# **11. Correlated electrons in complex transition metal oxides**

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# **11.1 Introduction**

Materials with strong electronic correlations are materials, in which the movement of one electron depends on the positions and movements of all other electrons due to the long-range Coulomb interaction. With this definition, one would naively think that all materials show strong electronic correlations. However, in purely ionic systems, the electrons are confined to the immediate neighborhood of the respective atomic nucleus. On the other hand, in ideal metallic systems, the other conduction electrons screen the long-range Coulomb interaction. Therefore, while electronic correlations are also present in these systems and lead for example to magnetism, the main properties of the systems can be explained in simple models, where electronic correlations are either entirely neglected (e.g. the free electron Fermi gas) or taken into account only in low order approximations (Fermi liquid, exchange interactions in magnetism etc.). In highly correlated electron systems, simple approximations break down and entirely new phenomena appear, possibly with related novel functionalities. These so-called emergent phenomena cannot be anticipated from the local interactions among the electrons and between the electrons and the lattice [1]. This is a typical example of *complexity*: the laws that describe the behavior of a complex system are qualitatively different from those that govern its units [2]. This is what makes highly correlated electron systems a research field at the very forefront of condensed matter research. The current challenge in condensed matter physics is that we cannot reliably predict the properties of materials with strong electronic correlations. There is no theory, which can handle this huge number of interacting degrees of freedom. While the underlying fundamental principles of quantum mechanics (Schrödinger equation or relativistic Dirac equation) and statistical mechanics (maximization of entropy) are well known, there is no way at present to solve the many-body problem for some  $10^{23}$ particles. Some of the exotic properties of strongly correlated electron systems and examples of emergent phenomena and novel functionalities are:

- *High temperature superconductivity*; while this phenomenon was discovered in 1986 by Bednorz and Müller [3], who received the Nobel Prize for this discovery, there is still no commonly accepted mechanism for the coupling of electrons into Cooper pairs, let alone a theory which can predict high temperature superconductivity or its transition temperatures. This lack of understanding is the more surprising, the more we consider the large number of solid-state physicists worldwide, which are trying to solve this problem. High temperature superconductivity has already some applications like in so-called SQUID (Superconducting Quantum Interference Device) magnetic field sensors, superconducting generators or motors, high field magnets etc but might in the future have even further applications for loss-free energy storage or -transport.
- *Colossal magnetoresistance effect CMR*, which was discovered in transition metal oxide manganites and describes a large change of the electrical resistance in an applied magnetic field [4]. This effect can be used in magnetic field sensors and could eventually replace the giant magnetoresistance field sensors<sup>1</sup>, which are employed for example in the read heads of magnetic hard discs.

<sup>&</sup>lt;sup>1</sup> The giant magnetoresistance effect [5] is an effect that occurs in artificial magnetic thin film multilayers. It was discovered independently by P. Grünberg and A. Fert, who received the Nobel Prize in 2007 for their discovery.

- *The magnetocaloric effect* [6], which describes a temperature change of a material in an applied magnetic field and can for example, be used for magnetic refrigeration without moving parts or a cooling fluid.
- *The multiferroic effect* [7], which describes the simultaneous occurring of various ferroic orders in one material. This could be ferromagnetism, ferroelectricity or ferroelasticity. If the respective degrees of freedom are strongly coupled, one can switch one of the orders by applying the conjugate field of the other order. In certain multiferroic materials, the application of a magnetic field can switch the ferroelectric polarization or the applications of multiferroic materials in computer storage elements are apparent. One could either imagine elements, which store several bits in form of a magnetic- and electric polarization, or one could apply the multiferroic properties for an easier switching of the memory element.
- Metal-insulator-transitions as observed e. g. in magnetite (Verwey transition [8]) or certain vanadites are due to strong electronic correlations and could be employed as electronic switches.
- Negative thermal expansion [9] is just another example of the novel and exotic properties that these materials exhibit.

It is likely that many more such emergent phenomena will be discovered in the near future. This huge potential is what makes research on highly correlated electron systems so interesting and challenging: this area of research is located right at the intersection between fundamental science investigations, striving for basic understanding of the electronic correlations, and technological applications, connected to the new functionalities [10].

# **11.2 Electronic structure of solids**

In order to be able to discuss the effects of strong electronic correlations, let us first recapitulate the textbook knowledge of the electronic structure of solids [11]. The description of the electron system of solids usually starts with the *adiabatic or Born-Oppenheimer approximation*. The argument is made that the electrons are moving so quickly compared to the nuclei that the electrons can instantaneously follow the movement of the much heavier nuclei and thus see the instantaneous nuclear potential. This approximation serves to separate the latticeand electronic degrees of freedom. Often one makes one further approximation and considers the nuclei to be at rest in their equilibrium positions. The potential energy seen by a single electron in the averaged field of all other electrons and the atomic core potential is depicted schematically for a one dimensional system in figure 11.1.





The following simple models are used to describe the electrons in a crystalline solid:

- *Free electron Fermi gas*: here a single electron moves in a 3D potential well with infinitely high walls corresponding to the crystal surfaces. All electrons move completely independent, i. e. the Coulomb interaction between the electrons is not considered explicitly, only the Pauli exclusion principle.
- *Fermi liquid*: here the electron-electron interaction is accounted for in a first approximation by introducing quasiparticles, so-called dressed electrons, which have a charge e, and a spin ½ like the free electron, but an active mass m\*, which can differ from the free electron mass m.
- *Band structure model*: this model takes into account the periodic potential of the atomic cores at rest i. e. the electron moves in the average potential from the atomic cores and from the other electrons.

Considering the strength of the long-range Coulomb interaction, it is surprising that the simple models of Fermi gas - or better Fermi liquid - already are very successful in describing some basic properties of simple metals. The band structure model is particularly successful to describe semiconductors. But all three models have in common that the electron is described with a single particle wave function and electronic correlations are only taken into account to describe phenomena like magnetism due to the exchange interaction between the electrons or BCS superconductivity [12], where an interaction between electrons is mediated through lattice vibrations and leads to Cooper pairs, which can undergo a Bose-Einstein condensation.

