma'}^{\alpha\beta}$ are proportional to the unitary matrix in indices $\alpha\beta$ in orbital space. Allowing for the possibility of formation of the ferromagnetic state with spontaneous magnetization along the *z* axis, the local Green's function is written as

$$\hat{G}_{L}(i\omega_{n}) = g_{0}(i\omega_{n}) + g_{1}(i\omega_{n})\sigma_{z}, \qquad (6.5)$$

and for the self-energy, in the same vein, we have

$$\hat{\Sigma}(\mathrm{i}\omega_n) = \Sigma_0(\mathrm{i}\omega_n) + \Sigma_1(\mathrm{i}\omega_n)\sigma_z$$

The quantities g_0 and g_1 are defined by the relationships

$$g_{0} = \frac{1}{4} \operatorname{Tr}^{(\alpha)} \operatorname{Tr}^{(\sigma)} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^{3}} \hat{G}_{\mathrm{L}},$$

$$g_{1} = \frac{1}{4} \operatorname{Tr}^{(\alpha)} \operatorname{Tr}^{(\sigma)} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^{3}} \hat{G}_{\mathrm{L}} \sigma_{z}.$$
(6.6)

For each momentum **k** we introduce the matrix $R_{\mathbf{k}}^{\alpha\beta}$ which diagonalizes the bare spectrum $\hat{\varepsilon}_{\mathbf{k}}$ as follows

$$\hat{\varepsilon}_{\mathbf{k}} = R_{\mathbf{k}} \begin{pmatrix} \varepsilon_{\mathbf{k}}^1 & 0\\ 0 & \varepsilon_{\mathbf{k}}^2 \end{pmatrix} R_{\mathbf{k}}^{-1} \,. \tag{6.7}$$

Using the theorem on the cyclic invariance of the trace of a matrix, Eqn (6.6) can be rewritten as

$$g_{0}(i\omega_{n}) = \frac{1}{4} \operatorname{Tr}^{(\alpha)} \operatorname{Tr}^{(\sigma)} \int d\varepsilon N(\varepsilon) \frac{1}{i\omega_{n} - \varepsilon + \mu - \hat{\Sigma}(i\omega_{n})},$$

$$(6.8)$$

$$g_{1}(i\omega_{n}) = \frac{1}{4} \operatorname{Tr}^{(\alpha)} \operatorname{Tr}^{(\sigma)} \int d\varepsilon N(\varepsilon) \sigma^{z} \frac{1}{i\omega_{n} - \varepsilon + \mu - \hat{\Sigma}(i\omega_{n})},$$

$$(6.9)$$

where the density of states $N(\varepsilon)$ is taken to be a half-disk of half-width W = 2t:

$$N(\varepsilon) = \frac{\sqrt{4t^2 - \varepsilon^2}}{2\pi t^2} \,. \tag{6.10}$$

Now let us derive equations for the basic quantities of the problem, $g_0(i\omega_n)$ and $g_1(i\omega_n)$ [93]. In the spirit of the DMF approximation, we introduce an effective one-site model characterized by a partition function of the form

$$Z_{\rm L} = \int r \, \mathrm{d}r \, \mathrm{d}\phi \int \mathrm{d}\mathbf{m} \exp\left[S_{\rm L}\right]. \tag{6.11}$$

Here, r and ϕ are the classical oscillator coordinates as defined above, $\mathbf{m} = \mathbf{S}/S$ is the unit vector of the localized spin, and all the integrals are ordinary — not functional — ones. The effective action $S_{\rm L}$ is clearly given by

$$S_{\rm L} = -\frac{1}{2} \frac{k}{T} r^2 + \sum_n \operatorname{Tr} \ln \left[a_0(\mathrm{i}\omega_n) + a_1(\mathrm{i}\omega_n) \sigma^z + J_{\rm H} S \mathbf{m} \cdot \boldsymbol{\sigma} + g \mathbf{r} \cdot \boldsymbol{\tau} \right] - \mathbf{h} \cdot \frac{S \mathbf{m}}{T} .$$
(6.12)

Here, the interaction energy between the localized spin and the external magnetic field \mathbf{h} has been added.

