Charge Order in Transition Metal Oxides

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1. INTRODUCTION

The design and synthesis of materials with adjustable physical properties is one of the most fascinating and challenging topics in modern condensed matter physics. Development of “smart” drugs and design of therapeutic macromolecules in biomolecular medicine, synthesis of magnetic, semi-, spin-, and super-conducting row materials in electronics, development of fuel cell elements, synthesis of fullerenes and carbon nanotubes – this is a not complete list of recent theoretical and technical advances in this field. Since the properties of matter are closely related to the configuration of its electrons, the effective design of materials with advanced properties requires a complete fundamental understanding of its electronic structure. The latter can be achieved through experimental and theoretical investigations, allowing a more direct approach to desirable properties.

X-ray diffraction, neutron scattering, x-ray absorption, bremsstrahlung isochromat and photoemission spectroscopy, nuclear and spin magnetic resonance, and many other experiments are extremely useful tools for exploring structural (e.g., crystal and magnetic) and dynamic (conductance and absorption) properties of materials. However, experiments provide an indirect probe of the true electronic structure of materials which can be obtained using a detailed quantum mechanical description of an interacting many-particle system. The calculations can be used for interpretation and prediction of experimental data which is of basic importance in science. Unfortunately even for a small cluster of atoms these calculations are very problematic and very time consuming. Moreover, the so-called Van Vleck catastrophe (Van Vleck 1936) states the exponential grow of required memory with the number of electrons and strongly limits the size of investigated clusters. It makes the interacting many-body systems hardly solvable in general.

During the past 80 years several methods have been developed to treat interacting many-body systems approximately (Kohn 1999). The first simplification which can be applied is that the electrons are moving in an effective potential produced by the heavy nuclei. In this so-called Born-Oppenheimer approximation (Born and Oppenheimer 1927), the nuclei and electrons are treated independently which significantly simplifies the calculations. However, the electronic Hamiltonian obtained within this approach cannot be solved exactly and further approximations are required. One of the most common of them is the one-electron approximation. Within this approximation, the many-electron system is described as a system of non-interacting electrons moving in an effective mean-field potential. This po-
potential depends on the interactions between electrons and, therefore, on the one-electron wave-functions which can be found by solving one-electron Schrödinger equation. Since initially neither potential nor wave-functions are known, it is necessary to solve these equations in a self-consistent manner. The effective potential can be defined using different approximations, among which Hartree and Hartree-Fock are the most famous examples (Hartree 1928, Fock 1930). In the Hartree approximation the potential describes only Coulomb repulsion between electrons, whereas its extension, the Hartree-Fock approximation includes both Coulomb and exchange electron correlations.

At present there are a couple of approaches to treat the effective potential. The most accurate description of properties of solids is provided by the density functional theory (Hohenberg and Kohn 1964, Kohn and Sham 1965) where the electron density distribution rather then the many-electron wave-function plays a crucial role. The limitation of this theory lies in the lack of knowledge of exact form of the exchange-correlation functional. In order to solve the DFT equations, approximations for this functional should be made. In the most widely used local density approximation (LDA), the many-body problem is mapped onto an effective non-interacting system with the one-electron exchange-correlation potential approximated by that of the homogeneous electron gas (von Barth and Hedin 1972, Jones and Gunnarsson 1989, Capelle 2002). This approach is very successful for explaining the properties of weakly correlated systems such as metals, band insulators and some semiconductors. Unfortunately, it generally fails to reproduce correctly the properties of strongly correlated electron systems like Mott and charge-orbitally ordered insulators. To overcome these disadvantages at least for the long-range ordered systems the LDA+U method was developed (Anisimov and Gunnarsson 1991, Anisimov, Zaanen and Andersen 1991, Liechtensten, Anisimov and Zaanen 1995). Its basic concept and profit with respect to the ordinary LDA approach is that the itinerant s, p and highly localized d (or f) electron states are treated differently. In particular, the former are generally well described by the LDA potential, whereas the one-site Hubbard interaction approximates well the Coulomb interaction between localized d (or f) electrons. During the last decade the LDA+U method has been successfully applied to many systems. Among them are the correlated metals, charge and orbitally ordered insulators (Liechtensten et al. 1995, Anisimov, Efimov, Hamada and Terakura 1996, Antonov, Harmon, Antrpov, Perlov and Yaresko 2001, Antonov, Harmon and Yaresko 2003). Particularly, the present thesis is devoted to investigation of the charge ordered mixed-valent transition-metal oxides.

The mixed-valent transition-metal oxides exhibit remarkable physical phenomena caused by interplay of spin, charge, and orbital degrees of freedom. In particular, the problem of metal-insulator phase transitions widely observed in many transition metal oxides (TMOs) is one of the most fascinating topics in condensed matter physics. This problem was first addressed by Verwey, de Bore, and Peierls
in the late 1930s; they pointed out the extremely important role of electron-electron correlations in the partially filled $d$-electron bands in transition metal oxides (see de Boer and Verwey (1937), Peierls (1937)), e.g., nickel oxide (NiO) and magnetite ($\text{Fe}_3\text{O}_4$) – the Mott insulator and charge ordered system, respectively. In both systems the finite temperature metal-insulator transitions occurs violating the Bloch-Wilson band-insulator concept, the only one known at that time (Bloch 1929, Sommerfeld 1928, Wilson 1931a, Wilson 1931b). These earlier observations launched the long and continuing history of the field of strongly correlated electrons. In the past 70 years, much progress has been achieved from both theoretical and experimental sides in understanding strongly correlated electrons and metal-insulator transitions (Imada, Fujimori and Tokura 1998). However, the charge ordering proposed by Verwey behind the metal-insulator transition in $\text{Fe}_3\text{O}_4$ remains at the focus of active debates (Wright, Attfield and Radaelli 2001, García, Subías, Proietti, Blasco, Renevier, Hodeau and Joly 2001).

Charge ordering in electron systems was first envisaged by Wigner in the 1930s (Wigner 1934). He proposed crystallization of carriers (electrons) in localized states in the uniform electron gas due to the long-range Coulomb repulsion (the so-called Wigner crystallization). This concept was applied by Verwey to explain the metal-insulator transition that occurs in mixed-valent magnetite ($\text{Fe}^{3+}\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_4^{-}$) at $\sim$120 K, the so-called the Verwey transition (Verwey 1939, Verwey and Haayman 1941). According to Verwey this transition is caused by the ordering of extra electron associated with $\text{Fe}^{2+}$ cation (see Fig. 1.1). It is driven by the mutual Coulomb repulsion between electrons in some sort of ordered arrangement below $\sim$120 K which is less conducting than the charge disordered state above the Verwey transition.

![Figure 1.1: Crystal structure and charge order in magnetite. Left panel, the structure of $\text{Fe}_3\text{O}_4$; right panel, the ordered structure of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ at the $B$ sublattice of the inverted spinel $\text{AB}_2\text{O}_4$ structure proposed by Verwey (1939).](image-url)
Charge ordering is characterized by the translational symmetry breaking with some finite value of appropriate order parameter, e.g., charge disproportion. The latter can be estimated from the bond valence sum (BVS) analysis of particular crystal structure (Brese and O’Keeffe 1991). Thus, an electron-rich metal site tends to expand the surrounding of anion, i.e., to increase the average length of cation-anion bonds. This gives rise to the appearance of distinct metal sites with remarkably different mean distances to the surrounding anions, which is a primary structural evidence for the charge order. The mean cation-anion distances can be extracted from the crystal structure data, whereas a valence can be evaluated through the BVS analysis of the mean bond lengths. It is interesting to note that the observed charge disproportion is significantly reduced from the ideal ionic value in all experimentally determined structures. In comparing several transition metal oxides that undergo a charge-ordering transition from a high-temperature charge-averaged state to a low-temperature charge ordered state, the charge separation estimated from BVS’s ranges from 24% in Y2Ni2+Ni4+O6 to 60% in YBaCo2+Co3+O5 of the ideal ionic value (Vogt, Woodward, Karen, Hunter, Henning and Moodenbaugh 2000). TbBaFe2O5 has 40% of the ideal charge separation between Fe2+ and Fe3+ (Karen, Woodward, Lindén, Vogt, Studer and Fischer 2001). Even less (only 20%) has been recently claimed in magnetite (Fe3O4) (Wright et al. 2001, Wright, Attfield and Radaelli 2002). This small charge disproportion cannot be considered as an ultimate proof of the charged ordered state below the Verwey transition in Fe3O4. Indeed, it was pointed out by García, Subías, Blasco and Proietti (2002) that the maximal limit of charge disproportion (0.2 e) has the same order as the total sensitivity (including experimental errors) of the BVS method. This contradiction has been a source of long-term debates which motivates us for detailed theoretical study.

In d (or f) electron systems orbital degeneracy is an important and unavoidable source of complicated behavior (Kugel and Khomskii 1975, Kugel and Khomskii 1982). The strong coupling between charge and orbital degrees of freedom that is widely observed in the CO systems gives rise to a simultaneous orbital ordering (OO) at the transition. The particular orbital occupation results in the strong anisotropy in the system’s properties occurred due to the spatial anisotropy of orbital electron distribution. It appears even if original structure is relatively isotropic. There are many examples of this phenomena and one of the most fascinating of them is the cooperative Jahn-Teller (JT) effect – a spontaneous lifting of degeneracy of the high symmetrical orbital-degenerated state (Jahn and Teller 1937). It leads to the occupation of particular orbital, i.e., in other words, orbital ordering, and simultaneously to the structural phase transition with lowering symmetry.

The particular orbital order leads to the corresponding distortions of anion surrounding of the metal site. In case of octahedral anion coordination the orbital ordering in eg systems brings to relative (in respect to the average value) ex-
pansion or contraction of the anion octahedra along \( z \)-axis. This corresponds to ordering of the \( 3z^2 - r^2 \) or \( x^2 - y^2 \) orbital, respectively. In \( t_{2g} \) systems due to the particular symmetry of occupied orbital the average metal-oxygen distance in the plane of the orbital (which is perpendicular to one of diagonals of the distorted octahedron) becomes considerably larger than the average distance in the others two. The distortions, however, are much smaller than in \( e_g \) systems, while an information about local structure distortion can be extracted from the crystal structure analysis.