What we have sketched so far is the textbook knowledge of introductory solid state physics courses. Of course there exist more advanced theoretical descriptions, which try to take into account the electronic correlations. The strong Coulomb interaction between the electrons is taken into account in density functional theory in the so-called "LDA+U" approximation or in so-called dynamical mean field theory DMFT or a combination of the two in various degrees of sophistication [13]. Still, all these extremely powerful and complex theories often times fail to predict even the simplest physical properties, such as whether a material is a conductor or an insulator.

Let us come back to the band structure of solids. In the so-called tight binding model one starts from isolated atoms, where the energy levels of the electrons in the Coulomb potential of the corresponding nucleus can be calculated. If such atoms are brought together, the wave functions of the electrons from different sites start to overlap, leading to a broadening of the atomic energy levels, which eventually will give rise to the electronic bands in solids. The closer the atoms are brought together, the more the wave functions overlap, the more the electrons will be delocalized, and the broader are the corresponding bands. This relationship is depicted graphically in figure 11.2.



**Fig. 11.2:** <u>Left</u>: The figure on the left shows the atomic potential of an electron interacting with the atomic core and the corresponding level scheme, which consists of sharp energy levels. The figure in the middle shows how these atomic energy levels broaden into bands, the more the wave functions of neighboring atoms overlap. <u>Right</u>: The figure on the right shows schematically the band width as a function of atomic number for the rare-earth- and transition metals. Underneath a certain width, the electrons remain localized. For partially filled shells such electrons can be magnetic. But even itinerant electrons can remain magnetic up to a certain band width. At band width over typically 8 eV, the electrons will be itinerant (the material will be metallic) and non-magnetic.

If electronic correlations are not too strong, the electronic properties can be described by a band structure, which allows one to predict, whether a material is a metal, a semiconductor or an insulator. This is shown in figure 11.3. At T = 0 all electronic states are being filled up to the Fermi energy. At finite T the Fermi-Dirac distribution describes the occupancy of the energy levels. If the Fermi energy lies somewhere in the middle of the conduction band, the material will be metallic. If it lies in the middle between valence band and conduction band and these two are separated by a large gap significantly larger than the energy equivalent of room temperature, the material will show insulating behavior. Finally, if the gap is small enough to allow thermal excitations of electrons from the valence band to the conduction band, we have semiconducting behavior. But again, this band structure model describes the electrons with single particle wave functions. Where are the electronic correlations?



Fig. 11.3: Schematic band structure for a simple metal, semiconductor and insulator.

# **11.3 Electronic correlations**

It turns out that electronic correlations are particularly important in materials, which have some very narrow bands. This occurs for example in transition metal oxides or transition metal chalcogenides<sup>2</sup> as well as in some light rare earth intermetallics (heavy fermion systems). Let us chose CoO as a typical and simple example of a transition metal oxide. CoO has the rock salt structure depicted in figure 11.4.



Fig. 11.4: CoO crystallizes in the rock salt structure.

The unit cell depicted in figure 11.4 is face centered cubic fcc and contains four formula units. The primitive unit cell of the fcc lattice, however, is spanned by the basis vectors

$$\underline{a}' = \frac{1}{2}a\left(\hat{\underline{e}}_x + \hat{\underline{e}}_y\right); \ \underline{b}' = \frac{1}{2}a\left(\hat{\underline{e}}_y + \hat{\underline{e}}_z\right); \ \underline{c}' = \frac{1}{2}a\left(\hat{\underline{e}}_z + \hat{\underline{e}}_x\right)$$
(11.1)

Here a is the lattice constant, and  $\underline{\hat{e}}_x$ ,  $\underline{\hat{e}}_y$ ,  $\underline{\hat{e}}_z$  are the unit basis vectors of the original fcc unit cell. Therefore the primitive unit cell contains exactly one cobalt and one oxygen atom. The electronic configurations of these atoms are: *Co:*  $[Ar]3d^74s^2$ ; *O:*  $[He]2s^22p^4$ . In the solid, the atomic cores of Co and O have the electronic configuration of Ar and He, respectively. These electrons are very strongly bound to the nucleus and we need not consider them on the usual energy scales for excitations in the solid state. We are left with nine outer electrons for the Co

<sup>&</sup>lt;sup>2</sup> Chalcogenides are compounds of the heavier chalcogens (group VI elements of the periodic table, particularly sulfides, selenides, tellurides). Even so, oxygen is in the same group of the periodic table, oxides are usually not considered chalcogenides.

and six outer electrons for the O atom in the solid, so that the total number of electrons per primitive unit cell is 9 + 6 = 15. Therefore we have an uneven number of electrons in the primitive unit cell. According to the Pauli principle, each electronic state can be occupied by two electrons, one with spin up and one with spin down. Therefore with an uneven number of electrons, we must have at least one partially filled band and according to figure 11.3, CoO must be a metal.

What does experiment tell us? Well, in fact, CoO is a very good insulator as the resistivity at room temperature amounts to  $\rho \sim 10^8 \ \Omega cm$ . This value can be compared to a good conductor like iron, which has a resistivity of about  $10^{-7} \ \Omega cm$ . The resistivity of CoO corresponds to activation energies of about 0.6 eV or a temperature equivalent of 7000 K, which means there is a huge band gap making CoO a very good insulator. To summarize these considerations: the band theory breaks down already for a very simple oxide consisting of only one transition metal and one oxygen atom!