For the density of states in the form (6.10), the mean field parameters a_0 and a_1 in Eqn (6.12) are determined as follows. First, from Eqns (6.8) and (6.9) one constructs equations for the combinations $g_0 \pm g_1$, which in turn depend on the combinations $\Sigma_0 \pm \Sigma_1$. Then both of these equations are integrated with respect to energy using an explicit densityof-states expression, after which the functions $\Sigma_0 \pm \Sigma_1$ are eliminated using the definition

$$\Sigma_0 \pm \Sigma_1 = a_0 \pm a_1 + (g_0 \pm g_1)^{-1},$$

and the resulting equations for $g_0 \pm g_1$ are solved. As a result, the functions a_0 and a_1 are given by the equations [93]

$$a_0(\mathrm{i}\omega_n) = \mathrm{i}\omega_n + \mu - \frac{t^2}{4} \frac{\delta \ln Z_\mathrm{L}}{\delta a_0(\mathrm{i}\omega_n)}, \qquad (6.13)$$

$$a_1(\mathrm{i}\omega_n) = -\frac{t^2}{4} \frac{\delta \ln Z_\mathrm{L}}{\delta a_1(\mathrm{i}\omega_n)}.$$
(6.14)

Here, the components of the local Green's function (6.5) have been expressed in terms of the variational derivatives: $g_{0,1} = (1/4)\delta \ln Z_L / \delta a_{0,1}$.

In the limit $J_{\rm H} \to \infty$, one can simplify Eqns (6.13) and (6.14). Let us write down the argument of the function Tr ln in Eqn (6.12) in the form $a_0 + (a_1\hat{z} + J_{\rm H}S\mathbf{m})\cdot\mathbf{\sigma} + g\mathbf{r}\cdot\mathbf{\tau}$. It is easy to see that the eigenvalues of this expression are $a_0 \pm |a_1\hat{z} + J_{\rm H}S\mathbf{m}| \pm gr$. The eigenvalues

 $a_0 - |a_1\hat{z} + J_H S\mathbf{m}| \pm gr$, which correspond to high-energy states for $J_H \ge t$, will be excluded from consideration. As may be seen from Eqn (6.14), the quantity a_1 is of order t, so that $a_1 \ll J_H S$ and hence $|a_1\hat{z} + J_H S\mathbf{m}| \approx J_H S + a_1 m_z$. We now redefine a_0 and μ by incorporating the constant $J_H S$ into them, introduce the new variables $x = r\sqrt{k/t}$, $b_{0,1} = a_{0,1}/t$, $\lambda = g^2/kt$, $h_0 = hS/t$, and take t as the unit of measurement for the quantities T, ω_n and μ . We then define the angle θ of a localized spin by the relation $m_z = \cos \theta$ and arrive at the following expression for the effective action [93]

$$S_{\rm L}(x,\theta) = -\frac{x^2}{2T} + \sum_{n} \ln\left[(b_0 + b_1 \cos \theta)^2 - \lambda x^2\right] + h_0 \frac{\cos \theta}{T}$$
(6.15)

For the mean field parameters we obtain

$$b_0 = \mathrm{i}\omega_n + \mu - \frac{1}{2} \int_0^\infty x \,\mathrm{d}x$$
$$\times \int_1^{-1} \mathrm{d}\cos\theta \, P(x,\theta) \frac{b_0 + b_1 \cos\theta}{(b_0 + b_1 \cos\theta)^2 - \lambda x^2} \,, \qquad (6.16)$$

$$b_1 = -\frac{1}{2} \int_0^\infty x \, dx$$

$$\times \int_1^{-1} d\cos\theta \, P(x,\theta) \cos\theta \frac{b_0 + b_1 \cos\theta}{(b_0 + b_1 \cos\theta)^2 - \lambda x^2} \,, \quad (6.17)$$

where

$$P(x,\theta) = \frac{1}{Z_{\rm L}} \exp\left[S_{\rm L}(x,\theta)\right].$$
(6.18)

