Orbital effects in manganites

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Abstract

In this paper I give a short review of some properties of the colossal magnetoresistance manganites, connected with the orbital degrees of freedom. Ions Mn^{3+}, present in most of these compounds, have double orbital degeneracy and are strong Jahn-Teller ions, causing structural distortions and orbital ordering. Mechanisms leading to such ordering are shortly discussed, and the role of orbital degrees of freedom in different parts of the phase diagram of manganites is described. Special attention is paid to the properties of low-doped systems (doping $0.1 \leq x \leq 0.25$), to overdoped systems ($x > 0.5$), and to the possibility of a novel type of orbital ordering in optimally doped ferromagnetic metallic manganites.

1 Introduction

When considering the properties of real systems with strongly correlated electrons, such as transition metal (TM) oxides, one often has to take into account, besides the charge and spin degrees of freedom, described e.g. by the

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[*]This paper is dedicated to Prof. E. Müller-Hartmann on the occasion of his 60th birthday

nondegenerate Hubbard model, also the orbital structure of corresponding TM ions. These orbital degrees of freedom are especially important in cases of the so-called orbital degeneracy—the situation when the orbital state of the TM ions in a regular, undistorted coordination (e.g. in a regular O_6-octahedron) turns out to be degenerate [1, 2, 3]. This is e.g. the situation with the ions Cu^{2+} (d^9), Mn^{3+} (d^4), Cr^{2+} (d^4), low-spin Ni^{3+} ($d^7 = t_{2g}^6 e_g^1$). This degeneracy gives rise in an isolated centre to the famous Jahn-Teller effect [4], and in concentrated systems—to the cooperative transition which may be viewed as simultaneous structural phase transition lifting this orbital degeneracy (cooperative Jahn-Teller transition), as an orbital ordering (OO) and as a quadrupolar ordering (this latter terminology is often used in rare earth compounds).

All these effects play very important role in the materials which became very popular recently—in manganites with the colossal magnetoresistance (CMR). The typical example is the system $La_{1-x}Ca_xMnO_3$ (there may be other rare earths, e.g. Pr, Nd, or Bi instead of La, or other divalent cations—Sr, Ba, Pb—instead of Ca; there exist also layered materials of this kind). The typical phase diagram of these systems is shown schematically on fig. 1. The starting undoped material $LaMnO_3$, which is an antiferromagnetic insulator, contains typical Jahn-Teller ions Mn^{3+} (electronic configuration $t_{2g}^3 e_g^1$)—i.e. it is orbitally doubly-degenerate, see fig. 2. Thus we can expect that the orbital degrees of freedom may significantly influence the properties of CMR manganites—the idea which is largely supported by experiments. In this short paper I will try to review some of the aspects of the physics of manganites connected with orbital degrees of freedom. This is actually already quite large and well developed field, and of course I will not be able to cover this whole field; much of the material presented will be based on the investigations in which I myself participated. Some of the general concepts used below are also presented in [8, 9].

This paper is dedicated to Prof. Erwin Müller-Hartmann on the occasion of his 60-th birthday. During many years of my acquaintance with him, especially during my stay in Cologne (1990–1992) I benefited a lot from many contacts with him. Also lately we had very interesting and fruitful discussions in connection with my recent, still controversial idea about "complex orbitals" ordering which is also presented below in this paper. I am happy to use this opportunity to wish him all the best in the years to come.

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2 Main features of the phase diagram of manganites: orbital effects

As already mentioned above, the undoped LaMnO$_3$ with the perovskite structure contains strong Jahn-Teller ions Mn^{3+}. They are known always to induce rather strong local distortion in all the insulating compounds containing them [2]. Also here it is well known that there exists an orbital ordering and concomitant lattice distortion in LaMnO$_3$: e_g-orbitals of Mn^{3+} ions are ordered in such a way that at the neighbouring Mn sites the alternating x^2 and y^2-orbitals are occupied, i.e. the local O$_6$-octahedra are alternatingly elongated along x and y-directions, see fig. 3.

Orbital ordering is also known to exist in most manganites in another well-defined region of the phase diagram—at half-doping $x = 0.5$. In this situation there occurs with decreasing temperature the charge ordering—the checkerboard arrangement of Mn^{3+} and Mn^{4+} ions in the basal plane, see fig. 4 [5, 6, 1]. The Mn^{3+}-ions with localized electrons again have an orbital degeneracy (Mn^{4+} ions are nondegenerate, cf. fig. 2) and develop the orbital ordering shown in fig. 4. Both the charge ordering (CO) and the OO occur simultaneously at the same temperature, although from some data it follows that probably the CO is the driving force, and the OO follows it [7]; this however is still an open question.

According to the well-known Goodenough–Kanamori–Anderson rules (see e.g. [1, 8, 9]) the magnitude and even the sign of the magnetic exchange depend on the type of orbitals occupied. Thus if the occupied by one electron (half-filled) orbitals are directed towards one another, one has a strong antiferromagnetic coupling; if however these orbitals are directed away from each other (are mutually orthogonal, as e.g. in fig. 3) we would have a ferromagnetic interaction. That is why the undoped LaMnO$_3$ (fig. 3) has the A-type magnetic ordering—the spins in the (x, y)-plane order ferromagnetically, the next xy-layer being antiparallel to the first one.

Similarly, the exchange between Mn^{3+} and Mn^{4+} ions is ferromagnetic if the orbital of Mn^{3+} ion is directed towards Mn^{4+} and antiferromagnetic if it looks away from it. This gives rise to the very specific CE-type magnetic structure for $x = 0.5$ manganites, shown in fig. 4: we have here the ferromagnetic zigzags, stacked antiferromagnetically. Recall now that according to the double-exchange picture ([10], see also [8]) electrons can easily move on

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the ferromagnetic background, but electron hopping is forbidden or at least strongly suppressed if the spins are antiparallel. Then one immediately sees that the motion of electrons in the CE-background shown in fig. 4 becomes essentially one-dimensional—it is confined to the ferromagnetic zigzags shown in this figure [11, 12]. One may show that due to a special topology of these zigzags (the presence of the edge and corner sites, different orbitals occupation), the gap opens in the $1d$ tight-binding spectrum of electrons even if we do not assume the charge ordering [11, 12]. Charge ordering appears when we add in this situation not even the intersite Coulomb repulsion (which would definitely prefer to stabilize the CO state), but the on-site Hubbard repulsion [12]. What is the actual mechanism leading to the CE-type (charge, orbital and magnetic) ordering in $x = 0.5$ manganites, will be discussed in the next section.