As was mentioned above, the crystal structure analysis provides a robust and useful tool to examine the charge and orbital state in CO systems (Attfield 1990). However, obtaining the atomic displacements within the unit cell has proven very difficult because of its complexity and the microtwinning that usually occurs below the transition. Together with a large number of unique metallic sites in the low-temperature phases this significantly reduces experimental resolution. Due to the difficulties to resolve the small atomic distortions (especially in \( t_{2g} \) systems) the prove of CO needs a consensus between the crystallographic and theoretical studies. The latter are usually based on the electronic structure calculations using the LDA+\( U \) method (Anisimov et al. 1996, Antonov, Yaresko, Perlov, Thalmeyer, Fulde, Oppeneer and Eschrig 1998, Antonov et al. 2001, Leonov, Yaresko, Antonov, Korotin and Anisimov 2004, Lee, Kuneš and Pickett 2004). Furthermore, the electronic structure calculations can usefully predict that such displacements are likely to be present even where experimental or materials difficulties have prevented the full structure from yet being observed (Leonov, Yaresko, Antonov, Attfield and Anisimov 2005).

The present work is devoted to the systematic theoretical study of the charge ordered mixed-valent transition metal oxides. Although the charge-ordering occurs in the wide range of mixed-valent systems in our work we focus only on three of them:

(i) Magnetite, \( \text{Fe}_3\text{O}_4 \), the archetypal charge ordering system;

(ii) Iron oxoborate, \( \text{Fe}_2\text{OBO}_3 \), which has been recently proposed as the prototype of “electrostatically driven” charge ordered system;

(iii) Titanium oxide, \( \text{Ti}_4\text{O}_7 \). In contrast to the above mentioned iron oxides which exhibit the on-site charge-ordering, it has the ordering of \( \text{Ti}^{3+}-\text{Ti}^{3+} \) dimers.

These are \( t_{2g} \) systems showing rich and complicated physics whose low-temperature properties have attracted considerable interest during the last decades.

The electronic structure of the above mentioned systems has been calculated within the LDA+\( U \) approach where the electronic correlations are taken on the static Hartree-Fock level (Anisimov and Gümürşsson 1991, Anisimov et al. 1991, Liechtensten et al. 1995). We focus our investigation on the ground
state properties of the long-range ordered insulators where dynamic correlations
are not very relevant. In this regard, an outstanding challenge for further
theoretical studies would be investigation of the charge-ordering itself. To do
this, more sophisticated methods (with respect to the static LDA+U) which
explicitly involve the spatial dynamic fluctuations are required. At present only
combination of LDA with the cluster expansion of dynamical mean-field the-
ory (LDA+CDMFT) gives such an opportunity (Anisimov, Poteryaev, Korotin,
Anokhin and Kotliar 1997, Kotliar and Vollhardt 2004, Georges, Kotliar, Krauth
and Rozenberg 1996, Maier, Jarrell, Pruschke and Hettler 2005). Therefore, a
realistic description of charge ordering remains a fascinating problem for further
investigations.

This thesis is organized as follows:

In the next chapter we introduce the ab initio Hamiltonian and discuss the ba-
sic concepts of the density functional theory. In this chapter we address some
practical aspects of its application, namely, the construction of the local-density
approximation (LDA) and its extension for correlated materials with a long-range
order (LDA+U).

The chapters 3, 4 and 5 present the detailed electronic structure study of the
ground state properties of the compounds mentioned above (Fe₃O₄, Fe₂OBO₃
and Ti₃O₇, respectively). Our calculations give microscopic explanation of the
strong and very remarkable discrepancy found between experimental estimations.
As you will see, the charge disproportion obtained in the calculations agrees well
with the experimental findings. This resolves the ambiguity of interpretations of
recent x-ray and neutron diffraction data which have been the source of strong
debates, and shows further perspectives for investigations.

Finally, we conclude this thesis with a summary and outlook.
2. THE LDA/LDA+$U$ APPROACH

2.1 Electronic Hamiltonian

Using the Born-Oppenheimer approximation (Born and Oppenheimer 1927) and neglecting relativistic effects (e.g. spin-orbit coupling) the electronic \textit{ab initio} Hamiltonian in general form can be written as

\[
\hat{H} = \sum_{\sigma} \int d^3r \, \hat{\Psi}^+(r, \sigma) \left[ -\frac{\hbar^2}{2m_e} \Delta + V_{\text{ion}}(r) \right] \hat{\Psi}(r, \sigma) + \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r \, d^3r' \, \hat{\Psi}^+(r, \sigma) \hat{\Psi}^+(r', \sigma') \, V_{\text{ee}}(r-r') \, \hat{\Psi}(r', \sigma') \hat{\Psi}(r, \sigma). \tag{2.1}
\]

Here, $\hat{\Psi}^+(r, \sigma)/\hat{\Psi}(r, \sigma)$ is the field creation/annihilation operator that create/destroy an electron at position $r$ with spin $\sigma$. $\Delta$ is the Laplace operator. $e$ and $m_e$ are the electron charge and electron mass, respectively. $V_{\text{ion}}$ denotes the one-particle ionic potential of all ions with charge $eZ_i$ at given positions $R_i$ via

\[
V_{\text{ion}}(r) = -e^2 \sum_i \frac{Z_i}{|r-R_i|},
\tag{2.2}
\]

and $V_{\text{ee}}(r-r')$ is the electron-electron interaction

\[
V_{\text{ee}}(r-r') = \frac{e^2}{2} \sum_{r \neq r'} \frac{1}{|r-r'|}.
\tag{2.3}
\]

The Hamiltonian (2.1) has a relatively simple form. However, if more than a few electrons are involved, it is impossible to solve it exactly without any approximation (Van Vleck 1936). Even the powerful numerical approaches like Green function Monte-Carlo method can only deal with a relatively modest number of electrons. In particular, an explicit numerical evaluations of the correlated wave-functions succeed only for the light atoms and molecules like hydrogen and helium, the simplest few-electrons chemical compounds. To overcome this complexity one can replace Eq. 2.1 with a strongly simplified model Hamiltonian containing several adjustable parameters.
An alternative ab initio method is the so-called density functional theory (DFT) in which total energy functional is expressed in terms of the total electron density (Hohenberg and Kohn 1964, Kohn and Sham 1965). In order to solve the DFT equations further approximations are required. One of the most successful of them is the local density approximation (LDA) where the many-body problem is mapped onto a non-interacting system with one-electron exchange-correlation potential taken as that of the homogeneous electron gas (Jones and Gummesson 1989, Capelle 2002). Although in LDA the correlation and exchange interaction are treated rudimentary, the method has proven to be highly successful for realistic solid-state calculation of weakly correlated systems such as large molecules and solids (Jones and Gummesson 1989). However, in materials with partially filled d (or f) electron shells where the Coulomb interaction is comparable to the bandwidth (e.g. transition-metal oxides or rare-earth metal compounds) application of this theory does not have a lot of success. One of the main reasons of this is that the orbital independent electron potentials contains a “self-interaction”, or, in the other words, an electron is moving in the average field of all other electrons including itself. In general, this assumption underestimates an energy gap in the band insulators. Another problem of the ordinary LDA method is that it takes into account only the N-electron ground state, i.e., both occupied and empty states are calculated with the same effective potential for N electrons. If we add one electron to the N electron system then effective potential diverges but this problem is not taken into account in the most of approximations of the electron density functional.

There were several attempts to improve on the LDA approach in order to take into account the strong electron-electron correlations. Among which is the self-interaction correction method (SIC) where the spurious self-interaction is approximately excluded. It reproduces well the localized nature of the d (or f) electrons in transition metal (rare-earth metal) compounds. However, one-electron energies obtained within SIC are usually in considerable disagreement with spectroscopy data.

The Hartree-Fock (HF) method (Hartree 1928, Fock 1930) is appropriate to describe the correlated electron systems with a long-range order (e.g. magnetic Mott insulators and charge ordered systems) because the HF equations contain a term that excludes the self-interaction. However, one of the serious problems of the Hartree-Fock method is that Coulomb interaction in this method is unscreened. The unscreened values of Coulomb parameter U is rather large (15-20 eV), while screening leads to much smaller value of 4-6 eV for 3d transition metals. Due to the neglecting of screening effects, the Hartree-Fock approximation ordinarily overestimates the energy gap by a factor of 2-3 comparing to experiment. This problem is overcome in the GW approximation which may be regarded as a Hartree-Fock theory with frequency and orbital dependent screened Coulomb interactions.
The GWA calculation scheme has been successfully applied to real systems like simple metals and some simple transition metal oxides. However, its application to more complex systems has not been feasible up to now because of large computation efforts. Another problem of the GWA method is the screened interaction (necessary to construct a response function) which is calculated using the energy bands and wave functions obtained from the LDA calculations. This procedure is valid only for systems with weak correlations effects.

Among others, the so-called LDA+$U$ method has proven to be highly successful for realistic solid-state calculation because of the non-local and energy-dependent self-energy, approximated by the frequency-independent and non-local screened Coulomb potential (Anisimov and Gunnarsson 1991, Anisimov et al. 1991, Liechtenstein et al. 1995). Although, the LDA+$U$ approach is designed for the long-range ordered insulating systems, e.g., charge ordered insulators and antiferromagnetic Mott insulators, the method has also been successfully applied to magnetic correlated metals (in order to explain magnetism) as well as for analysis of exchange interactions in the highly frustrated paramagnetic systems at the verge of magnetic transition. The one-electron static problem considered in the LDA+$U$ method usually fails to reproduce the systems near Mott-Hubbard metal-insulator transition. It also fails to explain the transition itself due to the neglecting of dynamical fluctuations which are very important at the verge of metal-insulator transition. However, due to the screened Coulomb potential and relatively moderate computational efforts, the LDA+$U$ is well suited for description of correlated metals and insulators with a long-range order. This is in remarkable contrast to the Hartree-Fock and GW approximations whose application have considerable limitations discussed above.