According to Eqn (6.5), the local Green's function G_L has only diagonal components

$$G_{L\uparrow\uparrow}(i\omega_n) = i\omega_n + \mu - b_0(i\omega_n) - b_1(i\omega_n), \qquad (6.19)$$

$$G_{\mathbf{L}\downarrow\downarrow}(\mathbf{i}\omega_n) = \mathbf{i}\omega_n + \mu - b_0(\mathbf{i}\omega_n) + b_1(\mathbf{i}\omega_n).$$
(6.20)

In terms of this Green's function, the spectral intensity and the conductivity are given by formulas

$$A(\omega) = -\frac{\operatorname{Tr}\operatorname{Im}\mathbf{G}_{L}(\omega + \mathrm{i}\delta)}{\pi}, \qquad (6.21)$$

$$\sigma(i\omega_n) = \frac{2}{i\omega_n} \int d\varepsilon_{\mathbf{k}} N_O(\varepsilon_{\mathbf{k}}) T$$
$$\times \sum_{i\omega_m} \operatorname{Tr}^{(\sigma)} \left[\mathbf{G}(\mathbf{k}, i\omega_m) \mathbf{G}(\mathbf{k}, i\omega_m + i\omega_n) \right]. \quad (6.22)$$

The numerical factor 2 in Eqn (6.22) came from the trace over the orbital states. In writing Eqn (6.21), the convention e = t = 1 was adopted.

Another quantity of interest is the average kinetic energy of the electrons *K*:

$$K = \operatorname{Tr}^{(\sigma)} \sum_{\alpha\beta} \int \frac{\mathrm{d}\mathbf{k}}{(2\pi)^3} \, \varepsilon_{\mathbf{k}}^{\alpha\beta} \langle a_{\mathbf{k}\alpha\sigma}^{\dagger} a_{\mathbf{k}\beta\sigma'} \rangle \,. \tag{6.23}$$

We can now express the averages of the Fermi operators in terms of the electron Green's function in the momentum representation, Eqn (6.4), and then go over to the local Green's function, taking into account the integral with respect to the momenta. Eventually we find

$$K = 2T \sum_{n} \left\{ \left[G_{L\uparrow\uparrow} \right]^2 + \left[G_{L\downarrow\downarrow} \right]^2 \right\}.$$
(6.24)

The magnetization *m* and the root-mean-square lattice displacement $\langle x^2 \rangle$ are written as

$$m = \int_0^\infty x \,\mathrm{d}x \int_{-1}^1 \,\mathrm{d}\cos\theta\cos\theta \,P(x,\theta)\,, \tag{6.25}$$

$$\langle x^2 \rangle = \int_0^\infty x \, \mathrm{d}x \int_{-1}^1 \, \mathrm{d}\cos\theta \, x^2 P(x,\theta) \,. \tag{6.26}$$

We now proceed to investigate the solutions (6.16) and (6.17) of the basic equations of the problem. In the DMF approximation, the main contribution to the integrals in these expressions at T = 0 is made by the region of small angles $(\cos \theta = 1)$, hence $b_1 = b_0 - \omega + \mu$, and from Eqn (6.19) it is easily seen that the function $G_{L\downarrow\downarrow}$ vanishes. The only nonzero function, it turns out, is that with components parallel to the magnetization vector. For $T > T_C$, there is no long-range order, and therefore $b_1 = 0$. The θ -angle dependence disappears in this case.