There are two more regions of the phase diagram of fig. 1 in which orbital effects apparently play an important role, although the detailed picture is less clear. These are the low-doped region $0.1 \leq x \leq 0.2 - 0.3$ (depending on the specific system considered) in which one often observes ferromagnetic insulating (FI) and often charge-ordered phase. This is the case of $La_{1-x}Ca_xMnO_3$ ($0.1 \leq x \leq 0.25$), $La_{1-x}Sr_xMnO_3$ close to $x = \frac{1}{8}$ ($0.1 \leq x \leq 0.18$) [13, 14] or $Pr_{1-x}Ca_xMnO_3$ ($0.15 \leq x \leq 0.3$) [6].

It is rather uncommon to have the FI state: typically insulating material of this class are antiferromagnetic, and ferromagnetism goes hand in hand with metallicity which finds natural explanation in the model of double exchange [10]. The only possibility to obtain the FI state in perovkites is due to a certain particular orbital ordering favourable for ferromagnetism [8] (FI state can appear also in systems in which there exists the 90°-superexchange—the TM–O–TM angle is close to 90°). But what is the detailed ordering in this low-doped region, is not completely clear, see below.

Another interesting, and much less explored, region is the overdoped manganites, $x > 0.5$. Typically in this case we have an insulating state, sometimes with the CO and OO state in the form of stripes [15] or bistripes [16], see fig. 5.

The choice between these two options is still a matter of controversy (see e.g. [15, 17]), as well as the detailed type of magnetic ordering in this case. I will return to this point in sec. 5; in any case we see that in this stripe-like phase the orbital degrees of freedom definitely play an important, and maybe decisive role—see sec. 5.

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Returning to magnetic properties of overdoped manganites $x > 0.5$, one should mention an important fact: the very strong asymmetry of the typical phase diagram of manganites. As seen e.g. from fig. 1, there usually exists a rather large ferromagnetic metallic region (FM) for $x < 0.5$, but nearly never for $x > 0.5$ (only rarely does one observe bad metal and unsaturated ferromagnetism in a narrow concentration range in some overdoped manganites [18]). However from the standard double-exchange model one can expect the appearance of a FM phase not only in hole-doped $LaMnO_3$ ($x < 0.5$) but in electron-doped $CaMnO_3$ ($x > 0.5$) as well. Orbital degeneracy may play some role in explaining this asymmetry [19]—see sec. 5.

There exists also a problem what are the orbitals doing in the optimally doped ferromagnetic and metallic manganites. Usually one completely ignores orbital degrees of freedom in this regime, at least at low temperatures; this is supported by the experimental observations that the MnO_6-octahedra are completely regular in this case. There is however a possibility that there still exists in this case an orbital ordering, but of completely novel type, not accompanied by any lattice distortion—an ordering of complex orbitals [40, 41]. This, still rather controversial point will be discussed in sec. 6.

Finally, one can also ask a question—which role do orbital degrees of freedom and Jahn-Teller play at elevated temperature, in particular in disordered states. These questions will be shortly discussed in sec. 7.

3   Mechanisms of Orbital Ordering

Before discussing particular situations in different doping ranges, it is worthwhile to shortly discuss the general question of possible interactions of degenerate orbitals which can lead to orbital ordering. In transition metal compounds there are essentially two such mechanisms. The first one is connected with the Jahn-Teller interaction of degenerate orbitals with the lattice distortions, see e.g. [20]. Another mechanism was proposed in 1972 [21], see also [2], and is a direct generalization to the case of orbital degeneracy of the usual superexchange [22].

A convenient mathematical way to describe orbital ordering is to introduce operators T_i of the pseudospin $\frac{1}{2}$, describing the orbital occupation, so that e.g. the state $|T^z = \frac{1}{2}\rangle$ corresponds to the occupied orbital $|z^2\rangle$, and

$|T^z = -\frac{1}{2}\rangle$—to $|x^2 - y^2\rangle$. The first one corresponds to a local elongation of the O_6-octahedra (distortion coordinate $Q_3 > 0$) and the second—to local contraction $Q_3 < 0$ [23]. The second degenerate E_g-phonon which can also lift electronic e_g-degeneracy, Q_2, corresponds to a pseudospin operator T^x. One can describe an arbitrary distortion and corresponding wave function by linear superpositions of the states $|T^z = +\frac{1}{2}\rangle$ and $|T^z = -\frac{1}{2}\rangle$

$$|\theta\rangle = \cos\frac{\theta}{2}|\frac{1}{2}\rangle + \sin\frac{\theta}{2}|-\frac{1}{2}\rangle \tag{1}$$

where θ is an angle in (T^z, T^x)-plane.

The first, Jahn-Teller mechanism of the orbital ordering starts from the electron–phonon interaction which in our case can be written in the form

$$H = \sum g_{iq}[T_i^z(b_{3q}^\dagger + b_{3,-q}) + T_i^x(b_{2q}^\dagger + b_{2,-q})] + \sum \omega_{\alpha q} b_{\alpha q}^\dagger b_{\alpha q} \tag{2}$$

where $\alpha = 2; 3$ and $b_3^\dagger$ and $b_2^\dagger$ are the phonon operators corresponding to Q_3 and Q_2 local modes. Excluding the phonons by a standard procedure, one obtains the orbital interaction having the form of a pseudospin–pseudospin interaction

$$H_{eff} = \sum_{ij} J_{ij}^{\mu\nu} T_i^\mu T_j^\nu \tag{3}$$

where

$$J_{ij} \sim \sum_q \frac{g_q^2}{\omega_q} e^{iq(R_i - R_j)} \tag{4}$$

and $\mu, \nu = x, y$. Due to different dispersion of different relevant phonon modes, and to anisotropic nature of electron–phonon coupling, the interaction (3) is in general anisotropic.

Similarly, the exchange mechanism of orbital ordering may be described by the Hamiltonian containing the pseudospins T_i, but also ordinary spins $\vec{S}_i$. It can be derived starting from the degenerate Hubbard model [21], and has schematically the form

$$H = \sum_{ij}\{J_1 \vec{S}_i \vec{S}_j + J_2(T_i T_j) + J_3(\vec{S}_i \vec{S}_j)(T_i T_j)\}. \tag{5}$$

Here the orbital part $(T_i T_j)$, similar to (3), is in general anisotropic, whereas the spin exchange is Heisenberg-like. In contrast to the Jahn-Teller induced interaction, the exchange mechanism describes not only the orbital and spin

orderings separately, but also the coupling between them (last term in (5)). This mechanism is rather successful in explaining the spin and orbital structure in a number of materials [21, 2], including $LaMnO_3$ (for the latter one has to invoke also the anharmonicity effects [21]—see also [24]).