In order to understand the reason for this dramatic breakdown of band theory, let us consider an even simpler example: the alkali metal sodium. It has the electronic configuration:  $Na: [Ne]3s^1=1s^22s^22p^63s^1$ . Following our argumentation for CoO, sodium obviously has a half-filled 3s band and is therefore a metal. This time our prediction was correct: the electrical resistivity at room temperature is about  $5 \cdot 10^{-6} \Omega cm$ . However, what happens if we pull the atoms further apart and increase the lattice constant continuously? Band theory predicts that for all distances sodium remains a metal, since the 3s band will always be half-filled. This contradicts our intuition and of course also the experiment: at a certain critical separation of the sodium atoms, there must be a transition from a metal to an insulator. It was Sir Nevill Mott (Nobel Laureate in physics of 1977), who predicted this metal-to-insulator transition, which is therefore called the Mott-transition [14]. The physical principle can be made clear with the illustration in figure 11.5.



*Fig. 11.5:* Illustration of the hopping process of an electron between two neutral sodium ions leading to charge fluctuations.

On the left of figure 11.5, two neutral sodium atoms are depicted. The atomic energy levels of the outer electrons correspond to an energy  $\varepsilon_{3s}$ . The wave functions of the 3s electrons will overlap giving rise to a finite probability that an electron can hop from one sodium atom to the other one. Such a delocalization of the electrons is favored according to the Heisenberg uncertainty principle

$$\Delta p \cdot \Delta x \ge \frac{\hbar}{2} \tag{11.2}$$

(11.2) shows that we can gain kinetic energy, if the electrons become more delocalized. Figure 11.5 on the right shows the situation after the electron transfer. Instead of neutral atoms, we have one Na<sup>+</sup> and one Na<sup>-</sup> ion. However, we have to pay a price for the double occupation of the 3s states on the Na<sup>-</sup> ion, namely the intra-atomic Coulomb repulsion between the two electrons denoted as  $U_{3s}$ . While this is a very simplistic picture, where we assume that the electron is either located on one or the other Na atom, this model describes the two main energy terms by just one parameter: the hopping matrix element *t*, connected to the kinetic energy, and the intra-atomic Coulomb repulsion *U*, connected with the potential energy due to the Coulomb interaction between the two electrons on one site. In this simple model, we have replaced the long range Coulomb potential proportional to  $\frac{1}{r}$  with its leading term, an onsite

Coulomb repulsion U. More realistic models would have to take higher order terms into account but already such a simple consideration leads to very rich physics. We can see from figure 11.5 that electronic conductivity is connected with charge fluctuations and that such charge transfer costs energy, where U is typically in the order of 1 or 10 eV. Only if the gain in kinetic energy due to the hopping t is larger than the penalty in potential energy U can we expect metallic behavior. If the sodium atoms are now being separated more and more, the intra-atomic Coulomb repulsion U will maintain its value, while the hopping matrix element t, which depends on the overlap of the wave functions, will diminish. At a certain critical value of the lattice parameter a, potential energy will win over kinetic energy and conductivity is suppressed. This is the physical principle behind the Mott transition.

More formally, this model can be cast into a model Hamiltonian, the so-called *Hubbard model* [15]. In second quantization of quantum-field theory, one can write down the so-called single band Hubbard Hamiltonian:

$$\mathbf{H} = -t \sum_{\substack{j,l\\ \in n.N.}} \sum_{\sigma} (\mathbf{c}_{j\sigma}^{+} \mathbf{c}_{l\sigma} + \mathbf{c}_{l\sigma}^{+} \mathbf{c}_{j\sigma}) + U \sum_{j} \mathbf{n}_{j\uparrow} \mathbf{n}_{j\downarrow}$$
(11.3)

The operator  $\mathbf{c}_{j\sigma}^+$  creates an electron in the tight binding (Wannier)-state  $\Phi(\underline{r}-\underline{R}_j)|\sigma\rangle$ ,  $\mathbf{n}_{j\sigma}$  is the occupation operator  $\mathbf{c}_{j\sigma}^+\mathbf{c}_{j\sigma}$  of the corresponding Wannier state; *U* is the Coulomb repulsion in one orbital at one site:

$$U = \int dr_1 \int dr_2 \frac{e^2 \left| \Phi(\underline{r}_1 - \underline{R}_j) \right|^2 \left| \Phi(\underline{r}_2 - \underline{R}_j) \right|^2}{4\pi \varepsilon_0 \left| \underline{r}_1 - \underline{r}_2 \right|}$$
(11.4)

*t* is the hopping amplitude

$$t = \int d\underline{r} \Phi(\underline{r} - \underline{R}_1) \frac{e^2}{4\pi\varepsilon_0 |\underline{r} - \underline{R}_2|} \Phi(\underline{r} - \underline{R}_2)$$
(11.5)

The Hubbard model is a so-called "*lattice fermion model*", since only discrete lattice sites are being considered. It is the simplest way to incorporate correlations due to the Coulomb interaction since it takes into account only the strongest contribution, the onsite Coulomb interaction. Still there is very rich physics contained in this simple Hamiltonian like the physics of ferromagnetic- or antiferromagnetic metals and insulators, charge- and spin density waves and so on [15]. A realistic Hamiltonian should contain many more inter-site terms due to the long range Coulomb interaction and it is quite likely that additional new physics would be contained in such a more realistic model.

The most direct consequence of the onsite Coulomb interaction is that additional so-called Hubbard bands are created due to possible hopping processes. This is illustrated in figure 11.6.



*Fig. 11.6:* Illustration of hopping processes between neighboring atoms together with their corresponding energy scales.

The first row in figure 11.6 shows hopping processes, which are connected with a change of the total Coulomb energy. The second row shows hopping processes without transition. The last row shows hopping processes, which are forbidden due to the Pauli principle. From figure 11.6 we can identify two different energy states. Configurations for which the onsite Coulomb repulsion comes into play have an energy which is higher by the onsite Coulomb repulsion U as compared to such configurations where the electrons are not on the same atom. In a solid these two energy levels will broaden into bands (due to the delocalization of the electrons on many atoms driven by the hopping matrix element t), which are called the *lower Hubbard* band and the upper Hubbard band. If these bands are well separated, i. e. the Coulomb repulsion U dominates over the hopping term t, we will have in insulating state, since only the lower Hubbard band is occupied. If the bands overlap, we will have a metallic state. Note however that lower and upper Hubbard band are totally different from the usual band structure of solids as they do not arise due to the interaction of the electrons with the atomic cores but due to electronic correlations. As a result the existence of the Hubbard bands depends on the electronic occupation. Figure 11.6 illustrates how in correlated electron systems the energy terms for simple hopping processes depend of the occupation of neighboring sites and how hopping transports spin information. The apparently simple single electron operator gets complex many body aspects.