Consider first the limit $\lambda = 0$. For T = 0, we have from Eqns (6.16) and (6.17):

$$b_0 + b_1 = \frac{1}{2} \left[\omega + \mu - i\sqrt{4 - (\omega + \mu)^2} \right].$$
 (6.27)

This result corresponds to the event of noninteracting electrons. The imaginary part of the local Green's function is different from zero in a semicircular band with a total width 4t. The spectral intensity has a maximum value at $\omega = -\mu$. The self-energy Σ in this case is zero.

For $T > T_{\rm C}$ and $\lambda = 0$, $b_1 = 0$ and the equation for b_0 takes the form

$$b_0 = \frac{1}{2} \left[\omega + \mu - i\sqrt{2 - (\omega + \mu)^2} \right].$$
 (6.28)

Here, the imaginary part of the local Green's function is nonzero in a semicircular band with a total width $2\sqrt{2}t$, the reduction in the band width by a factor of $\sqrt{2}$ reflecting the absence of correlations between localized spins. The selfenergy then takes the form

$$\Sigma(\omega) = -b_0 = \frac{i}{2}\sqrt{2 - (\omega + \mu)^2} - \frac{1}{2}(\omega + \mu).$$
 (6.29)

Notice that the expressions (6.27) and (6.28) are equivalent to the respective expressions (3.38) and (3.39) derived for the simplified DE model. For λ finite, Eqns (6.16) and (6.17) can only be solved numerically.

6.3 Comparison of the theory and experiment

Let us discuss the results of the numerical analysis made in Ref. [93]. We start by considering the Curie temperature, $T_{\rm C}$, shown in Fig. 17. As the coupling constant λ increases, $T_{\rm C}$ decreases, the rate of decrease being especially fast for $\lambda \approx 1$.

The temperature dependence of the resistivity for n = 1 is displayed in Fig. 18. The kinks in the curves correspond to the Curie temperature. Immediately below $T_{\rm C}$ the resistivity declines with decreasing *T*, presumably because the magnetic contribution to scattering is reduced and the effective electron-phonon coupling becomes weaker. The 'metal' $(d\rho/dT > 0)$ and 'semiconductor' $(d\rho/dT < 0)$ regimes can be recognized in the curves. For $T > T_{\rm C}$, the value $\lambda = 1$



Figure 17. Curie temperature versus electron – lattice coupling constant for n = 1 (heavy solid line), n = 0.75 (thin solid line), and n = 0.5 (thin dashed line). Analytical results for a zero coupling constant are shown as dots. Strong-coupling analytical results for n = 1 are shown as the dotted line [93].



Figure 18. Temperature variation of resistivity for n = 1 for a number of λ values: 0.32 (lower curve); 0.71, 1.00, 1.08, 1.12, 1.15, and 1.20 (upper curve) [93].

determines the boundary between these regimes $(d\rho/dT = 0)$, while for $T < T_C$ the boundary between them lies at higher values $\lambda \sim 1.15$. Calculations for n = 0.75 and n = 0.5 yield similar results. Comparison with Fig. 18 shows that in order for the curve $d\rho/dT$ to follow a semiconductor-type course the coupling constant λ in the case n = 0.75 must be larger than for n = 1, and in the case n = 0.5 even more so. Notice the close analogy between the behavior of $\rho(T)$ as a function of λ at a given electron concentration (see Fig. 18) and the behavior of $\rho(T)$ as a function of x in the manganite $La_{1-x}Sr_xMnO_3$ (see Fig. 4) [47, 94].

The temperature dependences of the mean square of lattice distortions calculated in Ref. [93] for the case n = 1 have been confirmed by measurements of the Debye–Waller factor in oxygen in Refs [95, 96]. The temperature $T_{\rm C}$ appears as a point of kink in two straight lines on the experimental graphs. For $T > T_{\rm C}$, the straight lines exhibit a smaller slope than for $T < T_{\rm C}$, which is attributed to the enhancement in the electron–phonon coupling.