As to the electron–lattice interaction, typically one includes mostly the coupling with the local—i.e. optical—vibrations [25]. However no less important may be the interaction with the long-wavelength acoustical phonons, or, simply speaking, with the elastic deformations. Generally, when one puts an impurity in a crystal, e.g. replacing the small Mn^{4+} ion in $CaMnO_3$ by the somewhat larger Mn^{3+} ion which in addition causes local lattice distortion due to Jahn-Teller effect (i.e. we replace a "spherical" Mn^{4+} ion by an "ellipsoidal" Mn^{3+}), this creates a strain field which is in general anisotropic and decays rather slowly, as $1/R^3$ [26, 27]. A second "impurity" of this kind "feels" this strain, which leads to an effective long-range interaction between them. This can naturally lead to the spontaneous formation of different superstructures in doped materials [28]. Thus, there may appear vertical or diagonal stripes, even for non-Jahn-Teller systems. In case of manganites one can show that there appears an effective attraction between e.g. x^2 and y^2-orbitals in x and y-direction; this immediately gives the orbital ordering of $LaMnO_3$-type shown in fig. 3. For $x = 0.5$, assuming the checkerboard charge ordering, one gets due to this mechanism the correct orbital ordering shown in fig. 4 [28]. And for overdoped manganites one can get either single or paired stripes, depending on the ratio of corresponding constants: One can show [25, 28] that for a diagonal pair like the ones in fig. 5, one gets an attraction of the same orbitals x^2 and x^2 or y^2 and y^2, but repulsion of x^2 and y^2. Thus, if one takes into account only these nearest neighbour diagonal interactions, the single stripe phase of fig. 5a would be more favourable than the paired stripes of the fig. 5b. However the latter may in principle be stabilizes by more distant interactions like those for a pair of Mn^{3+} ions along x and y-directions in fig. 5b. Which state is finally more favourable, is now under investigation.

4 Ferromagnetic insulating phase at low doping

As already mentioned in sec. 2, typically there exist a ferromagnetic insulating region at low doping ($0.1 < x < 0.18$ for the LaSr system, $x < 0.25$ for LaCa, $0.15 < x < 0.3$ for PrCa). The problem is to explain the origin of the FI state in this case. Apparently it should be connected with an orbital ordering of some kind; but what is the specific type of this ordering, is largely unknown.

The most complete data exist for the LaSr-system close to $x = 1/8$. There exists a superstructure in this system [29, 13], and an orbital ordering was detected in the FI phase in [14]. Certain orbital superstructure was also seen by the anomalous X-ray scattering in $Pr_{0.75}Ca_{0.25}MnO_3$ [30]. Both these systems however were looked at at only one k-point [300], which is not sufficient to uniquely determine the type of orbital ordering.

Theoretically two possibilities were discussed in the literature [31, 32]. First of all one can argue that when one puts a Mn^{4+} ion into Mn^{3+} matrix, the orbitals of all the ions surrounding the localized hole (Mn^{4+}) would be directed towards it, see fig. 6a [32, 33]. One can call such state an orbital polaron. These polarons, which according to Goodenough–Kanamori–Anderson rules would be ferromagnetic, can then order e.g. as shown in fig. 6b for $x = 0.25$. The calculations carried out in [32] show that this state is indeed stable, and it corresponds to a ferromagnetic insulator. Thus it is a possible candidate for a FI state at $x \simeq 1/4$ e.g. in Pr–Ca system.

However there exist an alternative possibility. The calculations show [31] that similar state with ordered polarons is also locally stable for $x \simeq 1/8$. But it turned out that the lower energy is reached in this case by different type of charge and orbital ordering, fig. 6c [31]: the holes are localised only in every second xy-plane, so that one such plane containing only Mn^{3+} ions develops the orbital ordering of the type of $LaMnO_3$, fig. 3, and the holes in the next plane concentrate in "stripes", e.g. along x-direction. This state also turns out to be ferromagnetic, and the superstructure obtained agrees with the experimental results of [29] and [13] for $La_{1-x}Sr_xMnO_3$, $x \simeq 1/8$. One can think that the situation can be also similar for $x \simeq 1/4$ which would agree with the data of [30]. This type of the charge ordering (segregation of holes in every second plane) may be favourable due to an extra stability of the

LaMnO$_3$-type orbital ordering, strongly favoured by the elastic interactions, as discussed in sec. 3.

5 Overdoped manganites

Now I will qualitatively discuss the role of orbital degrees of freedom in the overdoped regime, $x > 0.5$. The main question is why in this case the conventional double exchange, apparently responsible for the formation of the ferromagnetic metallic state for $x \sim 0.3 - 0.4$, does not lead to such a state in this case.

One reason may be the following. Usually we ascribe ferromagnetism in doped systems to a tendency to gain kinetic energy by maximal delocalization of doped charge carriers. These carriers are holes in lightly doped manganites $x \ll 1$, and electrons when we start e.g. from CaMnO$_3$ and substitute part of Ca by La or other rare earths, which corresponds to $x < 1$ in La$_{1-x}$Ca$_x$MnO$_3$.

There exist an important difference between these two cases, however. When we dope LaMnO$_3$, the orbital degeneracy in the ground state is already lifted by orbital ordering, and in a first approximation we can consider the motion of doped holes in a nondegenerate band. Then all the standard treatment, e.g. of de Gennes [10], applies, and we get the FM state. However, when we start from the cubic CaMnO$_3$, we put extra electrons into empty *degenerate e_g-levels*, which form degenerate bands. Therefore we have to generalize the conventional double-exchange model to the case of degenerate bands. This was done in [19], and the outcome is the following: At relatively low electron concentration ($x \simeq 1$) the anisotropic magnetic structures—C-type (chain-like) or A-type (ferromagnetic planes stacked antiferromagnetically)—are stabilised, and only close to $x \sim 0.5$ do we reach the ferromagnetic state. The C-phase occupies larger part of the phase space. The resulting theoretical phase diagram [19] is in surprisingly good agreement with the properties of Nd$_{1-x}$Sr$_x$ MnO$_3$ [34] in which there exist the A-type "bad metal" phase for $0.52 < x < 0.65$ and C-phase for $x > 0.65$.

Simple qualitative explanation of this tendency is the following. When we start from CaMnO$_3$ with Mn^4 (t_{2g})-ions and dope it by electrons, we put electrons into e_g-bands. The maximum energy we can gain is to put these electrons at the bottom of corresponding bands, so that one has to make these bands as broad as possible. But due to a specific character of

the overlap of different e_g-orbitals in different directions, the bottom of the bands coincides for different types of orbitals: one can easily check that if we make all the orbitals e.g. z^2, the energy $\epsilon(k)$ at the Γ-point $k = 0$ will be the same as for the bands made of $(x^2 - y^2)$-orbitals. (Actually it is a consequence of the degeneracy of e_g-orbitals in cubic crystals: the symmetry at the Γ-point should coincide with the point symmetry of local orbitals, i.e. at $k = 0$ the energies of the z^2-band and of the $(x^2 - y^2)$ one, or of a band made of any linear combinations thereof of the type (1), should coincide.)