Neither LDA nor LDA+$U$ are able to describe the many-body phenomena like Kondo-effect or quasiparticle peak in spectral function of strongly correlated metals. In order to resolve this problem the combination of LDA with one of the most successful non-perturbative many-body technics, dynamical mean-field theory (DMFT), has been recently formulated (Georges et al. 1996, Anisimov, Poteryaev, Korotin, Anokhin and Kotliar 1997, Kotliar and Vollhardt 2004). It combines together all positive aspects of both approaches. In this method all electrons are separated in two subsets: delocalized $s$, $p$ electrons which are well described using an orbital independent one-electron LDA potential and localized $d$ (or $f$) ones. DMFT is used to describe the on-site Coulomb correlations of $d$ (or $f$) electrons, whereas the long-range Coulomb interaction is well described by the LDA potential. A remarkable advantage of the LDA+DMFT theory with respect to the LDA/LDA+$U$ approach is that the former provides a realistic description for both weakly and strongly correlated materials. In particular, the LDA+DMFT in combination with quantum Monte Carlo (QMC) technics has proven to be reliable approach for realistic investigation of strongly correlated multi-band system (Keller 2005). However, a critical slowing down of the
DMFT(QMC) convergence process at low temperatures together with considerable increase of computational efforts with increase of the number of interacting orbitals (e.g., from one to three, or five in d electron systems) makes it problematic to study of charge-ordering systems. The lowest possible temperature as 300 K has been recently achieved in the single-site LDA+DMFT(QMC) calculations with five 3d orbitals in V₂O₃ (Mo, Denlinger, Kim, Park, Allen, Sekiyama, Yasumaki, Kadono, Suga, Saitoh, Muro, Metcalfe, Keller, Held, Eyert, Anisimov and Vollhardt 2003, Keller 2005). Therefore, the LDA+DMFT(QMC) investigation of the charge-ordering systems which ordinary have a complex low-temperature structure requires further increasing of computational efforts.

2.2 Density functional theory

In the past decades, DFT within the LDA approximation was successfully applied for realistic calculations in atoms, molecules and solids (Jones and Gunnarsson 1989). In order to calculate the electronic structure of a system it is necessary to solve Schrödinger equation ordinary using the variational principle. The important question rising in this case is how to build up corresponding basis functions which are the Bloch states of valence electrons. The main problem is that the wave functions have a qualitatively different behavior in the space close to ion and relatively far of it (in the interstitial region). In the first case a reasonably good approximation is a tight-binding formalism, i.e. the linear combination of atomic orbitals. In the second, these are the free-electron wave functions.

According to the fundamental Hohenberg-Kohn theorem of DFT (Hohenberg and Kohn 1964) all properties of the ground state of non-homogeneous interacting electron gas can be described in terms of functionals of electron density ρ(r). Instead of the Hamiltonian (Eq. 2.1) one introduces the following functional of the system

\[ E[\rho] = T[\rho] + \int d^3 r d^3 r' \frac{\rho(r)\rho(r')}{|r - r'|} + \int d^3 r \rho(r) v_{\text{ext}}(r) + E_{\text{xc}}[\rho], \]  (2.4)

where \( v_{\text{ext}}(r) \) is the external field including the kernel field, functional \( T[\rho] \) denotes a kinetic energy of the system of non-interacting electrons with density \( \rho(r) \), and functional \( E_{\text{xc}}[\rho] \) contains many-electron effects without taking into account the Hartree exchange and correlations. The total energy of the system can be found as minimum of the expectation energy functional with respect to all many-body wave functions at a given electron number \( N \) which yield the electron density \( \rho(r) \). On the other hand, in order to find the total energy of the system under investigation one needs to define functional \( E[\rho] \) and then find its
minimum. The electron density can be represented in the following manner

\[ \rho(r) = \sum_{i=1}^{N} |\varphi_i(r)|^2, \quad (2.5) \]

where \( \varphi_i(r) \) is the set of one-particle wave functions, and \( N \) is the electron number. Taking variation of the energy functional \( E[\rho] \) with respect to the set of one-particle wave functions \( \varphi_i(r) \) with condition Eq. 2.5 one obtains the Kohn-Sham equations

\[ \left[ -\frac{\hbar^2}{2m_e} \Delta + V_{\text{ion}}(r) + \int d^3r' V_{\text{ee}}(r-r')\rho(r') + V_{\text{xc}}(r) \right] \varphi_i(r) = \varepsilon_i \varphi_i(r), \quad (2.6) \]

were \( \varepsilon_i \) are the Langrange factors which imply energy spectra of one-electron state. The exchange correlation potential \( V_{\text{xc}}(r) \) is defined via the functional derivative of \( E_{\text{xc}}(\rho) \)

\[ V_{\text{xc}}(r) = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}. \quad (2.7) \]

Finally, the complicated many-body electron problem is mapped onto a set of non-interacting one-electron problems with an effective potential

\[ V_{\text{eff}}(r) = V_{\text{ion}}(r) + v_{\text{ext}}(r) + \int d^3r' V_{\text{ee}}(r-r')\rho(r') + V_{\text{xc}}(r). \quad (2.8) \]

The set of equations 2.4–2.8 should be evaluated in a self-consistent manner because \( V_{\text{xc}}(r) \) depends on a choice of orbitals \( \varphi_i(r) \) that are necessary to find. Equations 2.4 and 2.5 define the ground state energy and electron density exactly if the exchange correlation potential \( V_{\text{xc}}(r) \) is explicitly defined. For non-homogeneous electron gas \( E_{\text{xc}}[\rho] \) can be explicitly introduced as a Coulomb interaction between electron and exchange-correlation hole around it

\[ E_{\text{xc}}[\rho] = \frac{1}{2} \int d^3r \rho(r) \int d^3r' \frac{\rho_{\text{xc}}(r, r' - r)}{|r - r'|} \quad (2.9) \]

with the exchange correlation charge density \( \rho_{\text{xc}}(r, r' - r) \) defined via pair-correlation function \( g(r, r', \lambda) \) and coupling constant \( \lambda \)

\[ \rho_{\text{xc}}(r, r' - r) \equiv \rho(r') \int_{0}^{1} d\lambda [g(r, r', \lambda) - 1]. \quad (2.10) \]

It was found that \( E_{\text{xc}}[\rho] \) is independent from the exchange-correlation hole form and is the function of spherical charge density only. The physical idea of this phenomenon is that the Coulomb energy depends only on distance. Moreover, the hole charge density satisfies to the sum rule, i.e. the exchange correlation
First principles information:
atomic numbers, crystal structure (lattice, atomic positions)

Choose initial electronic density $\rho(r)$

Calculate effective potential using the LDA [Eq. (2.14)]

$$V_{\text{eff}}(r) = V_{\text{ion}}(r) + \int d^3r' \, V_{\text{ee}}(r-r')\rho(r') + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)}$$

Solve Kohn-Sham equations [Eq. (2.6)]

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) - \varepsilon_i \right] \varphi_i(r) = 0$$

Calculate electronic density [Eq. (2.5)],

$$\rho(r) = \sum_i^N |\varphi_i(r)|^2$$

Iterate to self-consistency

Calculate band structure $\varepsilon_i(k)$ [Eq. (2.6)], partial and total DOS, exchange couplings, self-consistent Hamiltonian, and etc.

**Figure 2.1:** Flow diagram of the DFT/LDA calculations, from Held et al. (2003)

hole corresponds to the charge decreasing around the electron on value that is equal to the value of electron charge

$$\int d\mathbf{r'} \rho_{\text{xc}}(\mathbf{r}, \mathbf{r'} - \mathbf{r}) = -1 \quad (2.11)$$

If the exchange correlation term $E_{\text{xc}}[\rho]$ would be known exactly, the DFT calculations could be performed without any approximation (see the flow diagram of Fig. 2.1).
2.3 Local density/spin-density approximation

In order to solve the DFT equations discussed above the explicit form of $E_{xc}[\rho]$ or exchange-correlation hole density $\rho_{xc}(r, r' - r)$ is required. However, a priori the exact form of this functional is unknown, i.e. some sort of approximation should be introduced to solve the DFT equations. The simplest one is the so-called local density approximation (LDA) where $\rho_{xc}(r, r' - r)$ is taken to be the same as in homogeneous electron gas with local charge density $\rho(r')$

$$\rho_{xc}(r, r' - r) \equiv \rho(r') \int_0^1 d\lambda \left[ g_0(r, r', \lambda, \rho(r)) - 1 \right].$$

(2.12)

Here, $g_0(r, r', \lambda, \rho(r))$ is the pair-correlation function of homogeneous electron system. This approximation satisfies the sum rule Eq. 2.11 which is one of the main reasons of its wide applicability. Substituting the exchange-correlation hole density in Eq. 2.9 one obtains

$$E_{xc}[\rho] = \int d^3 r \ \rho(r) \ \varepsilon_{xc}^{\text{LDA}}(\rho(r)),$$

(2.13)

where $\varepsilon_{xc}[\rho(r)]$ is the exchange correlation energy per electron of homogeneous interacting electron gas with charge density $\rho(r)$. This approximation corresponds to covering of each electron by exchange-correlation hole and valid for slow changing of $\rho(r)$. In theory of homogeneous systems there are several different ways to obtain $\varepsilon_{xc}[\rho(r)]$, e.g., the perturbative approach or numerical simulations of the jellium model which has a constant ionic background ($V_{\text{ion}}(r) = \text{const}$).

In the LDA approximation the effective potential transforms to

$$V_{\text{eff}}^{\text{LDA}}(r) = V_{\text{ion}}(r) + v_{\text{ext}}(r) + \int d^3 r' \frac{\rho(r')}{|r - r'|} + \mu_{xc}(r),$$

(2.14)

where $\mu_{xc}(r)$ is the exchange correlation part of the chemical potential of homogeneous interacting electron gas with local density $\rho(r)$. It is defined according to

$$\mu_{xc}(r) = \frac{\delta}{\delta \rho(r)} \left\{ \rho(r) \ v_{\text{xc}}[\rho] \right\}.$$  

(2.15)

To introduce a spin-polarization the exchange-correlation energy becomes functional of majority and minority spin densities (in spin-collinear case) leading to

$$E_{xc}[\rho_{\uparrow}, \rho_{\downarrow}] = \int d^3 r \ \rho(r) \ \varepsilon_{xc}^{\text{LDA}}(\rho_{\uparrow}(r), \rho_{\downarrow}(r)).$$

(2.16)

By construction the LDA/LSDA methods have no adjustable parameters. Moreover, there is no small parameter in the DFT theory, i.e., it is impossible to build
up an ordinary perturbative theory and to give theoretical estimation for the accuracy of approximation.