The interplay between the double exchange interaction and the electron-phonon coupling also explains other properties of the manganites, in particular, the behavior of the resistivity in a magnetic field [93]. The field aligns localized spins, increases the kinetic energy of the electrons, and decreases the effective electron-lattice coupling constant. As a result, increasing the magnetic field from zero changes the temperature dependence of the resistivity dramatically, 'smoothing out' the peaks and kinks in the dielectric and the metal regimes, respectively. The CMR effect is heightened with increasing coupling constant λ . It is worth noting that the electrical resistivity vs. magnetic field curves of Ref. [93] look like those for the magnetoresistivity of La_{1-x}Sr_xMnO₃ obtained in Ref. [97].

Interesting results have been found for optical conductivity in the n = 1 case. As the temperature and effective constant λ are increased, the Drude optical conductivity curve valid for the low temperatures and weak electron– lattice coupling goes over into a broad single peak at a nonzero frequency, which corresponds, ultimately, to electrons being localized by phonons [93]. The optical conductivity curves $\sigma(\omega)$ obtained in Ref. [93] are very much like the experimental ones of Refs [98, 99].

It should be noted that the question of the electron– lattice coupling has also been addressed in Ref. [100], using a variational wave function to study the role of the electron– phonon interaction in the DE model. To explain the isotope effect in the manganites [101], an original method based on the bipolaron model has been proposed in Refs [102, 103].

7. Open problems in the physics of manganites

7.1 Metal-insulator transition

One of the most remarkable physical properties of the manganites is the occurrence of a metal ferromagnetic phase within a certain region in the (T, n) phase plane. To cross the boundary of this region, whether by varying T or x, is to perform a metal-insulator type phase transition (or cross-over). The study of such transitions requires an understanding of the nature of the phases adjacent to the metal region.

One of the problems in the physics of the manganites is how to describe the paramagnetic phase for compositions at which the ferromagnetic state is realized. In the range $T > T_{\rm C}$, the manganites usually show a weak decrease in the electrical resistivity with temperature. This is not in serious disagreement with the DE-model DMF-approximation prediction that $\rho(T)$ is virtually constant for $T > T_{\rm C}$. At the same time, in the region about the onset of ferromagnetism at small x, $\rho(T)$ passes through a maximum near $T_{\rm C}$ and then decreases exponentially with temperature, as shown in Fig. 4. The same behavior of $\rho(T)$ is observed in ferromagnetic semiconductors [7]. An elegant explanation for this phenomenon has been given by Kogan and Auslender [104], based on the Anderson localization mechanism due to nondiagonal spin disordering in a system described within the framework of the DE model.

The effective DE-model Hamiltonian involves hopping over the lattice, with the matrix elements dependent on how the site spins are oriented relative to one another. It is assumed that in the absence of long-range magnetic order or near T_C , where large fluctuations in magnetization occur, this (nondiagonal) disorder may lead to the localization of the carriers. The transport properties of the system must then be determined by the position of the mobility edge E_c relative to the chemical potential μ ; in particular, the electrical resistivity should be given by formula

$$\rho(T) = \rho_0 \exp\left(\frac{E_c - \mu}{kT}\right). \tag{7.1}$$

The DE-model mobility edge has been calculated in the limit $S \ge 1$ as the radius of convergence of a series for the selfenergy part of the electron Green's function [104]. It was found that E_c depends on the temperature through two quantities, the magnetization and the pair correlation function $\langle S_0 S_1 \rangle$ for spins at nearest-neighbor sites. Substitution of the resulting expression for E_c into Eqn (7.1) leads to the following expression for the electrical resistivity

$$\rho(T) = \rho_0 \exp\left(\frac{1 - \langle \mathbf{S}_0 \mathbf{S}_1 \rangle / S^2}{1 + \langle S^z \rangle / S} \frac{W}{4kT}\right),\tag{7.2}$$

where W = 2zt is the bare band width. The two factors in the exponential depend on the temperature in an opposite manner. For $T < T_{\rm C}$, the first factor is small in the ferromagnetic region, and hence so also is $\rho(T)$. In the vicinity of $T_{\rm C}$, this factor very sharply increases and for $T > T_{\rm C}$ it levels off and remains constant. Thus we see that formula (7.2) does describe the observed maximum in $\rho(T)$ in the vicinity of the Curie point for x near the boundary of the metal phase.