But according to the double-exchange model electrons can move only if localised moments (t_{2g}-spins) of the corresponding sites are ordered ferromagnetically (although without doping, in $CaMnO_3$ ($x = 1$), the magnetic ordering is antiferromagnetic (G-type)). Now, if we make the band e.g. out of $(x^2 - y^2)$-orbitals, the band dispersion would have the form

$$\epsilon(\vec{k}) = -2t(\cos k_x + \cos k_y) \tag{6}$$

i.e. the electrons in this band move only in the xy-plane, but there is no dispersion in the z-direction. Therefore to gain full kinetic energy it is enough to make this plane ferromagnetic, and the adjacent planes may well remain antiparallel to the first one. But this is just the A-type magnetic structure (ferromagnetic planes stacked antiferromagnetically).

Note that in this case the electron occupy predominantly $(x^2 - y^2)$-states (or z^2-states in case of C-type ordering). Accordingly there will be corresponding lattice distortion (compression along c-axis, $c/a < 1$, for the A-type structure, and $c/a > 1$ for the C-type one). But I want to stress that these are strictly speaking not the localized orbitals, but rather *bands* of corresponding character. Whether we should call it orbital ordering, is a matter of convention (usually this terminology is applied to the case of localized orbitals). In any case, the feature mentioned above ([23, 24]), that due to higher-order effects, in particular lattice anharmonicity, only locally elongated MeO_6-octahedra are observed in practice, is valid only for orbital ordering of *localized* orbitals, and it is in general not true for the band situation considered here.

Thus the double exchange via degenerate orbitals may quite naturally lead to anisotropic magnetic structures (A-type or C-type): we gain by that the full kinetic energy without being forced to sacrifice all the exchange interaction of localised electrons (part of the bonds remain antiferromagnetic).

Which particular state will be stable at which part of the phase diagram, is determined by the competition between these terms, kinetic energy vs exchange energy, with the electron energy depending on the band filling sensitive to the density of states for the corresponding band.

There are several factors which can complicate this picture. Thus, one may in principle get in this case canted states, and not the fully saturated A- or C-type structures [19, 35]. There may appear also inhomogeneous phase-separated states. The possibility of the charge ordering (e.g. in the form of stripes) was also not considered in this treatment. But altogether it shows that the conventional double-exchange picture should be modified if double-exchange goes via degenerate orbitals, and overall tendency which results due to this is that not the simple ferromagnetic state, but more complicated magnetic structures may be stabilised, which agrees with the general tend observed in the experiment. This factor may be important in explaining strong qualitative asymmetry of the phase diagram of manganites for $x < 0.5$ (underdoped) and $x > 0.5$ (overdoped) regimes.

6   Orbital ordering in ferromagnetic metallic phase?

Finally we go over to the most important phase—that of optimal doping, $x \simeq 0.3 - 0.5$. In most cases the systems in this doping range at low temperatures are ferromagnetic and metallic, although the residual resistivity is usually relatively large.

Now, the question is: what are the orbitals doing in this phase ? Experimentally one observes that the macroscopic Jahn-Teller ordering and corresponding lattice distortion is gone in this regime. La–Ca system remains orthorhombic in this concentration range, but it is due to the tilting of the O_6 octahedra, octahedra themselves being regular (all the Mn–O distances are the same). The structure of the La–Sr manganites in this regime is rhombohedral, but again all the Mn–O distances are equal. Moreover even the local probes such as EXAFS or PDF (pair distribution function analysis of neutron scattering) [36], which detect local distortions above and close to T_c, show that for $T \to 0$ they completely disappear, and MnO_6-octahedra are regular even locally.

What happens then with the orbital degrees of freedom ? There are several possibilities. One is that in this phase the system may already be an ordinary metal, electronic structure of which is reasonably well described by the conventional band theory. In this case we should not worry about orbitals at all: we may have band structure consisting of several bands, some of which, not necessarily one, may cross Fermi-level, and we should not speak of orbital ordering in this case, the same as we do not use this terminology and do not worry about orbital ordering in metals like Al or Nb which often have several bands at the Fermi-level.

If however there exist strong electron correlations in our system (i.e. the Hubbard's on-site repulsion U is bigger that the corresponding bandwidth)—one should worry about it. The orbital degrees of freedom should then do something. There exists then two options. One is that the ground state would still be disordered due to quantum fluctuations, forming an orbital liquid [37], similar in spirit to the RVB state of the spin system (we can speak of the pseudospin RVB state). This is of course in principle possible. I however see some problems with this picture. One is that typically the orbital (pseudospin) interaction is not Heisenberg-like, but rather anisotropic, see Eqs. (3), (5). Whether it is good or bad for the orbital liquid state, remains at present highly controversial [38, 39]. Another factor is that due to a rather strong Jahn-Teller interaction (or pseudospin–phonon coupling) one may expect strong suppression of quantum fluctuations by the polaron effects. And finally, an argument against this picture is the already mentioned experimental observation that the lattice structure is undistorted even on a local level (these two latter factors may however be explained if we assume that the orbital quantum fluctuations are very fast, i.e. occur at a time scale much shorter that the phonon times $\sim \hbar/\omega_D$).

There exists however yet another, alternative possibility: there may in principle occur in this case an orbital ordering of a novel type, without any lattice distortion, involving not the orbitals of the type (1), but the *complex* orbitals—linear superpositions of the basic orbitals z^2 and $(x^2 - y^2)$ with the complex coefficients, e.g.

$$|\pm\rangle = \frac{1}{\sqrt{2}}\Big(|z^2\rangle \pm i|x^2 - y^2\rangle\Big). \qquad (7)$$

This possibility was first suggested in [40, 41] and explored in [42]; independently similar conclusion was reached a bit later in [43].

Why can such state be favourable and what are its properties ? My initial arguments were based on the analogy with the double-exchange model and with the well-known phenomenon of Nagaoka's ferromagnetism [44]. When we introduce holes into strongly correlated Hubbard system, $U \gg t$, $n < 1$, the tendency to gain kinetic energy forces the system to become ferromagnetic, at the expense of losing the antiferromagnetic exchange energy of localised spins.

One can show that pseudospins play the role similar to ordinary spins: one gains kinetic energy when one makes the orbitals ordered. For very low doping $x \ll 1$, when all the holes are at the bottom of the band, one would get a ferro. ordering of orbitals. For finite x, due to a finite band filling and different behaviour of the density of states for different bands, some other types of orbital ordering may become preferable, e.g. the staggered (antiferro.) orbital ordering—this would be determined by which structure minimizes total band energy for a given band filling (this is the same factor which determines the stability of one or another magnetic phases in the situation considered in sec. 5 [19]).