#### 11.4 Example: doped CMR manganites

In what follows we will discuss one example of highly correlated electron systems, the mixed valence manganites (see e.g. [16]). Their stoichiometric formula is  $A_{1-x}B_xMnO_3$ , where A is a trivalent cation (A = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y, Bi) and B is a divalent cation (B = Sr, Ca, Ba, Pb). The doping with divalent cations leads to a mixed valence on the manganese sites. If we neglect covalency<sup>3</sup> and describe these compounds in a purely ionic model, charge neutrality requires that manganese exists in two valence states: Mn<sup>3+</sup> and Mn<sup>4+</sup> according to the respective doping levels:

$$A_{l-x}B_{x}MnO_{3} \rightarrow \left[A_{l-x}^{3+}B_{x}^{2+}\right]\left[Mn_{l-x}^{3+}Mn_{x}^{4+}\right]O_{3}$$

$$(11.6)$$

<sup>&</sup>lt;sup>3</sup> an assumption which is often made but certainly not entirely adequate this class of materials!

This is why one speaks of mixed valence manganites as Mn exists in two valence states with the following electronic configurations:

 $Mn^{3+}$ : [Ar] $3d^4$  /  $Mn^{4+}$ : [Ar] $3d^3$  (11.7) The structure of these mixed valence manganites is related to the perovskite structure depicted in figure 11.7.



*Fig. 11.7:* The perovskite structure. <u>Left</u>: The ideal cubic structure; <u>middle</u>: the cubic structure in orthorhombic setting; <u>right</u>: the distorted perovskite structure with rotated and tilted oxygen octahedra.

Perovskite is a mineral CaTiO<sub>3</sub>, which has a cubic crystal structure, where the smaller Ca<sup>2+</sup> metal cation is surrounded by six oxygen atoms forming an octahedron; these corner sharing octahedra are centered on the corners of a simple cubic unit cell and the larger Ti<sup>4+</sup> metal cation is filling the interstice in the centre of the cube. This ideal cubic perovskite structure is extremely rare. It only occurs when the sizes of the metal ions match to fill the spaces between the oxygen atoms ideally. Usually there is a misfit of the mean ionic radii of the A and B ions, which leads to sizeable tilts of the oxygen octahedra. The resulting structure is related to the perovskite structure as illustrated in figure 11.7: in the middle of figure 11.7 the cubic perovskite structure is related to this structure by a tilting of the corner shared oxygen octahedra as shown on figure 11.7 on the right. Such an orthorhombic structure is for example realized in LaMnO<sub>3</sub> with space group Pbnm. Orthorhombic or rhombohedral structures occur if the so-called *tolerance factor T*, which is the measure for the misfit of the ionic radii deviates significantly from the value 1, where *T* is defined as:

$$T = \frac{1}{\sqrt{2}} \frac{\langle R_{A,B} \rangle + \langle R_{O} \rangle}{\langle R_{MN} \rangle + \langle R_{O} \rangle}$$
(11.8)

For the manganites the octahedral surrounding of the Mn ions leads to so-called crystal field effects. To explain these we stay in the ionic model and describe the oxygen atoms as  $O^{2^-}$  ions. The outer electrons of the Mn ions, the 3d electrons, experience the electric field created by the surrounding  $O^{2^-}$  ions of the octahedral environment. This leads to a splitting of the electronic levels as depicted in figure 11.8, the so-called *crystal field splitting*. Those 3d orbitals, which have loops of the electron density pointing towards the negatively charged oxygen ions, will have higher energies with respect to those 3d orbitals, where the loops point in directions between the oxygen atoms. This leads to a splitting of the d-electron levels into three so-called  $t_{2g}$  and two so-called  $e_g$  crystal field levels. For the manganites this crystal field splitting is typically in the order of 2 eV. If we now consider a Mn<sup>3+</sup> ion, it depends on the ratio between the crystal field splitting and the intra-atomic exchange, how the electrons will occupy these crystal field levels. According to Hunds' rule, electrons tend to maximize the

total spin i. e. occupy energy levels in such a way that the spins of all electrons are parallel as far as Pauli principle permits. This is a consequence of the Coulomb interaction within a single atom and is expressed by the Hunds' rule energy  $J_{H}$ . If the crystal field splitting is much larger than Hunds' coupling, a low spin state will result where all electrons are in the lower t<sub>2g</sub> level and two of these t<sub>2g</sub> orbitals are single occupied, while one orbital is double occupied. Due to Pauli principle the spins in the doubly occupied orbital have to be antiparallel giving rise to a total spin S = 1 for this low spin state. Usually, however, in the manganites Hunds' rule coupling amounts to about 4 eV, and is stronger than the crystal field splitting. In this case the high spin state shown in figure 11.8 is realized, where four electrons with parallel spin occupy the three  $t_{2g}$  levels plus one of the two  $e_g$  levels. The high spin state has a total spin of S = 2 and the orbital angular momentum is quenched<sup>4</sup>. This state has an orbital degree of freedom. The eg electron can either occupy the  $3z^2 r^2$  or the  $x^2 y^2$  orbital. Nature does not like such degenerate states. The MnO<sub>3</sub> octahedra will undergo a geometric distortion that removes this degeneracy and lowers the overall energy of the complex. This is called the Jahn-Teller effect, which is depicted in figure 11.8 as a further splitting of the d-electron levels. For the case shown in the figure, the c-axis of the octahedron has been elongated thus lowering the energy of the  $3z^2 r^2$  orbital with respect to the energy level of the  $x^2 y^2$  orbital. The Jahn-Teller splitting in the manganites has a magnitude of typically some 0.6 eV.