Another possible mechanism for metal-insulator phase transitions was suggested by Gor'kov [9]. When a parent compound is doped with a bivalent element, the manganite is known to remain in the dielectric state until a certain doping level is achieved. Thus for $La_{1-x}Sr_xMnO_3$ the metallization occurs only at $x_c = 0.16$. It is assumed that an isolated Sr atom produces a hole in the 3d states of a Mn ion, which cannot be localized on any particular ion but rather belongs to all the eight Mn ions (i.e. becomes collectivized) nearest to the Sr. Coulomb forces keep the hole near the charged impurity center. At a certain electron concentration x_c , the overlapping of the wave functions of the impurity-center d states gives rise to an infinite cluster, in which the spins on the centers are all aligned due to the delocalization of the hole states. For $x > x_c$, a macroscopic volume of the ferromagnetic phase appears, sprouting up through the antiferromagnetic dielectric matrix. Thus we see that the metallicity and the ferromagnetic state appear in a manganite as a consequence of a percolation process. For the cubic lattice, the critical percolation concentration is $x_c = 0.31$, but because of the delocalization of a hole on Mn atoms adjacent to the Sr atom the percolation limit is expected to be lower. This percolation concept can be extended to the case in which holes do not localize near an impurity center but instead a phase separation to ferromagnetic phase islands occurs within an antiferromagnetic dielectric matrix. The metallization of the system in this case can also be thought of as a percolation process in an uncompensated finely divided ferromagnetic phase. There exists some experimental evidence to back up this percolation idea. In particular, this concept provides a natural way to explain the critical concentration $x_c = 0.16$ for lanthanum-strontium manganite.

A third possible mechanism for the metal-insulator transition involves the Jahn-Teller polaron concept already discussed in the preceding section. According to the calculations of Ref. [105], which are based on the Hamiltonian (6.3) and thus take into account the interaction of degenerate electrons with local atomic displacements, charge carriers in the paramagnetic phase are small-radius polarons, whose

localized nature makes it possible for the paramagnetic phase to become insulating. Experimentally this idea is supported by the observation of large Jahn – Teller distortions [106], and also by the data of Refs. [107, 108] which show small-radius polarons to determine the transport properties at high temperatures.

The essence of the polaron mechanism is as follows [105]. At high enough values of the effective electron-lattice coupling λ , electrons become localized polarons outside the region of the metal ferromagnetic phase, i.e. for $T > T_C(x)$ and $x < x_c$. In the ferromagnetic phase, charge carriers are delocalized because the effective coupling λ , i.e. the ratio of the polaron energy to the band width, decreases due to the increase of the band width in the ferromagnetic phase. The decrease of λ below a certain critical value results in the delocalization of the carriers.

The above concept was developed in Ref. [109] using the reasonable assumption that at given x and T only some of the carriers become localized polarons above $T_{\rm C}(x)$. If $n_{\rm p}$ is the concentration of the polarons, then $n_{\rm c} = n - n_{\rm p}$ is the number density of delocalized electrons. In the study of the transition between the PI (paramagnetic insulator) and FM (ferromagnetic metal) phases it is essential to determine the balance between these two carrier types. For this purpose, the simplest possible statistical model is proposed, which includes spin polarization in a lattice gas of Fermi carriers with free energy