Why then the complex orbitals (7) and not the conventional real combinations (1) ? One can show that, similar to the treatment of sec. 5, the bottom of the band for the complex orbitals (7) will be *exactly the same* as for any real combination (1), so that in this sense the orbitals (7) are at least not worse than the conventional ones. On the other hand, they may be better from the point of view of the exchange interaction.

One can show that for undoped systems the ordinary orbitals are always better: they are stabilised by both the exchange and Jahn-Teller interactions (5), (3), and formally it is reflected in the fact that these effective Hamiltonians contain only pseudospin operators T^z, T^x. One can easily show however that the state (7) is an eigenstate of the third operator $T^y = \frac{1}{2} \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} = \frac{1}{2}\sigma_y$, where σ_y is the corresponding Pauli matrix. As these operators do not enter the Hamiltonians (3), (5), the corresponding pseudospin (orbital) ordering for undoped systems would be the one in (T^z, T^x)-sector, i.e. it would be the ordering of real orbitals.

But just the fact that the T^y-operators do not enter the pseudospin exchange interactions (3), (5), which are typically "antiferromagnetic" (antiferroorbital!) tells us that if we *force* our system to change the type of orbital ordering, e.g. making it "ferromagnetic", so as to gain maximum kinetic energy—then it may be favourable to make it T^y-ferro.orbital ordering: we

gain by that *the same* kinetic (band) energy, and lose *less exchange* energy.

The real Hartree-Fock calculations carried out in [41, 42] indeed confirm that there exist conditions at which the ordering of complex orbitals is energetically preferable to that of the real ones. Thus, for the realistic values of parameters (electron hopping t, Hubbard interaction U) the staggered ordering of complex orbitals may be realized at doping level $x \sim 0.35 - 0.4$ — just in the most important region of the phase diagram of manganites (the ferro.ordering of complex orbital could be realized at larger values of U/t at small doping [40, 41]).

The properties of this novel type of orbital ordering were investigated in [40, 41]. One may easily see that the distribution of the electron density in this state is the same in all three directions, x, y and z. Thus this ordering does not induce any lattice distortion—the MnO_6 octahedra remain regular, and the system is cubic (if we ignore tilting of the octahedra). On the other hand, the state (7), as always is the case with complex wave functions, breaks time-reversal invariance, i.e. this state is in some sense magnetic. One can show however that the magnetic dipole moment in this case is zero—it is well known that the orbital moment is quenched in e_g-states (these states are actually $|l^z = 0\rangle$ and $\frac{1}{\sqrt{2}}(|2\rangle + |-2\rangle)$ states of the $l = 2$ d-orbitals). Similarly, magnetic quadrupole moment is also zero, by parity arguments. The first nonzero moment in this state is a magnetic octupole. Indeed, the actual order parameter in this case is the average

$$\eta = \langle M_{xyz} \rangle = \langle \mathrm{S} L_x L_y L_z \rangle \neq 0 \qquad (8)$$

where l_α are the components of the orbital moment $l = 2$ of d-electrons, and S means the symmetrization. This operator is actually proportional to the T^y-operator of pseudospin, i.e. the order parameter of this type of orbital ordering is indeed $\eta = \langle T^y \rangle$.

One can visualize this state as the one in which there exist orbital currents at each unit cell. But these currents have rather high symmetry, so that the resulting magnetic fields are of octupole character, see fig. 7.

One can analyze some other properties of the state (7) with octupole ordering [40, 41]). The main problem is to find an experimental probe which could directly check the existence of this octupole ordering. This is indeed not easy, but if successful, such experiments would allow us to verify whether such novel state is indeed realized in optimally doped ferromagnetic metallic

manganites. If correct, this would mean that this state is perfectly ordered not only with respect of spins but also as to the orbitals, but with "strange" orbitals (7). (Relatively large residual resistivity in this case may be due to the (small scale and possibly dynamic) phase separation.) If not, this would probably mean that the ground state in this case is a quantum orbital liquid. In both cases we lose (or rather do not gain) Jahn-Teller energy. Whether quantum effects are sufficiently strong to overcome the factors discussed above which stabilize complex orbitals, is still not clear at present.

7 Orbital polarons and properties of manganites at finite temperatures.

In this last section I want to shortly discuss some of the issues which are rather actively investigated nowadays—those of the short-range orbital correlations and local Jahn-Teller effect at finite temperatures, in situations where there is no long-range orbital ordering. Specifically, these effect are often observed above and close to the phase transitions. As we already saw, there exists an orbital ordering of one or another type in manganites in most of the cases. Consequently, one should expect that there will exist at least local orbital correlations in disordered phases above corresponding T_c's. Such correlations were indeed observed e.g. in [7].

The most important however are the recent observations that such correlations exist above T_c and are enhanced in approaching T_c (but rapidly disappear below it) even in optimally doped manganites with $x \sim 0.3 - 0.4$ [36, 45]—in situation where there exists no orbital ordering at low temperatures. Actually the idea of the possible importance of such correlations in the paramagnetic phase of the CMR manganites was first put forth by Millis and his coworkers already in 1995 [46]; they argued that the double exchange alone is not sufficient to explain transport properties of manganites in this regime, and suggested that they may be largely dominated by the Jahn-Teller interaction.

The real direct indications that it may indeed be the case were obtained only recently; the most spectacular one is that the intensity of the diffuse neutron scattering attributed to Jahn-Teller polarons closely follows the temperature dependence of the resistivity [45] (it grows with decreasing temper-

ature, has a maximum at T_c and rapidly disappears for $t < T_c$).

There are now many other experiments which are interpreted in terms of these Jahn-Teller polarons (although this very notion is often not well defined). This is quite a big field in itself, and I have no space to discuss it here in details. Suffice it to say that the orbital degrees of freedom apparently play very important role in many properties of manganites not only in phases in which there exists an orbital ordering, but also in disordered states.

8   Conclusions

In conclusion I can only repeat that orbital effects play very important role in the physics of manganites, and also in many other transition metal oxides [2, 3]. Together with charge and spin degrees of freedom they determine all the rich variety of the properties of manganites in different doping regions. Orbital effects also play very important role in disordered phases, determining to a large extent their transport and other properties.

An important recent achievement in this field is the development of the method to directly study orbital ordering using the anomalous resonant X-ray scattering, initiated by the pioneering work of Murakami et al. [47]. This method was successfully applied to a number of problems in manganites as well as to several other systems. And although there is still a controversy as to the detailed microscopic explanation of these observations [48, 49], this method will be definitely of great use in the future.