The Hamiltonian Eq. 2.1 within the LDA approximation can be written as

\[
\hat{H}_{\text{LDA}} = \sum_\sigma \int d^3r \, \hat{\Psi}^+(r, \sigma) \left[ -\frac{\hbar^2}{2m} \Delta + V_{\text{ion}}(r) + \int d^3r' \, \rho(r') V_{\text{ee}}(r-r') \right. \\
\left. + V_{xc}^{\text{LDA}}(r) \right] \hat{\Psi}(r, \sigma)
\]  

(2.17)

where the exchange-correlation LDA potential is

\[
V_{xc}^{\text{LDA}}(r) = \frac{\delta E_{xc}^{\text{LDA}}[\rho]}{\delta \rho(r)}.
\]  

(2.18)

To proceed further, the field operators \( \hat{\Psi}(r, \sigma) \) have to be expanded in a suitable set of basis functions \( \Phi_{ilm}(r) \)

\[
\hat{\Psi}^+(r, \sigma) = \sum_{ilm} c_{ilm}^\sigma \Phi_{ilm}(r).
\]  

(2.19)

Although a rich variety of different basis sets \( \Phi_{ilm}(r) \) have been proposed, e.g., plane waves (PW), augmented plane waves (APW), augmented spherical waves (ASW), linear augmented plane waves (LAPW), muffin-tin orbitals (MTO), linear muffin-tin orbitals (LMTO), the linear methods have been widely adopted because of its moderate computational time consuming together with a relatively good accuracy (Andersen 1975). In the following we consider only the LMTO basis set because of its remarkably simple formulation and small computational efforts with respect to the LAPW method. The latter is very important in sense of the apparent complexity of electron systems of the interest.

### 2.4 Linear Muffin-Tin Orbital (LMTO) formalism

The LMTO’s calculation scheme is based on the concept of muffin-tin potential which has proven to be a highly successful approximation of potential of realistic close-packed systems. In this concept the potential for a solid is approximated by series of non-overlapping atomic-like spherical symmetric potentials inside a sphere with radius \( S \), and a constant potential in the interstitial region between the spheres

\[
V(r) = \begin{cases} 
V(|r|), & r \leq S \\
V_c, & r > S.
\end{cases}
\]  

(2.20)
Therefore, the Schrödinger equation can be solved exactly in both regions \(r \leq S\) and \(r > S\). These solutions are matched at the boundaries of the spheres to produce the muffin-tin orbitals. To reduce the effect of interstitial region one introduces the overlapping atomic spheres which fill the whole volume of the crystal. In this the so-called atomic sphere approximation (ASA) the volume of interstitial region equals to zero, i.e. the electron kinetic energy \(\kappa^2 = \varepsilon - V_e\) in this region becomes a free parameter which can be taken equal to zero. In this case wave function inside a sphere (for \(r \leq S\)) satisfies to the radial Schrödinger equation, whereas outside it corresponds to the solution of Laplas equation \(\nabla^2 \Phi = 0\). Therefore, the radial part of the wave function can be written as

\[
\Phi_l(r, \varepsilon) = \begin{cases} 
  u_l(r, \varepsilon), & r \leq S \\
  \left[ \frac{D_l + l + 1}{2l + 1} \left( \frac{r}{S} \right)^l + \frac{l - D_l}{2l + 1} \frac{(r/S)^{-l-1}}{u_l(S, \varepsilon)} \right] u_l(S, \varepsilon), & r > S,
\end{cases}
\]

where \(u_l(r, \varepsilon)\) is the exact radial solution of Schrödinger equation which is normalized by one in the MTO sphere with radius \(S\). These functions are not convenient to use as basis functions because of its divergence for large \(r\). In order to construct decaying for large \(r\), continuous and smooth in the whole space basis functions one has to subtract the divergent wave \(\frac{D_l + l + 1}{2l + 1} \left( \frac{r}{S} \right)^l\) from both parts of Eq. 2.21

\[
\Phi_l(r, D) = \begin{cases} 
  \Phi(r, D) - \frac{D_l + l + 1}{2l + 1} \frac{\Phi_l(S, D)}{\Phi_l(S, l)} \Phi_l(r, l), & r \leq S \\
  \frac{l - D_l}{2l + 1} \frac{r^{-l-1}}{u_l(S, \varepsilon)} \Phi_l(S, D), & r > S,
\end{cases}
\]

where \(D_L(\varepsilon)\) is the logarithmic derivative of the radial part of wave function at the sphere radius \(S\)

\[
D_L(\varepsilon) = S \frac{\dot{u}_l(r, \varepsilon)}{u_l(r, \varepsilon)} \bigg|_{r=S}.
\]

The obtained functions are not any more the solutions of Schrödinger equation inside the atomic sphere. However, it is convenient to use them to built up the Bloch sums of the crystal. Taking into account all tails of basis functions from the other sites in central sphere at \(R_s\), the Bloch sums can be written as

\[
\chi^k_L(r, D) = \sum_{R_s \neq 0} e^{i k \cdot R_s} \Phi_L(r - R_s, D),
\]

where tails from the center with radius-vector \(R_s\) are defined by

\[
\Phi_L(r - R_s, D) = i^l Y_L(r - R_s) \left| \frac{r - R_s}{S} \right|^{-l-1} \frac{l - D}{2l + 1} \Phi_l(S, D).
\]
Taking tails expansion in partial waves at the center of sphere and making the Bloch basis functions continuous and differentiable on the sphere surface, one obtains

\[
\chi^k_L(r, D) = \begin{cases} 
\Phi_L(r, D) - \Phi_l(S, D) \frac{r^l}{r^l} \sum_{L'} \left[ S^k_{L'L} - \frac{D + l + 1}{l - D} \times \right. \\
\times 2(2l + 1) \delta_{LL'} \left\{ \frac{\Phi_L(r, D')}{2(2l' + 1)} \Phi_l(S, D'), \right. \\
\left. \right. \\
\left. \Phi_l(S, D) \frac{r^l}{r^l} \sum_{L'} S^k_{L'L} \times \right. \\
\times \frac{1}{2(2l' + 1)} \left[ \frac{r^l}{r^l} + \frac{1}{S} \right] \right] \\
\end{cases} \\
(2.26) \\
r \leq S,
\]

\[
\Phi_l(S, D) \frac{r^l}{r^l} \sum_{L'} S^k_{L'L} \times \frac{1}{2(2l' + 1)} \left[ \frac{r^l}{r^l} + \frac{1}{S} \right]. \\
r > S.
\]

Here, \( \chi^k_L(r, D) \) are the so-called muffin-tin orbitals, and \( S^k_{L'L} \) are the structural constants which are defined via

\[
S^k_{L'L} = \sum_R e^{ik \cdot R} S_{L'L'}, \text{ and}
\]

\[
S^R_{L'L} = -\frac{8\pi(2l + 2l' - 1)!!}{(2l - 1)!!(2l' - 1)!!} \sum_{L''} C_{L''L'}(-i)^{l''} \left( \frac{R}{S} \right)^{l''-l-1} Y_{l''}(R), \hspace{1cm} (2.27)
\]

where \( C_{L''L'} \) are the Gaunt's coefficients. \( Y_L(R) \) are the corresponding spherical harmonics. The solution of Schrödinger equation of the whole crystal is a linear combination of MT-orbitals

\[
\Psi_k(r) = \sum_L C_L(k) \sum_{R_s \neq 0} e^{ik \cdot R_s} \chi^k_L(r - R_s, D_1(\varepsilon)) \hspace{1cm} (2.28)
\]

which must be exact solution of the radial Schrödinger equation inside of atomic spheres. According to this condition all tails from other sites and unphysical terms in MT-orbital, that is proportional to \( [i' Y_L(r) r^l] \), have to eliminate each other inside of all atomic spheres, i.e. the second term in \( \chi^k_L(r, D) \) (Eq. 2.26) will turn to zero. This gives a set of linear homogeneous equations

\[
\sum_L (S^k_{L'L'} - \delta_{LL'} P_l(\varepsilon)) C_L(k) \Phi_L(S, D) = 0, \hspace{1cm} (2.29)
\]

where the total information about crystal potential is included in the potential functions

\[
P_l(\varepsilon) = 2(2l + 1) \frac{D_l(\varepsilon) + l + 1}{D_l(\varepsilon) - l}. \hspace{1cm} (2.30)
\]

The crystal structure information is contained in the structural constants \( S^k_{L'L'} \) (Eq. 2.27). Therefore, the main problem of band structure calculations is to find eigenvalues and eigenvectors for single atomic sphere with spherically symmetric
potential and $k$-dependent boundary conditions which appears from neighboring spheres.

By construction the MTO basis set $\chi_{L}^{k}(r, D)$ is an energy dependent. This considerably complicates numerical evaluation of the secular equation whose solution defines the energy spectra of the system

$$\det||\langle \chi_{L}^{k}(r, D)|\hat{H} - \varepsilon \hat{O}|\chi_{L}^{k}(r, D)\rangle|| = 0.$$  \hspace{1cm} (2.31)

Here, $\hat{H}$ and $\hat{O}$ are the Hamiltonian and overlap operators, respectively.

To resolve such a difficulty the linear MTO (LMTO) method was introduced which is based on the power expansion of the original MTO’s up to the linear order in energy (Andersen 1975). The energy independent LMTO basis set provides a rapid convergence of the method. Taking into account only linear term in the Taylor expansion for the MTO basis wave function in an arbitrary energy point $\varepsilon_\nu$ one obtains

$$\Phi(r, D) = \Phi_\nu(r) + w(D)\Phi_\nu'(R).$$  \hspace{1cm} (2.32)

Here, $\Phi_\nu(r)$ is the value of wave function at the energy point $\varepsilon_\nu$, i.e. $\Phi_\nu(r) = u_l(\varepsilon_\nu, r)$. $\Phi_\nu'(r)$ is the energy derivative of the wave function at the expansion point $\Phi_\nu(r) = \frac{\partial}{\partial \varepsilon} u_l(\varepsilon, r)|_{\varepsilon = \varepsilon_\nu}$ which is normalized by one in the atomic sphere with radius $S$. $w(D)$ is calculated as follows

$$w(D) = -\frac{\Phi_\nu(r)}{\Phi_\nu'(r)} \frac{D - D_\nu}{D - D_\nu},$$  \hspace{1cm} (2.33)

where $D$ is the logarithmic derivative on the atomic sphere surface

$$D = \frac{\Phi'(r, D)}{\Phi(r, D)}|_{r=S}.$$  \hspace{1cm} (2.34)

$D_\nu$ and $D_\nu'$ are defined via $D_\nu = S \frac{\Phi_\nu'(S)}{\Phi_\nu(S)}$ and $D_\nu' = S \frac{\Phi_\nu'(S)}{\Phi_\nu(S)}$, respectively.