**Fig. 11.8:** Energy level diagram for a  $MnO^{3+}$  ion in an oxygen octahedron. For the free ion, the four 3d electron levels are degenerate. They split in a cubic environment into  $t_{2g}$  and  $e_g$  levels. If Hunds' rule coupling is stronger than crystal field splitting, a high spin state results. The degeneracy of the  $e_g$  level is lifted by a Jahn-Teller distortion, which results in an elongation of the oxygen octahedra. On the right of the figure, the 3d orbitals corresponding to the different orbital magnetic quantum numbers are depicted.

The Jahn-Teller effect demonstrates nicely how in these transition metal oxides electronic degrees of freedom and lattice degrees of freedom are coupled. Only the  $Mn^{3+}$  ion with an even number of electrons (the so-called *Kramer ion*) exhibits the Jahn-Teller effect, while the  $Mn^{4+}$  ion with only three d electrons does not. A transfer of charge between neighboring manganese ions is accompanied with a change of the local distortion of the oxygen octahe-

<sup>&</sup>lt;sup>4</sup> i.e. vanishes: L=0

dron: a so-called lattice polaron. Due to the Jahn-Teller effect, charge fluctuations and lattice distortions become coupled in these mixed valence transition metal oxides.



**Fig. 11.9:** Orbital order in LaMnO<sub>3</sub>. Below the Jahn-Teller transition temperature of 780 K, a distinct long range ordered pattern of Jahn-Teller distortions of the oxygen octahedra occurs leading to orbital order of the  $e_g$  orbitals of the  $Mn^{3+}$  ions as shown. Also shown is the antiferromagnetic spin order which sets in below the Néel temperature  $T_N \sim 145$  K. Oxygen atoms are represented by filled circles, La is not shown.

Having explained the Jahn-Teller effect, we can now introduce an important type of order occurring in these transition metal oxides: orbital order. Let us look at the structure of the LaMnO<sub>3</sub> parent compound. Here all manganese are trivalent and are expected to undergo a Jahn-Teller distortion. In order to minimize the elastic energy of the lattice, the Jahn-Teller distortions on neighboring sites are correlated. Below the Jahn-Teller transition temperature  $T_{JT} \sim 780$  K, a cooperative Jahn-Teller transition takes place, with a distinct pattern of distortions of the oxygen octahedra throughout the crystal lattice as shown in figure 11.9. This corresponds to a long range orbital order of the eg electrons, which should not be confused with magnetic order of an orbital magnetic moment. In fact, the orbital magnetic moment is quenched i. e. totally suppressed by the crystal field surrounding the Mn<sup>3+</sup> ions. Orbital ordering instead denotes a long range ordering of an anisotropic charge distribution around the nuclei. As the temperature is further lowered, magnetic order sets in at the Néel temperature of 145 K. In LaMnO<sub>3</sub> the spin degree of freedom of the Mn<sup>3+</sup> ion orders antiferromagnetically in so-called A-type order: spins within the a-b plane are parallel, while spins along c are coupled antiferromagnetically. This d-type orbital ordering and A-type antiferromagnetic ordering results from a complex interplay between structural-, orbital- and spin degrees of freedom and the relative strengths of the different coupling mechanisms in LaMnO<sub>3</sub>.

The situation becomes even more complex for doped manganites, where the charge on the manganese site becomes an additional degree of freedom due to the two possible manganese valances  $Mn^{3+}$  and  $Mn^{4+}$ . In order to minimizes the Coulomb interaction between neighboring manganese sites, so-called *charge order* can develop. This is shown for the example of half-doped manganites in figure 11.10.



<u>Fig. 11.10:</u> Charge-, orbital- and spin-order in the half-doped manganite  $\begin{bmatrix} La_{1/2}^{3+}Sr_{1/2}^{2+} \end{bmatrix} \begin{bmatrix} Mn_{1/2}^{3+}Mn_{1/2}^{4+} \end{bmatrix} O_3$ 

These half-doped manganites show antiferromagnetic spin order, a checkerboard-type charge order with alternating  $Mn^{4+}$  and  $Mn^{3+}$  sites and a zigzag orbital order of the additional  $e_g$  electron present on the  $Mn^{3+}$  sites. This is only one example of the complex ordering phenomena that can occur in doped mixed valence manganites. These ordering phenomena result from a subtle interplay between lattice-, charge-, orbital-, and spin degrees of freedom and can have as a consequence novel phenomena and functionalities like the colossal magnetoresistance effect.

How are these ordering phenomena related with the macroscopic properties of the system? To answer this question, let us look at the resistivity of doped Lanthanum-Strontium-Manganites, see figure 11.11.



**Fig. 11.11:** Resistivity in the  $La_{1-x}Sr_xMnO_3$  series, taken from [17]. <u>Left</u>: resistivity in zero field for various compositions from x = 0 to x = 0.5. <u>Right</u>: resistivity for x = 0.15 in different magnetic fields as well as the magnetoresistance defined as the change in resistivity relative to its value for field equal zero.

The zero field resistance changes dramatically with composition. The x = 0 compound shows insulating - or better semiconducting - behavior as the resistivity increases with decreasing temperature. The higher doped compounds e. g. x = 0.4 are metallic as the resistivity decreases with decreasing temperature. Note however that the resistivity of these compounds is still about three orders of magnitude higher than for typical good metals. At an intermediate composition x = 0.15, the samples are insulators at higher temperatures down to about 250 K, then a dramatic drop of the resistivity indicating an insulator-to-metal transition and again an upturn below about 210 K with typical insulating behavior. The metal-insulator transition occurs at a temperature, where the ferromagnetic long-range order sets in. Around this temperature we also observe a very strong dependence of resistivity on external magnetic field. This is the so-called *colossal magnetoresistance effect*. In order to appreciate the large shift in the maximum of the resistivity curve with field shown in figure 11.11, one should remember that the energy scales connected with the Zeeman interaction of the spin  $\frac{1}{2}$  electron in an applied magnetic field are very small: the energy equivalent of 1 Tesla for a spin  $\frac{1}{2}$  system corresponds to 0.12 meV, which in turn corresponds to a temperature equivalent of 1.3 K.