The last point I want to mention is that until now I discussed in this paper mostly the static (ground state) properties connected with orbital ordering. However each time we have certain ordering in solids, there should appear corresponding excitations in them. In our case these excitations—we may call them orbitons—were first discussed shortly in [21, 2] (and in more details in the PhD thesis by K. I. Kugel in 1975) and recently were studied theoretically in several papers, e.g. in [50, 51]. One of the problems which, in my opinion, could have made an experimental observation of these excitations difficult, is the usually rather strong Jahn-Teller coupling of orbital degrees of freedom with the lattice distortions. I was afraid that it could make very difficult, if not impossible, to "decouple" orbitons from phonons. And indeed the experimental efforts to observe orbitons were unsuccessful for many years. The breakthrough was made only recently when the group of Y. Tokura

managed to observe orbital excitations by Raman scattering in untwinned single crystals of $LaMnO_3$ [52]. And although many questions here still remain unclear, this work will definitely open a new chapter in the study of orbital effects in oxides, in particular in manganites. Thus the field of orbital physics is still capable of producing important new results, and sometimes—surprises.

In conclusion I want to thank many of my colleagues with whom I had a pleasure to collaborate and to discuss the exciting questions of orbital physics. Among many good friends and colleagues I would like to single out three: K. I. Kugel with whom we started long collaboration in this field already quite a while ago and continue it until now, and my recent collaborators J. van den Brink and G. A. Sawatzky who contributed a lot to the recent development of this field. And, once again, I want to use this opportunity to congratulate E. Müller-Hartmann with his jubilee and to wish him many fruitful and happy years.

References

[1] J. B. Googenough, Magnetism and Chemical Bond, Interscience Publ., New York–London, 1963

[2] K. I. Kugel and D. Khomskii, Sov. Phys–Uspekhi **25**, 231 (1982)

[3] Y. Yokura and N. Nagaosa, Science **288**, 462 (2000)

[4] H. J. Jahn and E. Teller, Proc. Roy. Soc. A**161**, 220 (1937)

[5] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955)

[6] Z. Jirak et al., J. Magn. Magn. Mater. **53**, 153 (1985)

[7] M. v. Zimmermann et al., Phys. Rev. Lett. **83**, 4872 (1999)

[8] D. Khomskii and G. Sawatzky, Solid State Comm. **102**, 87 (1997)

[9] D. Khomskii, chapter in "Spin Electronics", Springer, in press (2001)

[10] P. G. de Gennes, Phys. Rev. **118**, 141 (1960)

[11] I. V. Solovyev and K. Terakura, Phys. Rev. Lett. **83**, 2825 (1999)

[12] J. van den Brink, G. Khaliullin and D. Khomskii, Phys. Rev. Lett. **83**, 5118(1999)

[13] T. Niemöller et al, Eur. Phys. J. **B8**, 5 (1999); R. Klingerer et al., preprint (2001)

[14] Y. Endo et al., Phys. Rev. Lett. **82**, 4328 (1999)

[15] P. G. Radaelli et al., Phys. Rev. B **59**, 14440 (1999)

[16] S. Mori, C. H. Chen and S.-W. Cheong, Nature **392**, 479 (1998)

[17] R. Wang et al., Phys. Rev. B **61**, 11946 (2000)

[18] C. Martin et al., J. Solid State Chem. **134**, 198 (1997)

[19] J. van den Brink and D. Khomskii, Phys. Rev. Lett. **82**, 1016 (1999)

[20] G. A. Gehring and K. A. Gehring, Rep. Progr. Phys. **38**, 1 (1975)

[21] K. I. Kugel and D. Khomskii, JETP Lett. **15**, 446 (1972); K. I. Kugel and D. Khomskii, Sov. Phys.–JETP **37**, 725 (1973)

[22] P. W. Anderson, Phys. Rev. **115**, 2 (1959)

[23] J. Kanamori, J. Appl. Phys. (Suppl.) **31**,14S 91960)

[24] D. Khomskii and J. van den Brink, Phys. Rev. Lett. **85**, 3229 (2000)

[25] R. Englman and B. Halperin, Phys. Rev. B **2**, 75 (1970); B. Halperin and R. Englman, Phys. Rev. B **3**, 1698 (1971)

[26] J. D. Eshelby, Solid State Phys., ed. F. Seitz and D. Turnbull, Academic Press, New York, v. 3, p. 79 (1956)

[27] A. G. Khachaturyan, Theory of Phase Transformations and the Structure of Solid Solutions, Nauka, Moscow, 1974

[28] D. Khomskii and K. I. Kugel, cond-mat/0103317; Europhys. Lett. in press (2001)

[29] Y. Yamada et al., Phys. Rev. Lett. **77**, 904 (1996)

[30] M. v. Zimmermann et al., cond-mat/0007321 (2000)

[31] T. Mizokawa, D. Khomskii and G. Sawatzky, Phys. Rev. B **61**, R3776 (2000)

[32] T. Mizokawa, D. Khomskii and G. Sawatzky, Phys. Rev. B **63**, 24403 (2000)

[33] R. Kilian and G. Khaliullin, Phys. Rev. B **60**,13458 (1999)

[34] H. Kuwahara et al., Mat. Res. Soc. Symp. Proc., v. 494, 83 (1998)

[35] I. Solovyev and K. Terakura, Phys. Rev. B in press (2001)

[36] D. Louca and T. Egami, J. Appl. Phys. **81**, 5484 (1997)

[37] S. Ishihara, M. Yamanaka and N. Nagaosa, Phys. Rev. B **56**, 6861 (1997)

[38] G. Khaliullin and V. Oudovenko, Phys.Rev. B **56**, R14243 (1997)

[39] L. F. Feiner, A. M. Oles and J. Zaanen, J. Phys. Condens. Matter **10**, L555 (1998)

[40] D. Khomskii, cond-mat/0004034 (2000)

[41] J. van den Brink and D. Khomskii, Phys. Rev. B **63**, 1401416(R), (2001)

[42] R. Maezono and N. Nagaosa, Phys. Rev. B **62**, 11576 (2000)

[43] A. Takahashi and H. Shiba, J. Phys. Soc. Jap. **69**, 3328 (2000)

[44] Y. Nagaoka, Phys.Rev., **147**, 392 (1966)

[45] L. Vasiliu-Doloc et al., Phys. Rev. Lett. **83**, 4393 (1999)

[46] A. J. Millis, P. B. Littlewood and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995)

[47] Y. Murakami et al., Phys. Rev. Lett. **80**, 1932 (1998)

[48] S. Ishihara and S. Maekawa, Phys. Rev. Lett. **80**, 3799 (1998)