The expansion energy point $\varepsilon_\nu$ is selected within the region of energies occupied by the valence electrons which is obtained from the solution of the Schrödinger equation within the atomic sphere. Therefore, if we consider an arbitrary energy $\varepsilon$, then the LMTO’s have an error of order $(\varepsilon - \varepsilon_\nu)^2$ within the spheres.

In the LMTO basis set matrix elements of the Hamiltonian and overlap matrix inside of sphere can be written as

$$\langle \Phi_{L}'(D', S)|\hat{H} - \varepsilon \hat{O}|\Phi_{L}(D, S)\rangle = \delta_{L,L'} w_l(D),$$

$$\langle \Phi_{L}'(D', S)|\Phi_{L}(D, S)\rangle = \delta_{L,L'} (1 + \langle \Phi_\nu^2|\Phi_{L}(D, S)\rangle w_l(D)w_l(D')).$$  \hspace{1cm} (2.35)
where $\Phi_L(r, D)$ is orthogonal to $\hat{\Phi}_L(r)$ because of the normalization condition 
$\langle \Phi(r, \varepsilon) | \hat{\Phi}(r, \varepsilon) \rangle = 1$ and $\frac{\partial}{\partial \varepsilon} \langle \Phi(r, \varepsilon) | \hat{\Phi}(r, \varepsilon) \rangle = 2 \langle \Phi(r, \varepsilon) | \Phi(r, \varepsilon) \rangle = 0$.

The Hamiltonian Eq. 2.36 describes a single atomic sphere. In order to build up a crystal where each sphere affects to the energy spectra one introduces a set of potential parameters $w_i(D_1), S\Phi^2(D_1), \Phi^2(D_1)/\Phi^2(D_2)$ with $D_1 = -l - 1$ and $D_2 = l$. Using these potential parameters the basis orbitals $\chi^k_L(r, D)$ can be written as

$$\chi^k_L(r, D) = \frac{w_i(l) - w_i(D)}{w_i(l) - w_i(-l - 1)} \chi^k_L(r) = \alpha_i(D) \chi^k_L(r),$$

where $\chi^k_L(r)$ is defined according to

$$\chi^k_L(r) = \Phi_L(r, -l - 1) - \Phi_l(S, -l - 1) \sum_{L'} S_{LL'}^k \frac{\Phi'_{L'}(r, l')}{2(2l' + 1)\Phi_l(S, l')},$$

The Hamiltonian and overlap matrix of the crystal are

$$H^k_{LL'} = \langle \chi^k_L(r) | \hat{H} | \chi^k_L(r) \rangle = H^{(1)}_{LL'} \delta_{LL'} + \left[ -(H^{(2)}_{LL'} + H^{(2)}_{L'L}) \right],$$

$$O^k_{LL'} = \langle \chi^k_L(r) | \chi^k_L(r) \rangle = O^{(1)}_{LL'} \delta_{LL'} + \left[ -(O^{(2)}_{LL'} + O^{(2)}_{L'L}) \right],$$

with

$$H^{(1)}_{L} = w_i(-l - 1) + \varepsilon_{VL} O^{(1)}_{L};$$

$$H^{(2)}_{L} = \frac{1}{2} \frac{w_i(l)}{w_i(-l - 1) - w_i(l)} + \varepsilon_{VL} O^{(2)}_{L};$$

$$H^{(3)}_{L} = \frac{w_i(l)}{2S[(2l + 1)\Phi_l(S, l)]^2} + \varepsilon_{VL} O^{(3)}_{L},$$

where $H^{(1)}, H^{(2)},$ and $H^{(3)}$ terms can be treated like one-, two-, and three-centers integrals respectively.
2.5 The LDA+U method

As was previously established, application of the ordinary LDA theory is very successful in explaining properties of the weakly correlated electron systems. However, this theory fails to reproduce the correct ground state properties of many systems with partially filled d or f electron shells. To overcome these disadvantages the LDA+U method was proposed (Anisimov, Aryasetiawan and Lichtenstein 1997). The basic concept of this method and its profit with respect to the LDA approach is that the localized and itinerant electron states are treated in different ways. In particular, the delocalized s, p electron states are usually well described by the LDA potential, whereas the Coulomb interaction between localized d (or f) electrons in the LDA+U is approximated by the on-site Hubbard interaction \( \frac{U}{2} \sum_{m \neq m'} n_m n_{m'} \), where \( n_m \) is the d (or f) orbital occupation in the spinless formalism. In order to keep the consistency of the LDA+U functional, the Coulomb interaction energy of d (or f) electrons originally presented in the LDA potential has to be eliminated. This so-called double counting energy contribution \( E_{dc} \) can be reasonably well approximated by the average interaction of \( N_d \) electrons via

\[
E_{dc} = \frac{U}{2} N_d (N_d - 1),
\]

where \( N_d = \sum n_m \) is the total number of electrons. Furthermore, neglecting for simplicity the exchange and non-sphericity the LDA+U functional can be written as

\[
E_{LDA+U} = E_{LDA} - \frac{U}{2} N_d (N_d - 1) + \frac{U}{2} \sum_{m \neq m'} n_m n_{m'}.
\]

With respect to the ordinary LDA approach the LDA+U potential depends on the orbital occupancy and reproduces the qualitatively correct Mott-Hubbard physics where the lower and upper Hubbard bands are separated by the value of Coulomb interaction parameter \( U \). The orbital-dependent correction to the LDA potential shifts an orbital energy by \( -U/2 \) and \( U/2 \) for occupied states \( (n_m = 1) \) and empty states \( (n_{m'} = 0) \), respectively,

\[
V_i(r) = V_{LDA}(r) + U \left( \frac{1}{2} - n_i \right).
\]

Taking into account the direct and exchange Coulomb interactions inside a partially occupied d (or f) atomic shell the generalized LDA+U functional \( E_{LDA+U}[\rho_\sigma(r), n_\sigma] \) can be written as

\[
E_{LDA+U}[\rho_\sigma(r), n_\sigma] = E_{LSDA}[\rho_\sigma(r)] + E_U[n_\sigma] - E_{dc}[n_\sigma],
\]
where \( \rho_\sigma(r) \) is the charge density of \( d \) (or \( f \)) electrons with spin \( \sigma \) and \( E_{\text{LSDA}}[\rho_\sigma(r)] \) is the ordinary LSDA functional. The electrons of density matrix \( n_\sigma \) are defined via integration of the Green function of particular \( nl \) orbital in a localized orthonormal basis \( \left| inlm\sigma \right\rangle \)

\[
n^\sigma_{mm'} = -\frac{1}{\pi} \int \epsilon^\prime \text{Im} G^\sigma_{inlm, inlm'}(\epsilon) \, d\epsilon,
\]

(2.44)

where \( i \) denotes the particular site, \( n, l, \) and \( m \) are the principal, orbital and magnetic quantum numbers, respectively. \( \sigma \) is the spin index. The elements of the Green function matrix in this localized representation are defined by \( G^\sigma_{inlm, inlm'}(\epsilon) = \langle inlm\sigma| (\epsilon - \hat{H})^{-1} |inlm'\sigma\rangle \). Equation asserts that the LSDA suffices in the absence of orbital polarizations while the latter are driven by

\[
E_U[n_\sigma] = \frac{1}{2} \sum_{\{m\}, \sigma} \left\{ \langle m, m''|V_{ee}|m', m''\rangle n^\sigma_{m', m''} n^\sigma_{m''', m'''} - \langle m, m''|V_{ee}|m', m''\rangle n^\sigma_{m', m''} n^\sigma_{m'''', m''''} \right\},
\]

(2.45)

where \( V_{ee} \) are the screened Coulomb interactions among the \( nl \) electrons. The double counting correction term can be written as

\[
E_{\text{dc}}[n_\sigma] = \frac{U N_d(N_d - 1)}{2} - \frac{1}{2} \left\{ J N_1(N_1 - 1) + N_1(N_1 - 1) \right\}.
\]

(2.46)

Here, \( N_\sigma = \text{Tr}(n^\sigma_{mm'}) \) and \( N = N_1 + N_\uparrow \). \( U \) and \( J \) are the screened Coulomb and exchange interaction parameters, respectively. Remarkably that in the absence of orbital polarization the LDA+U functional \( E_{\text{LDA+U}} \) reduces to the LSDA one (\( E_{\text{LSDA}} \)).

The one-particle LDA+U Hamiltonian becomes

\[
\hat{H} = \hat{H}_{\text{LSDA}} + \sum_{mm'} \left| inlm\sigma \right\rangle V^\sigma_{mm'} \left\langle inlm'\sigma \right|,
\]

(2.47)

where the LDA+U potential is defined according to

\[
V^\sigma_{mm'} = \sum_{\{m\}} \left\{ \langle m, m''|V_{ee}|m', m''\rangle n^\sigma_{m', m''} - \langle m, m''|V_{ee}|m', m''\rangle n^\sigma_{m', m''} \right\} - \langle m, m''|V_{ee}|m', m''\rangle n^\sigma_{m', m''} - U \left( N - \frac{1}{2} \right) + J \left( N_\sigma - \frac{1}{2} \right).
\]

(2.48)

The matrix elements of screened Coulomb interactions can be expressed in terms of complex spherical harmonics and effective Slater integrals \( F^k \) as

\[
\langle m, m''|V_{ee}|m', m''\rangle = \sum_k a_k(m, m', m'', m''') F^k
\]

(2.49)
where \( 0 \leq k \leq 2l \) and coefficients \( a_k(m, m', m'', m'''') \) are defined by

\[
a_k(m, m', m'', m'''') = \frac{4\pi}{2k + 1} \sum_{q=-k}^{k} \langle lm|Y_{kq}|lm'\rangle \langle lm''|Y_{kq}^*|lm'''\rangle
\]  

(2.50)

For 3d electrons one needs to know \( F^0 \), \( F^2 \), and \( F^4 \) which can be estimated through the Coulomb and Stoner exchange interaction parameters, \( U \) and \( J \): \( U = F^0 \) and \( J = (F^2 + F^4)/14 \) with a ratio \( F^2/F^4 \) for 3d compounds with well accuracy equals to 0.625. Furthermore, \( U \) and \( J \) can be obtained by the constrained LDA calculations for supercell or estimated from experiment.