$$F = -tn_{\rm c} + (T - tn_{\rm c})m^2 + \frac{\beta}{2}tn_{\rm c}m^4 - \varepsilon_{\rm p}n_{\rm p}$$
$$+ T(n_{\rm c}\ln n_{\rm c} + n_{\rm p}\ln n_{\rm p}), \qquad (7.3)$$

where ε_p is the polaron energy. The magnetization *m* and the polaron concentration n_p should be considered as two interacting order parameters. The analysis of minimization equations for the energy (7.3) shows that the phase transition $PI \rightarrow FM$ occurs at any *n*, provided $\beta < 1/(n \ln 2)$, with $T_{\rm C}(x)$ increasing monotonically with *n*. For $\beta > 1/(n \ln 2)$, the ferromagnetic phase exists if n is above a certain critical value. For ε_p and t of order 1 eV, the electrical resistivity calculated from the model (7.3) sharply increases as the temperature approaches $T_{\rm C}$, and then falls off rapidly for $T > T_{\rm C}$. In this temperature range, the CMR effect takes place. However, not all predictions of this model are in agreement with the experimental findings on the manganites. For example, the model predicts a first-order phase transition $PI \rightarrow FM$ with fairly large jumps in the quantities m and $n_{\rm p}$, and this issue is inconsistent with experiment. Also, it predicts too large intensities (~ 50 T) for the magnetic field at which a marked CMR effect is observed.

The authors of Ref. [109] therefore proposed another model, which involves large-radius polarons unlike those just outlined, and uses the Varma approach [68] complemented by the introduction of the Jahn – Teller effect. It is believed that percolation in a system of such polarons gives rise to a more adequate model for describing $PI \rightarrow FM$ phase transitions in manganites.

The mechanism of metal-insulator transitions in manganites is still to be understood. Another unresolved problem concerns the so-called charge ordering phenomena observed in these materials.

7.2 Charge ordering

The idea of charge ordering in manganites dates back to Goodenough [110] and was prompted by the discovery in neutron diffraction data [2] of superstructural peaks of no relation to magnetism. Specifically, the ordering process in question involves the Mn^{3+} and Mn^{4+} ions. Half-doping with a bivalent ion (x = 0.5) may clearly lead to the lattice period doubling of the crystal (Fig. 19a). Charge ordering must also be accompanied by orbital ordering, one possible realization of which is shown in Fig. 19b. In this figure, distorted octahedrals of oxygen ions surrounding lattice sites occupied by Jahn-Teller Mn^{3+} ions are shown schematically. The orbital ordering appears as a regular array of alternately long and short octahedral axes. Clearly, charge ordering also forms two spin sublattices, because the Mn^{3+} and Mn^{4+} ions have spin 2 and 3/2, respectively.



Figure 19. Charge ordering (a) and one possible mode of orbital ordering (b) for a manganite at x = 0.5.

Referring the reader to a recent review article [20] for a more detailed discussion of charge ordering, we should mention here one further aspect of this phenomenon, the socalled striped structures discovered in the manganites [111, 112]. Unlike high-temperature superconductors, where such structures had been found previously, in the manganites they exist in the insulating phase. Specifically, they look like alternating chains of Mn³⁺ and Mn⁴⁺ ions, the most common element being three nearest-neighbor chains of identical ions in the succession $Mn^{3+} - Mn^{4+} - Mn^{3+}$. Such chains appear to result from the elastic interactions due to the Jahn-Teller-distorted environment of the Mn³⁺ ions. It is believed that between such three-chain stripes already formed in the material there exist repulsion forces which prevent them from sticking together. The stripes are observed in 'commensurate' compositions, when the ratio between Mn³⁺ and Mn^{4+} concentrations — i.e. between x and 1 - x — is that of some of the least positive integers. 'Incommensurate'composition material breaks up into domains with the nearest stable compositions. It was observed, for example, that at x = 5/8 the system breaks up into domains with x = 2/3 and x = 1/2, occupying 75% and 25% of the volume, respectively [113]. It has also been observed that the striped structure disappears when a magnetic field or pressure is applied [113, 114]. Since striped structures in weakly doped manganites have only been found experimentally (Fig. 20) but not predicted theoretically, neither their formation mechanisms nor their impact on the physical properties of the manganites are as yet known.