[49] I. S. Elfimov, V. A. Anisimov and G. Sawatzky, Phys. Rev. Lett. **82**, 4264 (1999)

[50] S. Ishihara, J. Inoue and S. Maekawa, Phys. Rev. B **55**, 8280 (1997)

[51] J. van den Brink et al., Phys. Rev. B **58**, 10276 (1998)

[52] E. Saitoh et al., Nature **410**, 180 (2001)

Figure Captions

Fig. 1.   Phase diagram of $La_{1-x}Ca_xMnO_3$ (after to S.-W. Cheong). O—orthorhombic phase with rotated regular octahedra; O′—orthorhombic phase with Jahn-Teller distortions,

Fig. 2.   The splitting of $3d$-levels in a cubic crystal field (regular MnO_6-octahedron). Electron occupation of $4d$-electrons in Mn^{3+} is shown by arrows

Fig. 3.   The orbital ordering of $LaMnO_3$. Arrows show shifts of oxygen ions

Fig. 4.   Charge, orbital and spin ordering in the basal (xy)-plane of manganates at $x = 0.5$. Arrows denote the spin ordering. The spin zigzags are shown by thick lines

Fig. 5.   (a) Single stripes ("Wigner crystal") and (b) paired stripes, or bistripes in $La_{1-x}Ca_xMnO_3$ for $x = \frac{2}{3}$. O—ions Mn^{4+}; 8, ∞—ions Mn^{3+} with the corresponding orbitals

Fig. 6.   Orbital polarons and possible types of orbital ordering in low doped manganites: (a) Orbital polaron close to a Mn^{4+} ion; (b) Ordering of orbital polarons for $x = 0.25$ in a bcc-lattice; (c) An alternative charge and orbital ordering, obtained for $x = 1/8$ in [31]. Notations are the same as in figs. 4, 5. Shaded lines—"stripes" containing holes.

Fig. 7.   The distribution of magnetic field around each Mn in the ordered state with the complex orbitals (7). The $+$ and $-$ signs show the direction of the magnetic field (outward and inward). One sees that the local symmetry axes are 4 cube diagonals [111], in accordance with (8)
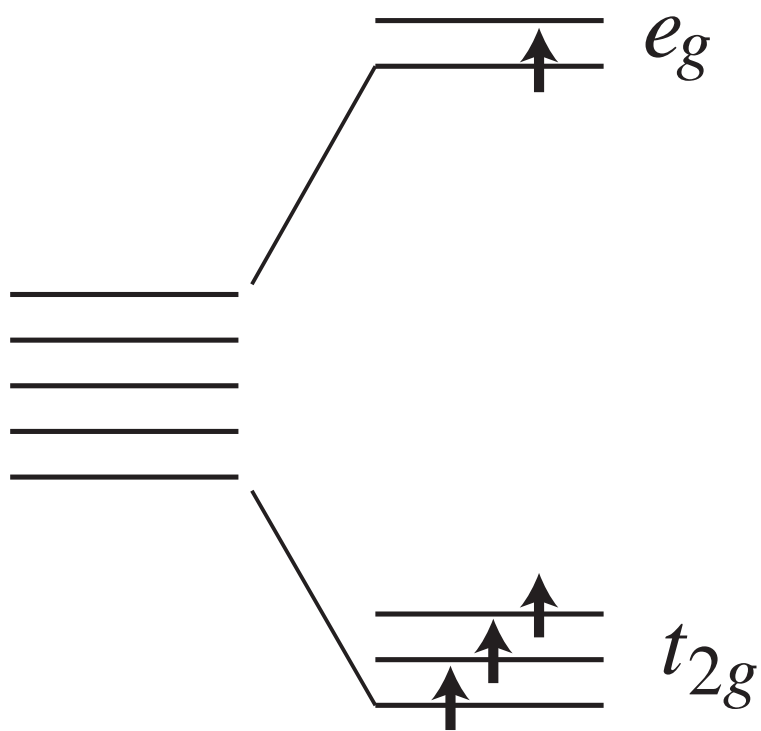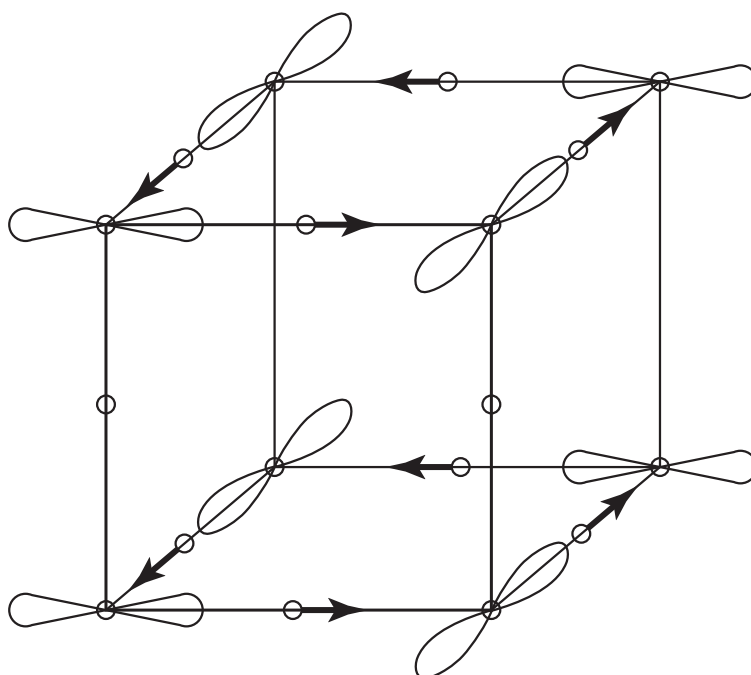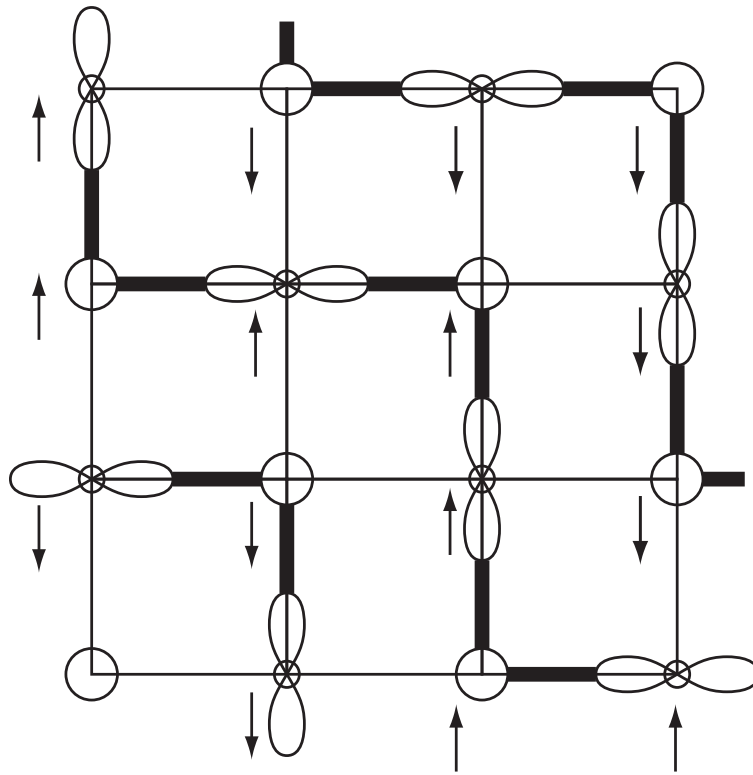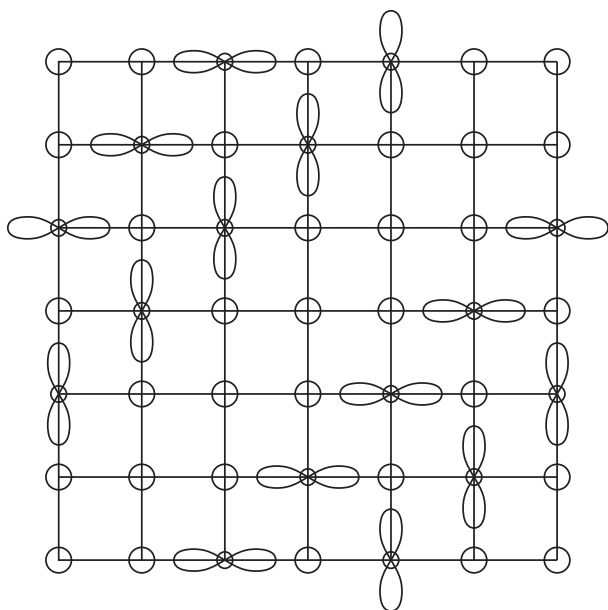
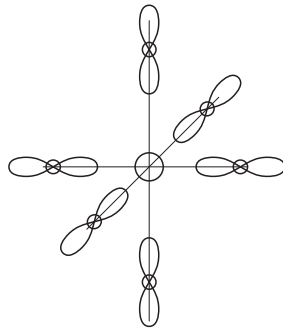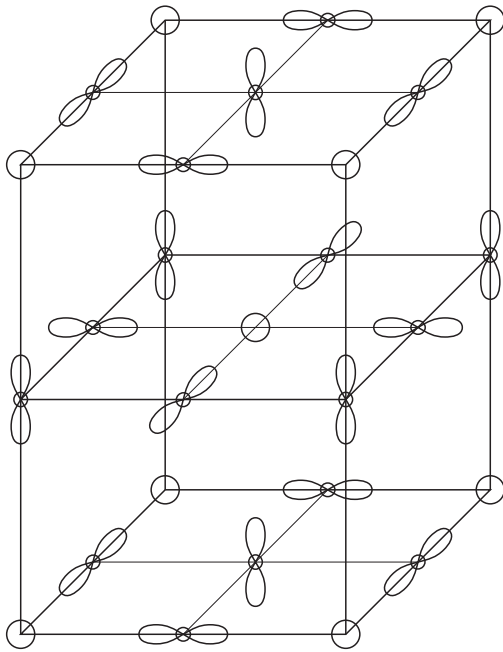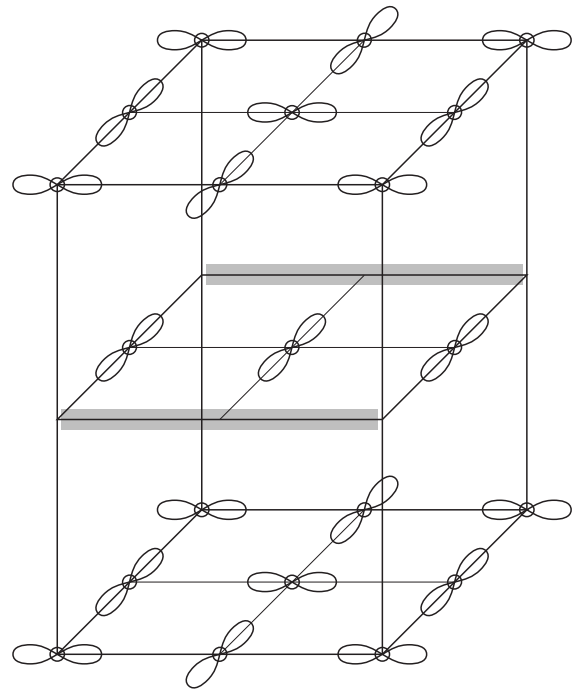Fig. 1