### 2.6 Calculation of exchange interaction parameters within the LDA+U method

The LDA+U approach presented in the previous section can be further used for estimation of the exchange interaction parameters \( J_{ij} \) of the effective Heisenberg model Hamiltonian

\[
\hat{H} = -\sum_{i<j} J_{ij} \vec{S}_i \cdot \vec{S}_j
\]  

(2.51)

Using the Green function formalism (Liechtenstein, Katsnelson, Antropov and Gubanov 1987) the effective exchange couplings can be evaluated as a second variation of the ground state energy with respect to the rotation angle of magnetic moment on the corresponding magnetic sublattices (Liechtensten et al. 1995). In combination with Eqs. 2.43-2.46 one obtains

\[
J_{ij} = \sum_{\{m\}} I_{mm'}^{ij} \chi_{mm'm''m'''}^{ij} I_{m''m'''}^{ij},
\]  

(2.52)

where the spin-dependent potentials \( I^i \) for the \( i \)th atom in the unit cell are expressed in term of the LDA+U potentials \( V_{m\sigma}^{i\sigma} \) (see Eq. 2.48)

\[
I_{mm'}^{i\sigma} = V_{mm'}^{i\sigma} - V_{mm'}^{i\sigma}.
\]  

(2.53)

The effective susceptibility between the magnetic sublattices is given in terms of the LDA+U eigenfunctions \( \psi_{n\kappa\sigma}^{m\sigma} \) and corresponding energies \( \varepsilon_{n\kappa\sigma} \) as

\[
\chi_{mm'm''m'''}^{ij} = \sum_{k\kappa\sigma} \frac{\theta_{n\kappa\sigma} - \theta_{n'\kappa\sigma}}{\varepsilon_{n\kappa\sigma} - \varepsilon_{n'\kappa\sigma}} \left| \psi_{n\kappa\sigma}^{m\sigma} \right|^* \left| \psi_{n\kappa\sigma}^{m\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m'\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m'\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m''\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m''\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m'''\sigma} \right| \left| \psi_{n'\kappa\sigma}^{m'''\sigma} \right|,
\]  

(2.54)

where \( \theta_{n\kappa\sigma} \) depicts an occupation of the \( n\kappa\sigma \) state and equals to 0 and 1 for empty and occupied state, respectively. This method provides a more sophisticated way of calculating of the exchange couplings parameters than direct comparison of the total energies of ferro- and antiferromagnetic configurations (Kübner, William and Sommers 1983). The accuracy of this method depends only on approximation used to obtain the one-particle potentials \( V_{m\sigma}^{i\sigma} \).
2. The LDA/LDA+ $U$ approach
3. CHARGE ORDER IN Fe₃O₄

The magnetic properties of magnetite (Fe₃O₄), the famous permanent natural magnet, have fascinated mankind for several thousand years already (Mattis 1988). The first ancient written source related to magnetite was recorded by Greek writers ~800 B.C. The mineral’s name of magnetite comes from the large deposits found in the district of Magnesia in Asia Minor. Since the beginning of the Iron Age it is one of the important ores of iron. Magnetite lodestones were used as a compass by earlier navigators, probably first made in China during the Qin dynasty (221-206 B.C.). In 1600 one of the first attempts of systematic study of magnetite was performed by William Gilbert, the famous English scientist. He published a book (recently republished, see Gilbert (1991)) on magnetism “De magnete” (“On the Magnet”) which contains the fruits of the earlier researches on electricity and magnetism, indeed provided the basis for a new science. During the 20th century, magnetite and spinel ferrites were intensively applied in industry, and its magnetoresistivity properties are of current interest for spintronics (Coey, Berkowitz, Balcels, Putris and Parker 1998).

Comprehensive investigation of magnetite started in 1913 when the first indication of the first-order transition was obtained by a susceptibility measurements on a synthetic polycrystals (Renger 1913, Weiss and Renger 1914).¹ They found an anomalous transition peak at ~130 K in addition to the already known para-ferromagnetic order transition on cooling through ~850 K. Extended magnetic measurements, performed during these early years by Weiss and Forrer (1929), Li (1932), and Okamura (1932), revealed that the observed variations of magnetic properties at the transition are only part of a fundamental transformation process in Fe₃O₄, giving rise to similar anomalies on a variety of other inter-related system parameters (see Fig. 3.1). In addition, an anomalous specific heat maximum occurred in Fe₃O₄ at ~113-115 K was observed by Okamura (1932), Parks and Kelly (1926), Millar (1929), and finally summarized by Ellefson and Taylor (1934).

Followed these earlier reports on the susceptibility and heat-capacity anomaly in Fe₃O₄ at 120 K, Verwey made the fundamental discovery that magnetite undergoes a sharp, first-order transition on cooling below \( T_V \sim 120 \) K (see Figs. 3.2, 3.3). At the transition the conductivity abruptly decreases by two orders

¹ These measurements were performed by Karl Renger in the course of his thesis (Renger 1913), with Pierre Weiss and Albert Einstein as advisers, at the ETH Zürich, Switzerland.
of magnitude and structure distorts from cubic to the orthorhombic symmetry. In addition, Verwey proposed a first theoretical model according to that the transition is caused by the ordering of Fe$^{2+}$ cations on the octahedral $B$ sublattice of the inverted spinel AB$_2$O$_4$ structure (Bragg 1915, Bragg and Brown 1926, Claassen 1926)$^2$, with a simple charge arrangement of (001) planes, indexed on the cubic cell, alternately occupied by 2+ and 3+ Fe$_B$ cations. This particular orthorhombic the so-called Verwey charge-ordering model was apparently confirmed not only by extensive anisotropy (Bickford 1953, Williams, Bozorth and Goertz 1953), magnetization and conductivity measurements (Domenicali 1950, Calhoun 1954), but also by x-ray (Abrahams and Calhoun 1953, Abrahams and Calhoun 1955) and neutron diffraction (Hamilton 1958). Thus, neutron diffraction measure-

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$^2$ Bragg (1915), this is one of the first publications on x-ray diffraction measurements. In the same year (1915) Sir William Henry Bragg and his son William Lawrence Bragg “for their services in the analysis of crystal structure by means of X-rays” jointly earned the Nobel Prize for Physics.
ments performed by Hamilton (1958) by carefully suppressing crystal twinning below the transition temperature, had been able to clearly resolve a (002) reflection which was regarded as ultimate proof for an orthorhombic symmetry of the low-temperature Fe₃O₄ phase.

![Graph](image_url)

**Figure 3.2:** Verwey’s original resistivity measurements on polycrystalline Fe₃O₄ bars, containing increasing amount of octahedral vacancies, as indicated by the varying Fe₃O₃:FeO ratios of the inset (Verwey and Haayman 1941); according to Walz (2002).

However, later diffraction studies disproved this model. Thus, Tombs and Rooksby (1951) and Rooksby and Willis (1953) were the first who deduced a non-orthorhombic symmetry for the low-temperature phase of Fe₃O₄. They found a rhombohedral symmetry by x-ray powder diffraction. Afterwards, the orthorhombic symmetry underlying the Verwey model was disproved by electron diffraction (Yamada, Suzuki and Chikazumi 1968, Chiba, Suzuki and Chikazumi 1975), x-ray (Yoshida and Iida 1977, Yoshida and Iida 1979), and neutron (Shapiro, Iizumi and Shirane 1976, Iizumi and Shirane 1975, Fujii, Shirane and Yamada 1975) diffraction. These experiments have clearly established the rhombohedral distortions of the cubic unit cell which was first detected by Tombs and Rooksby (1951) and Rooksby and Willis (1953) from x-ray powder diffraction. Furthermore, the detailed neutron diffraction measurements (Shirane, Chikazumi, Akimitsu, Chiba, Matsui and Fujii 1975) proved that the intensity of (002) reflections
Figure 3.3: Typical temperature dependence of the electrical conductivity in Fe₃O₄; according to Miles et al. (1957).

is actually zero when the contribution from simultaneous reflections is carefully removed. Further observation of superstructure reflections revealed half-integer satellite reflections, indexed as \((h, k, l + \frac{1}{2})\) on the cubic unit cell, which point to a doubling of the lattice cell along the \(c\)-axis and show the symmetry to be monoclinic (Yamada et al. 1968, Chiba et al. 1975, Samuelsen, Bleker, Dobrzynski and Riste 1968). The monoclinic lattice symmetry was also confirmed by single-crystal x-ray diffraction, whereas a magnetoelastic effect observed in magnetite indicates that the symmetry in the low-temperature phase is lower than \(P1\) (Miyamoto and Shindo 1993).

The most detailed structure refinement below the Verwey transition was performed by Iizumi, Koetzle, Shirane, Chikazumi, Matsui and Todo (1982) through neutron-diffraction study of almost fully detwinned single crystal of Fe₃O₄. The authors reported centric space group \(Pmca\) and acentric \(Pmc2_1\) subcell refinements of the \(Cc\) unit cell. By grouping the observed superstructure reflections according to symmetry requirements it was shown that these high-symmetry models account for the bulk of the atomic displacements, and any further distortions are very small. Although large atomic displacements of iron and oxygen atoms were found, no charge ordered arrangement was identified in the refined structure. This is in strong qualitative contrast to the recent structure refinement performed by Wright et al. (2001) where a clear evidence of charge-ordering below the Verwey transition has been found. This refinement confirms the correctness
of the symmetry approximations used by Iizumi et al. (1982), however, the refined parameters differ from those in the latter study, leading to different values for Fe-O bond distances. In particular, for octahedral Fe\(_B\) cations they fall into two groups, with larger average bond distance value for 2+ and smaller for 3+ Fe cations. Estimation of the charge difference between these two groups of Fe\(_B\) sites using bond valence sum (BVS) method results in a small charge separation of 0.2 \(\varepsilon\) between larger and smaller sites. This provides direct crystallographic evidence of at least partial long-range charge-ordering on the \(B\) sublattice below the Verwey transition.