8. Conclusions

A very fundamental question which remains to be discussed is how adequately the DE model describes the physics of CMRrevealed manganites. Several dynamical mean field calculations [11, 61] show good qualitative agreement with the



experimental data. This is true, in particular, of the general structure of the temperature–electron concentration phase diagram containing a homogeneous ferromagnetic phase, various metal or insulating antiferromagnetic phases, and inhomogeneous separated phases. Also magnetization and various transport properties are well accounted for by the DE model, including the temperature, electron-concentration, and field variation of electrical resistivity and optical conductivity.

When it comes to quantitative comparison, the situation is different, however. It was pointed out long ago [13] that the DE model overpredicts the Curie temperature and underpredicts the electrical resistivity, and since the reason for this is electron scattering by magnetization fluctuations, corrections for the interaction of electrons with lattice degrees of freedom had to be introduced into the theory. This gives a much better agreement with experiment for the Curie temperature and $\rho(T)$. Moreover, the inclusion of Jahn-Teller distortions, easy to observe experimentally, makes it possible to understand the nature of the paramagnetic insulating phase in the electron concentration range where ferromagnetic ordering exists. The possibility of polaron localization allows a new approach to the problem of finding the mechanism of the metal-insulator transition, currently the most important in the physics of the manganites.

Thus, as far as the most general physical properties of the manganites are concerned, it can be argued that the DE model with an electron-lattice interaction is good to describe the physics of the manganites, but when it comes to the details and quantitative aspects, instead of answers, it is questions which turn out to dominate the subject. To clear things up, further detailed experimental research is needed, the top priority being the physics of the metal-insulator transition and whatever has relevance to it.

Our primary concern in this review was with the DE model, which together with the Hubbard model [115] and the tJ model [116] is one of the fundamental investigation tools in the theory of strongly correlated systems. The question of whether and how far this model encompasses the physics of the manganites is too large for one review article to resolve. Experimental studies of the manganites are far from over, and further attempts at understanding this broad subject theoretically are of course expected to be made occasionally down the road.

The manganites are a unique system, whose electronic, magnetic, and lattice properties are all intertwined and may be controlled by varying the chemical composition and the doping level. We have begun, in the last few years or so, to witness research interest in magnetic materials shifting from metals and alloys to the transition metal oxides, as the manganites with their CMR features and cuprates with high-temperature superconductivity most clearly exemplify.

These two classes of oxides have much in common. Oxides in either class have a perovskite structure, their parent compounds are antiferromagnetic insulators, and the physics of electrons in them is determined by Mn and Cu ions surrounded by oxygen ligands. Substitution of a bivalent element for a trivalent one creates holes in a system of Mn ions in the manganites or in a system of Cu ions in cuprates, the holes acting as charge carriers in either case. The similarities end there, however, and the difference in the interactions involved — i.e. the strong sd-exchange in the former case, and the strong on-site Coulomb interaction in the latter — comes into play giving rise to two different and totally unrelated phenomena: CMR in the manganites and HTSC in the cuprates.

Even though the major interactions operating in the manganites and cuprates are different, the two classes often share common physical properties. Among them are phase separation and the unusual, stripe-structured charge ordering — presumably a manifestation of the strong electron correlation existing in either class. The two systems are very complicated. Note that in the case of the cuprates, fifteen years of extensive study has left many important questions of their low-energy physics unanswered. For the manganites, the period of intense research activity (apart from the long prehistory of the current explosive growth) has been only half as long, so it comes as no surprise that more time is needed to better understand them.

We conclude by referring the reader to Refs [117-119] as the most recent theoretical works on the subject of this review.

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