22

e_g

t_{2g}

Fig. 2
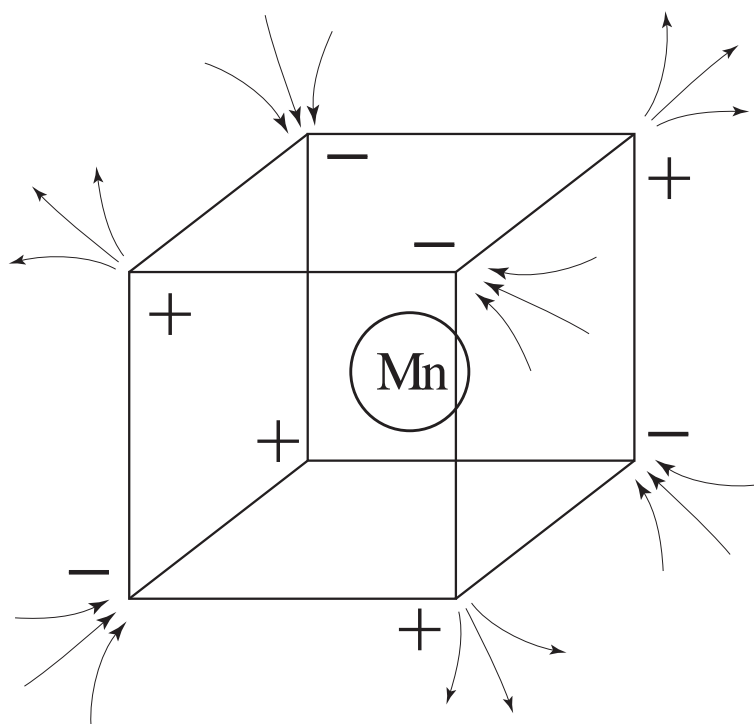
Fig. 3

Fig. 4

(a)

(b)

Fig. 5

(a)

(b)   (c)

Fig. 6

27

Fig. 7