This refined structure analysis has recently been found to be controversial (García et al. 2002). The lack of atomic long-range order and, as a result, an intermediate valence regime below the Verwey transition were proposed (García et al. 2001). Indeed, a difference between averaged Fe-O distances of compressed and expanded FeO\(_6\) octahedra corresponds to the maximum limit of charge disproportion (0.2 \(\varepsilon\)), which has the same order as the total sensitivity (including experimental errors) of BVS method. Together with recent spectroscopic investigations which are failed to observe the Raman and infrared phonon modes that should be active if the low-temperature phase lack inversion symmetry, remains the symmetry of the low-temperature phase to be controversial (Gasparov, Tanner, Romero, Berger, Margaritondo and Forró 2000). However, any distortion from the \(P2/c\) monoclinic cell is to be very small, compared to the distortion from cubic to monoclinic symmetry, and roughly of 0.01 Å.

![Figure 3.4: Valence band photoemission (PES) and bremsstrahlung isochromatic (BIS) and O 1s x-ray absorption (XAS) spectra. The XAS spectrum is aligned with the BIS spectrum by a 529.1 eV shift; according to Park et al. (1997).](image)
Another controversial issue refers to the electronic properties of the high-temperature phase of Fe₃O₄. In particular, originating from the high-resolution photoemission above the Verwey transition two possible scenarios were proposed. Chainani, Yokota, Morimoto, Takahashi and Todo (1995) found finite spectral weight at the Fermi level and concluded on a metallic state above \( T_V \), i.e. identified the Verwey transition as insulator-to-metal transition with increasing temperature. In contrast, Park et al. (1997) found a remarkable change of the activation energy at the transition with finite energy gap above \( T_V \). However, low photon energies have been used in previous experiments made them very surface-sensitive. The probing depth was small (\( \sim 15 \, \text{Å} \)) and surface effects may dominate in both spectra. Only recent photoemission experiment performed by Schrupp, Sing, Tsunekawa, Fujiwara, Kasai, Sekiyama, Suga, Muro, Brabers and Claessen (2005) were able to resolve surface and volume contribution to the spectra.

![Figure 3.5](image_url)

**Figure 3.5:** (a) Valence band spectra of termally treated (111) surface, a similarly prepared (100) surface, and an unoriented surface obtained by crystal fracture. (b) Detailed of the (111) spectrum as function of temperature above and below the Verwey transition (\( T_V \approx 122 \, \text{K} \)). (c) Same for the fractured surface; according to Schrupp et al. (2005).

Using different surface preparations and sample orientations no indication of the metallic Fermi edge or quasiparticle feature was observed in the high-temperature phase, in notable contrast to the Mott transition (Mo et al. 2003). They found
a broad maximum at -0.6 eV and a strong suppression of intensity towards the chemical potential. While below $T_V$ an insulating spectra was clearly observed, above the Verwey transition the spectral onset is shifted towards or even right at the chemical potential (see Fig. 3.5). Remarkably, with increasing temperature they found quite different spectra behavior for different surfaces. In particular, for (100) surface and for fractured sample a finite activation energy above $T_V$ of $\sim 50 \text{ meV}$ was found, whereas for (111) sample the spectra onset shifts continuously towards the chemical potential and reaches it at $\sim T_V$. Moreover, the activation energy for (100) sample remains finite even up to 190 K, well above $T_V$. It was tempting to relate this finding to earlier reports of room-temperature charge order at the (100) surface of Fe$_3$O$_4$ (Wiesendanger, Shvets, Bürgler, Tar-rach, Güntherodt, Coey and Gräser 1992).

Figure 3.6: Cubic spinel $Fd3m$ crystal structure of Fe$_3$O$_4$ above the Verwey transition. Two structurally distinct tetrahedral Fe$_A$ and octahedral Fe$_B$ iron sites are shown in red and blue colors, respectively. [110] and [110] chains of Fe$_B$ atoms are connected by the green lines. Oxygen atoms are denoted by small dark shading spheres.
3.1 Crystal and magnetic structure of Fe₃O₄

Above the Verwey transition magnetite crystallizes in the face-centered cubic (fcc) inverse spinel crystal structure with space group Fd3m (shown in Fig. 3.6). The iron atoms occupy the interstitial positions of the closed-packed fcc structure formed by the oxygen atoms. According to the chemical formula of the inverse spinel, AB₂O₄, there are two different iron sublattices (A and B) distinguished by the point symmetry (T₄ and D₃d) as well as by the averaged Fe-O distance (1.876 and 2.066Å) and the valence state of iron cations. In particular, the A sublattice is formed by Fe³⁺ cations tetrahedrally coordinated by four oxygen ions, whereas the so-called B sublattice consists of iron sites octahedrally coordinated by six oxygen ions. The octahedral B-sites are occupied by an equal number of randomly distributed 2⁺ and 3⁺ Fe cations which results in an average valence value of 2.5⁺ per each Fe⁺⁺ cation. The B-sublattice is highly frustrated and can be considered as a diamond lattice of Fe⁺⁺ cations tetrahedra, sharing corners with each other.

![Diagram](image)

**Figure 3.7:** The scheme of magnetic structure in Fe₃O₄. Only tetrahedral A and octahedral B-sites are shown.

Magnetite is a ferrimagnet with anomalous high Curie temperature of ~850 K. The A-site magnetic moments are being aligned antiparallel to the B-site moments. The strong antiferromagnetic coupling between A and B sublattices give rise to the strong exchange splitting between majority and minority 3d Fe states schematically presented in Fig. 3.7. In addition to the exchange splitting 3d Fe states are split due to crystal field. In octahedral oxygen coordination of Fe⁺⁺ atoms (D₃d point symmetry), the crystal field lifts the five fold degeneracy of 3d
shell and causes 3d orbitals to split into a lower-energy triplet \( t_{2g} \) and higher-energy doublet \( e_g \) states which form two separated nonoverlapping bands. In addition, the small trigonal component of the crystal field splits \( t_{2g} \) orbitals into a lower-energy singlet \( a_{1g} \) and doublet \( e_{g'} \). In tetrahedral oxygen coordination, 3d \( Fe_A \) states are split into a lower-energy doublet \( e \) and higher-energy triplet \( t_2 \) (see Fig. 3.8 and 3.9).

**Figure 3.8:** 3d electronic levels splitting of octahedral \( Fe_B^{3.5+} \) cation. While \( e_g \) states form strong \( \sigma \)-bonds with \( O \) \( p \) states, \( t_{2g} \) form relatively weak \( \pi \)-bonds. 2.5+ valence of \( Fe_B \) cation corresponds to 3d\(^{5.5} \) state.

**Figure 3.9:** 3d electronic levels splitting of tetrahedral \( Fe_A^{3+} \) 3d\(^5 \) cation. \( Fe_A \) 3d minority and majority states are completely occupied and empty, respectively.

At room temperature \( Fe_3O_4 \) is a poor metal with an electronic resistivity of 4 m\( \Omega \) cm which is remarkably higher than resistivity of simple metals (for instance, the resistivity of Cu is only 1.7 \( \mu \Omega \) cm). Upon further cooling a first-order metal-insulator transition (the so-called Verwey transition) occurs at \( \sim 120 \) K where conductivity abruptly decreases by two orders of magnitude. The experiments show that the Verwey transition is accompanied by a structural distortion from cubic to the monoclinic structure which has not been fully resolved so far (Iizumi et al. 1982, Zhuo, Spence and Petuskey 1990). The low-temperature structure have a \( \sqrt{2}a \times \sqrt{2}a \times 2a \) supercell with space group \( Cc \). However, recent structural refinement (at 90 K) was only possible in the centric monoclinic space group \( P2/c \) with \( \frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a \) of the cubic spinel subcell which contains 8 formula units in
the primitive unit cell. Although \( P2/c \) space group was found to be unstable the additional \( Pmca \) orthorhombic symmetry constrain was also applied.

![Diagram](image)

**Figure 3.10:** Relationships between the unit cells referred to in the text.

This symmetry constrain is equivalent to the averaging the true superstructure over additional symmetry operators. Therefore, each \( B \)-site in \( P2/c \) unit cell is averaged over four nonequivalent subsites in the large \( \sqrt{2}a \times \sqrt{2}a \times 2a \) \( Cc \) supercell, although further distortions from \( P2/c \) subcell to the \( Cc \) monoclinic structure are small (less then 0.01Å). Previous structure refinement below \( T_V \) obtained by Iizumi et al. (1982) resulted in \( \frac{a}{\sqrt{2}} \times \frac{a}{\sqrt{2}} \times 2a \) subcell of the \( Cc \) unitcell and imposed orthorhombic symmetry constrains on the atomic positions. In particular, refinements based on approximation of the true crystal structure by the centric space group \( Pmca \) or polar \( Pmc2_1 \) where proposed. However, a charge ordered arrangement has not been identified which is in strong qualitative contrast to the recent structure refinement proposed by Wright et al. (2001).

### 3.2 The Verwey charge-ordering model

One of the first attempts to explain the simultaneous metal-insulator and structural transition at \( \sim 120 \)K in \( Fe_3O_4 \) was performed by Verwey and Haayman (1941). According to Verwey this transition is caused by the order-disorder transformation of \( Fe^{2+} \) cations on the \( B \)-sublattice of the inverted spinel \( AB_2O_4 \) structure. The insulating state below the Verwey transition corresponds to the long-range order of \( Fe^{2+} \) cations on the octahedral \( B \)-sites and its disorder above \( T_V \) gives rise to the steep increasing in conductivity by two orders of magnitude. Moreover, Verwey and Haayman (1941) proposed the first theoretical CO model according to that \( 2+ \) and \( 3+ \) \( Fe_B \) cations alternately occupy (001) planes of the cubic \( Fd3m \) cell leading to the orthorhombic distortion.