Can we understand this strong dependence of the resistance on an external field in simple terms? Indeed there is a mechanism for a magnetic exchange interaction which can give rise to a ferromagnetic order and at the same time is connected with conductivity. This mechanism is called *double exchange* and is depicted schematically in figure 11.12. This exchange interaction can only occur between transition metals of different valences. In the case depicted in figure 11.12, an eg electron from a Mn<sup>3+</sup> ion hops into the oxygen 2p orbital while the other oxygen 2p electron hops on the Mn<sup>4+</sup> site. Since eg and t<sub>2g</sub> electrons are strongly coupled through the Hund's rule coupling, this transfer of an electron from Mn<sup>3+</sup> to Mn<sup>4+</sup> can only occur if the spins of the t<sub>2g</sub> electrons are parallel.



**Fig. 11.12:** Schematic representation of the double exchange interaction. On the left, the transfer of an  $e_g$  electron through the intervening 2p orbitals from a  $Mn^{3+}$  to a  $Mn^{4+}$  ion is shown. On the right, this process is illustrated in an energy level diagram for the manganese atoms. There is an antiferromagnetic exchange interaction  $J_{AF}$  between the  $t_{2g}$  electrons. Within the Mn atoms, Hund's rule coupling  $J_H$  is assumed to be larger than the crystal field splitting. t represents the hopping term between the two Mn sites. Only if the  $t_{2g}$  spins of both Mn atoms are parallel can the  $e_g$  electron hop between the two sites. If the  $t_{2g}$  spins are anti-parallel, hopping is suppressed by the strong Hund's rule coupling between  $e_g$  and  $t_{2g}$  spins. As double exchange is stronger than  $J_{AF}$ , the Mn spins tend to align parallel.

For an anti-parallel orientation of the  $t_{2g}$  spins hopping is suppressed due to the penalty of the Hund's rule coupling energy  $J_{H}$ . Therefore the double exchange between Mn<sup>3+</sup> and Mn<sup>4+</sup> ions is ferromagnetic and this ferromagnetic exchange is connected with conductivity. In terms of

the double exchange mechanism, we can now explain the insulator-to-metal transition occurring at  $T_C$ : in the paramagnetic states, the spins of the  $t_{2g}$  electrons fluctuate, thus suppressing the hopping of the  $e_g$  electron due to Hund's rule coupling. The system behaves like an insulator. As soon as ferromagnetism sets in, hopping between neighboring manganese sites can occur and the resistivity drops. An applied external field aligns the Mn spins even above the Curie temperature. This induced magnetization permits an increased hopping of the  $e_g$  electrons and thus to a decrease of resistivity. Thus in this simple model of the double exchange interaction, magnetoresistance can be explained qualitatively. However, it has been shown [18] that the double exchange interaction alone gives the wrong magnitude for the magnetoresistance effect. Other effects, such as the electron-phonon interaction, have to be taken into account.

It is also clear that our entire discussion starting from ionic states is only a crude approximation to the real system. Therefore we now have to pose the question how can we determine the true valence state? Or more general, which experimental methods exist to study the complex ordering and excitations of the charge-, orbital-, spin- and lattice- degrees of freedom in these complex transition metal oxides?

### 11.5 Experimental techniques: Neutron and x-ray scattering

In this chapter we will give a first glimpse into how these various ordering phenomena can be studied experimentally. Obviously we need probes with atomic resolution which interact as well with the spins as with the charges in the system. Therefore neutron and x-ray scattering are the ideal microscopic probes to study the complex ordering phenomena and their excitation spectra. The lattice and spin structure can be studied with neutron diffraction from a polycrystalline or single crystalline sample as detailed in the chapter on "Structure determination" of this course. Figure 11.13 shows as an example a powder spectrum of a  $La_{7/8}Sr_{1/8}MnO_3$  material.



**Fig. 11.13:** High resolution neutron powder diffractogram of a powdered single crystal of  $La_{7/8}Sr_{1/8}MnO_3$ . Circles are the data points, the solid line is the result of the structural refinement. Structural and magnetic Bragg reflections are located at the  $2\theta$  values indicated by the vertical lines below the spectrum. The solid line underneath shows the difference between the observed and simulated spectrum. Inserts show details in certain  $2\theta$  regions e.g. a magnetic Bragg reflection at very low Q.

Preferably the structure determination from polycrystalline material is done by a simultaneous refinement of neutron and x-ray powder diffraction spectra, as the two probes have different contrast mechanisms. For example an x-ray spectrum contains less precise information on the structural parameters for the oxygen atoms, since these rather light atoms scatter much weaker than the heavier metal atoms. Neutrons have the added advantage of a vanishing form factor for nuclear scattering and therefore give information up to larger momentum transfer. This is particularly useful for the determination of the thermal parameters (Debye-Waller factors). Neutrons also allow one to determine the magnetic structure from a powder diffraction pattern. As a result of such a refinement, one can show that the low temperature structure of this compound is monoclinic or even triclinic<sup>5</sup>, i.e. there exists an additional distortion from the Pnma structure introduced in chapter 11.4. Ferromagnetic order becomes visible by intensity on top of the structural Bragg peak. Antiferromagnetic order is usually (but not always!) connected with an increase in the unit cell dimension, which in turn shows up in the diffractogram by additional superstructure reflections between the main nuclear reflections. It is beyond the scope of this lecture to discuss the experimental and methodological details of such a structure analysis or to present detailed results on specific model compounds. For this we refer to the literature, e.g. [16]. We just want to mention that with detailed structural information, we cannot only determine the lattice- and spin structure, but also the charge- and orbital order and can relate them to macroscopic phenomena such as the CMR effect. At first sight it might be surprising that neutron diffraction is able to give us information about charge order. We have learnt in the introductory chapters that neutrons interact mainly through the strong interaction with the nuclei and through the magnetic dipole interaction with the magnetic induction in the sample. So how can neutrons give information about charge order? Obviously charge order is not determined directly with neutrons. However in a transition metaloxygen bond, the bond length will depend on the charge of the transition metal ion. The higher the positive charge of the transition metal, the shorter will be the bond to the neighboring oxygen, just due to Coulomb attraction. This qualitative argument can be quantified in the so-called bond valence sum. There exists an empirical correlation between the chemical bond length and the bond valence:

$$s_{ij} = \exp\left(\frac{R_0 - R_{ij}}{B}\right)$$
(11.9)

Here, the  $R_{ij}$  are the experimentally determined bond lengths, *B* is a constant (B = 0.37 according to [19]) and  $R_0$  are tabulated values for the cation-oxygen bonds see e. g. [19]. Table 11.1 reproduces some of these values.

Ions	La <sup>3+</sup>	Pr <sup>3+</sup>	Nd <sup>3+</sup>	$\mathrm{Sm}^{3+}$	Eu <sup>3+</sup>	Gđ <sup>3+</sup>	Tb³+	Dy <sup>3+</sup>	Er <sup>3+</sup>
<i>R</i> <sub>0</sub>	2.172	2.138	2.105	2.090	2.074	2.058	2.032	2.001	1.988
Ions	Tm <sup>3+</sup>	Yb <sup>3+</sup>	Y <sup>3+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>	
$R_0$	1.978	1.965	2.019	1.967	2.118	2.285	1.760	1.753	

**<u>Tab. 11.1</u>**:  $R_0$  values of cation-oxygen bonds in manganese perovskites needed for the bond valence calculation (11.9); taken from [19].

<sup>&</sup>lt;sup>5</sup> Highest resolution synchrotron x-ray powder diffraction is best suited to solve the problem of the metric of the low temperature structure, as peak splitting can be detected much better with this method than with laboratory x-ray- or neutron powder diffraction which has generally less resolution

Finally the valence or oxidation state of the cation can be determined by the sum of the bond valences around the respective atom i according to:

$$V_i = \sum_{ij} s_{ij} \tag{11.10}$$

Even though this method to determine the valence state is purely empirical, it proves to be rather precise, if compared to other techniques. The values of the valences found with this method differ significantly from a purely ionic model. Instead of integer differences between charges on different transition metal ions, one finds more likely differences of a few tenth of a charge of an electron.

Just like charge order, orbital order is not directly accessible to neutron diffraction techniques since orbital order represents an anisotropic charge distribution and neutrons do not directly interact with the charge of the electron. However, we have seen in the discussion of the Jahn-Teller effect (figure 11.8 and figure 11.9) that an orbital order is connected with a distortion of the local environment visible in different bond lengths within the anion complex surrounding the metal cation. In this way, by a precise determination of the structural parameters from a combined neutron and x-ray powder diffraction experiment, one can determine in favorable cases the ordering pattern of all four degrees of freedom: lattice, spin, charge and orbitals.

One can ask, whether there is not a more direct way to determine charge- and orbital order. The scattering cross section of x-rays contains the atomic form factors, which are Fourier transforms of the charge density distribution of an atom. Naively one would think therefore that charge and orbital order can be easily determined with x-ray scattering. However, as discussed in the last paragraph on bond valence sums, it is usually only a fraction of an elementary charge, which contributes to charge- or orbital ordering. If we take the case of the Mn atom, the atomic core has the Ar electron configuration i. e. 18 electrons are in closed shells with spherical charge distributions. For the Mn<sup>4+</sup> ion, three further electrons are in the t<sub>2g</sub> levels. Since in scattering, we measure intensities and not amplitudes, these 21 electrons contribute  $21^2 r_0^2$  to the scattered intensity<sup>6</sup>. If the difference in charge between neighboring Mn ions amounts to 0.2e, this will give an additional contribution to the scattered intensity of  $0.2^2 r_0^2$ .

The effect of charge ordering in x-ray scattering is therefore  $\frac{0.2^2}{21^2} \sim 1 \times 10^{-4} = 0.1$  ‰. In this

simple consideration, we have completely ignored the scattering from all the other atoms, so that detection of charge- or orbital ordering becomes even more difficult in reality. There is, however, a way to enhance the scattering from non-spherical charge distributions, the so-called *anisotropic anomalous x-ray scattering*. It was first discussed by Templeton and Templeton [20] and applied for orbital order in manganites by Murakami et al. [21]. The principle of this technique is shown in figure 11.14.

 $<sup>^{6}</sup>$  The classical electron radius  $r_{0}$ =e/mc<sup>2</sup>=2.82 fm is the natural unit for the scattering amplitude of x-ray Thomson scattering



**Fig. 11.14:** Illustration of the principle of anisotropic anomalous x-ray scattering for a hypothetical 2-dimensional compound consisting of two atoms with different number of electrons. On the left a possible reconstruction of the charge distribution from a laboratory x-ray source is shown. Non resonant x-ray scattering is sensitive mainly to the spherical charge distribution and a unit cell as shown by the white lines is being deduced from this experiment. In the middle the principles of a resonance x-ray scattering is depicted in an energy level diagram (see text). On the right, the charge distribution deduced from such an anomalous x-ray scattering experiment is shown. Now an orbital ordering pattern becomes apparent, which could not be detected with non-resonant x-ray scattering. The unit cell is evidently larger, giving rise to superstructure reflections which appear at resonance.

The figure shows scattering from a hypothetical two dimensional compound consisting of two atoms with different number of electrons. Non resonant x-ray scattering as it can be done on a laboratory x-ray source is sensitive mainly to the spherical charge distribution. A reconstruction of the charge distribution done from such an experiment might look schematically as shown on the left of figure 11.4. The corresponding crystal structure can be described with a primitive unit cell indicated by the white lines. In order to enhance the scattering from the non spherical part of the charge distribution, an experiment can be done at a synchrotron radiation source. There the energy of the x-rays can be tuned to the energy of an absorption edge as shown in the middle of figure 11.4. Now second order perturbation processes can occur, where a photon induces virtual transitions of an electron from a core level to empty states above the Fermi energy and back with re-emission of a photon of the same energy as the incident photon. Since second order perturbation processes have a resonant denominator, this scattering will be largely enhanced close to an absorption edge. If the intermediate states in this resonant scattering process are somehow connected to orbital ordering, scattering from orbital ordering will be enhanced. Thus in the resonant scattering experiment, orbital order can become visible as depicted schematically on the right of figure 11.14. With the shown arrangement of orbitals, the true primitive unit cell of this hypothetical compound is obviously larger than the unit cell that was deduced from the non resonant scattering experiment (shown on the left), which was not sensitive enough to determine the fine details of the structure. An increase of the unit cell dimensions in real space, however, is connected with a decrease of the distance of the reciprocal lattice points, i. e. an increase in the number of Bragg reflections. Therefore orbital order is visible by a resonant scattering process in the appearance of additional superstructure reflections. The intensity of these reflections has strong energy dependence as we would expect for a second order perturbation process. This type of scattering experiment is called anisotropic anomalous x-ray scattering, since it is sensitive to the anisotropic local charge distribution around an atom.

Figure 11.15 shows data from such a resonant scattering experiment [22] together with its interpretation in terms of an orbital polaron lattice [23].



**Fig. 11.15:** The figure on the left shows the dependence of the intensity of resonant superlattice reflections from La<sub>7/8</sub>Sr<sub>1/8</sub>MnO<sub>3</sub> as a function of the energy of the incident photons. Clearly visible is the strong resonant enhancement at the K-absorption edge of Mn (note the logarithmic intensity scale). Several reflections with half indices along c become visible at resonance. The interpretation of this experiment is given in real space on the right of the figure. There is an alternating arrangement of Mn<sup>3+</sup> and Mn<sup>4+</sup> ions. The additional electron of the Mn<sup>3+</sup> ion occupies an e<sub>g</sub> orbital, which points towards the Mn<sup>4+</sup> ion. This arrangement is called an orbital polaron. In the ferromagnetic insulating phase of La<sub>7/8</sub>Sr<sub>1/8</sub>MnO<sub>3</sub> below 155 K, these orbital polarons arrange into a long ranged ordered orbital polaron lattice.

The figure gives a nice example of how anisotropic anomalous x-ray scattering gives detailed information on charge- and orbital ordering in solids. Its advantage is that it is element specific (due to the different absorption edge energies for the different elements) and that it combines diffraction and spectroscopy. This can also be seen in figure 11.15: there is a distinct fine structure in the resonance above the absorption edge, which gives information about the density of states of the unoccupied orbitals above the Fermi level.

So far we have discussed some powerful experimental techniques to determine the various ordering phenomena in complex transition metal oxides. Scattering can give much more information than just on the time averaged structure. Quasielastic diffuse scattering gives us information on fluctuations and short range correlations, i. e. short range correlations of polarons above the phase transition, magnetic correlations in the paramagnetic state, local dynamic Jahn-Teller distortions above the Jahn-Teller transition etc. Studying these correlations and fluctuations help us to understand what drives the respective phase transitions into long range order. The relevant interactions, which give rise to these ordering phenomena, can be determined from inelastic scattering experiments as we have learnt in the chapter on "Inelastic neutron scattering". For example, one can determine the exchange interactions from measurements of the spin wave spectra and compare with models for superexchange interactions and double exchange in order to verify or falsify the simple model explanations for the CMR effect discussed in chapter 11.4. Since there is a huge amount of such experiments definitely goes far beyond the scope of this introductory lecture.

## 11.6 Summary

This chapter gave a first introduction into the exciting physics of highly correlated electron systems, restricted to the complex transition metal oxides and -chalcogenides. The main message can be summarized in figure 11.16.



Fig. 11.16: Illustration of complexity in correlated electron systems. Meaning of the symbols is: H, E: magnetic and electric field, respectively; μ: chemical potential (doping); T: temperature; P: pressure; σ: strain (epitaxial growth); d: dimensionality (e. g. bulk versus thin film systems); CO: charge order; OO: orbital order; SO: spin order; JT: Jahn-Teller transition.

The complexity in these correlated electron systems arises from the competing degrees of freedom: charge, lattice, orbit and spin. The ground state is a result of a detailed balance between these different degrees of freedom. This balance can be easily disturbed by external fields or other thermodynamical parameters, giving rise to new ground states or complex collective behavior. Examples are the various ordering phenomena discussed, Cooper pairing in superconductors, so-called spin Peierls transitions in one dimensional systems etc. This high sensitivity to external parameters as well as the novel ground states of the systems gives rise to novel functionalities, such as the colossal magnetoresistance effect, high temperature superconductivity, multiferroic behavior and many more. A theoretical description of these complex systems starting from first principles, like Schrödinger equation in quantum mechanics or the maximization of entropy in statistical physics, is bound to fail due to the large number of strongly interacting particles. Entirely new approaches have to be found to describe the emergent behavior of these complex systems. Therefore highly correlated electron systems are a truly outstanding challenge in modern condensed matter physics. We have shown in this lecture that neutron and x-ray scattering are indispensable tools to disentangle this complexity experimentally. They are able to determine the various ordering phenomena as well as the fluctuations and excitations corresponding to the relevant degrees of freedom. No other experimental probe can give so much detailed information on a microscopic level as scattering experiments.

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