The mutual Coulomb repulsion between electrons is one of the driving forces
of charge ordered state formation in mixed-valent systems. In particular, another key to understanding charge ordered structure in Fe$_3$O$_4$ is provided by the Anderson criterion of electrostatic repulsion energy minimum (Anderson 1956). According to Anderson, each tetrahedron formed by octahedral $B$-sites of the spinel structure is occupied by two 2+ and two 3+ Fe cations in order to minimize the inter-site electrostatic repulsion ("charge frustration"). Thus, within a $Cc$ supercell of the cubic Fe$_3$O$_4$, there are ten independent cationic arrangements and only one of them coincides with the Verwey model (Zuo et al. 1990). However, the Verwey CO pattern has the overall lowest classical electron repulsion energy. Moreover, Anderson (1956) interpreted the Verwey transition as a transformation from short-range to long-range electronic order. Indeed, the observed entropy change in the transition has been found to be a little more than 0.3 $R$ per mole of octahedral sites rather than the $R \ln 2 = 0.69 \ R$ to be expected in a transition from complete disorder to complete order. This value is in rough agreement with 0.202 $R$ expected for short-range order to complete order transition. Note, however, that a value 0.202 $R$ of the entropy change corresponds to the lower limit estimate, whereas the true value probably is 10-20% larger and is in good agreement with experimental observation.

Since the Verwey CO model was disproved by diffraction experiments which revealed the existence of a more complicated than orthorhombic structure below $T_v$, a wide variety of other CO models has been proposed (Mizoguchi 1978, Zuo et al. 1990, Kucza 2001). However, all make use of the Anderson criterion.
3.3 Evidence for charge-ordering

The charge-ordering state below the Verwey transition has been evidenced by different experimental technics. In particular, in addition to the tetrahedral iron signal Mössbauer spectra demonstrate presents of localized 2+ and 3+ Fe cations situated on the octahedral B-sites. The spectra were best fitted with five magnetic components: one corresponds to Fe\textsuperscript{3+} on the A-sites, and four magnetic components correspond to Fe\textsuperscript{2+} and Fe\textsuperscript{3+} cations situated on two non-equivalent octahedral sites. This finding is in agreement with structural properties as well as the charge-ordering concept in the low-temperature magnetite.

The charge-ordering below \( \sim 120 \text{ K} \) has been also evidenced by the nuclear magnetic resonance (NMR) spectra analysis performed below and around the Verwey transition. The NMR spectrum of \(^{57}\text{Fe} \) on \( \text{Fe}_3\text{O}_4 \) single crystal above \( T_V \) consists of two lines as expected for the cubic symmetry and magnetization along the (100) direction (see Fig. 3.12). The very narrow line at 69.95 MHz corresponds to Fe\textsuperscript{3+} cations on the A sites, while Fe\textsubscript{B} cations give rise to the line at 66.297 MHz. With further increasing temperature, at \( \sim 125 \text{ K} \) the system undergoes a (100) to (111) spin reorientation transition, which leads to the splitting of the Fe\textsubscript{B} line in two lines with ideal intensity ratio 1:3. The line at lower frequency corresponds to the B-sites for which the local trigonal axis is parallel to the magnetization, while the remaining B-sites contribute to the higher frequency line (see Fig. 3.12).

Below \( T_V \) the NMR spectrum of \(^{57}\text{Fe} \) in \( \text{Fe}_3\text{O}_4 \) single crystal is changed dramatically. At 121K the spectrum collapse to the set of narrow lines presented in Fig. 3.14. The Fe\textsubscript{B} site line split out in 15 unique lines (B1-B15). Therefore, it can be concluded that 15 distinct octahedral Fe\textsubscript{B} environments are presented in the low-temperature structure of \( \text{Fe}_3\text{O}_4 \). Although, the spectra resolve only 7 unique Fe\textsubscript{A} environments it was concluded that the line at 69.606 MHz is a double line. It retains the doubled intensity also at higher temperatures up to \( \sim 118-121 \text{ K} \) as seen in Fig. 3.14. With possible exception of the line A3, relative intensities of the NMR lines are similar indicating that the lines originate from the same number of \(^{57}\text{Fe} \) nuclei. Although, it might be that one missed Fe\textsubscript{B} line is hidden in the rather large intensity of line A3. Thus, the \(^{57}\text{Fe} \) NMR spectra analysis below the Verwey transition is in accord with the \( \text{Cc} \) crystal symmetry which contains 8 and 16 magnetically inequivalent Fe cations on A and B-sites, respectively. The NMR relaxation shows that Fe\textsubscript{B} cations have intermediate between ideal 2+ and 3+ chemical shift which qualitatively agree with the bond valence sum analysis indicating a small charge difference between Fe\textsuperscript{2+} and Fe\textsuperscript{3+} cations (Wright et al. 2001, Wright et al. 2002).

Diffuse streaking in electron and neutron scattering together with diffuse resonant x-ray scattering at the Fe K-edge experiment above the Verwey transition were explained as a 1:3 (or 3:1) ordering of 2+ and 3+ cations along [110] directions,
Figure 3.12: The nuclear magnetic resonance (NMR) spectra of $^{57}$Fe in Fe$_3$O$_4$ single crystal above the Verwey temperature $T_V$. At 122 K the magnetization is along $\langle 100 \rangle$ and the left-right arrow indicates the region of the Fe$^4_\ell$ spectrum below $T_V$. At 133 K the magnetization is along $\langle 111 \rangle$ direction. $\delta_{\text{trig}}$ is the splitting caused by the trigonal anisotropy of the hyperfine field. The measurements were performed for synthetic Fe$_3$O$_4$ single crystal with $T_V = 121.5$ K; according to Novak et al. (2000).

suggesting that the charge disproportion is coupled to the phonon modes softening above $T_V$ (Chiba et al. 1975, Shapiro et al. 1976). Differential anomalous fine structure (DAFS) measurements of the (002) and (004) reflections above $T_V$ indicate that the Fe$^4_\ell$ sites are equivalent on a time scale of $10^{-16}$ s, suggesting that the valence electrons are delocalized, rather than hopping rapidly above $T_V$ (García, Subías, Proietti, Reniever, Joly, Hodeau, Blasco, Sánchez and Béra 2000). Also measurements of $(0 4 \frac{1}{2})$ superstructure peak intensities as a function of x-ray energy around the Fe $K$-edge showed features that strongly suggest charge-ordering (Toyoda, Sasaki and Tanaka 1999). Furthermore, several proposed charge ordered models have been compared to electron-diffraction data (Zuo et al. 1990). In particular, all those CO models make use of the Anderson criterion of minimum electrostatic repulsion leading to a short range CO pattern where tetrahedra of $B$-sites consists of two Fe$^{2+}$ and two Fe$^{3+}$ cations (Anderson 1956). One of the first attempts to reconstruct a charge-ordering model was performed by Mizoguchi (2001) using decomposition of the $^{57}$Fe NMR data from a single crystal which resolves all 16 Fe$^2_\ell$ sites and measure their angular dependence. But the primary evidence for charge-ordering transition that the
Figure 3.13: The NMR spectrum of $^{57}$Fe obtained at 121 K. The right figure shows Fe$_A^{3+}$ lines region around 70 MHz at 118 K. The arrows indicate the frequency of eventual motionally narrowed spectrum at 122 K (the narrow line at 69.59 MHz in Fig.3.12); according to Novak et al. (2000).

Figure 3.14: The NMR spectrum of $^{57}$Fe in Fe$_2$O$_4$ single crystal obtained at 4.2 K. The right figure shows region of Fe$_A^{3+}$ lines around 70 MHz at 4.2 K. The measurements were performed for synthetic Fe$_2$O$_4$ single crystal with $T_V = 121.5$ K; according to Novak et al. (2000).
3.3. Evidence for charge-ordering

appearance of distinct metal sites with significantly different mean Fe-O distances in the low-temperature phase has not been resolved so far. Only in recent structural refinement performed by Wright et al. (2001), two distinct, in sense of the average Fe$_B$-O distances octahedral iron sites, have been resolved. This direct structural observation of charge-ordering was obtained from a combined x-ray and neutron powder diffraction study of the $P2_1/c$ subcell structure with $Pmca$ symmetry constrain as used before. According to the refinement, as shown in Table 3.3, the octahedral Fe$_B$ sites are split into two groups with different values of the averaged Fe-O bond distances where B2 and B3 sites are being significantly smaller (2.039 and 2.053 Å) then B1 and B4 (2.071 and 2.062 Å, respectively). B1-B4 are crystallographically independent Fe$_B$ sites according to the Wright et al. (2001) notation.

A different averaged Fe-O bond distance is a sensitive experimental indicator of the cation charge state. Quantitative analysis of the valence state of both Fe$_B$ groups using bond valence sum (BVS) method shows that the octahedral Fe$_B$ sites fall into two clear groups in respect to the estimated value of valence. It results in a charge disproportion of 0.2 $\bar{e}$ between large [B1 and B4] and small [B2 and B3] sites (which has been referred as class-I CO model). Another possible class of CO arise from the symmetry-averaging orthorhombic constrain. There are 32 charge ordered models which refer to class-II CO because large [B1 and B4] and small [B2 and B3] sites could be averaged over $[3$ Fe$^{2+} +$ Fe$^{3+}]$ and [Fe$^{2+} + 3$ Fe$^{2+}]$ subsites, respectively (see Fig. 3.15). The symmetry averaging results in decreasing of the more pronounced charge separation of 0.4 $\bar{e}$ in the full $Cc$ superstructure (class-II CO) down to 0.2 $\bar{e}$ in $P2_1/c$ subcell. The Anderson criterion (Anderson 1956) is not satisfied by any of class-I or class-II CO models. However, class-II as was shown from electrostatic repulsion energy estimations appear to be more plausible then the class-I CO arrangement.

The charge-ordering has been recently confirmed by the analysis of Fe $K$-edge resonant x-ray diffraction (Goff, Wright, Attfield and Radaelli 2005) data which revealed a scattering difference in agreement with the Wright et al. (2001) refinement. Moreover, the differences in scattering factors between the nominal 2+ and 3+ Fe states are small, in keeping with the reduced magnitude of real charge separation in symmetry-broken, charge ordered, transition metal oxides.

An important feature in this structural refinement is that the Fe$_B$ sites charges follow a pronounced [001] charge density wave modulation. Remarkably, the [001] atomic displacement wave of amplitude $\sim$0.05 Å was noted previously by Iizumi et al. (1982) and has been recently confirmed by diffuse scattering experiments. But a [001] modulation which is originated from alternating chains of “occupied” Fe$^{2+}$ cations on the octahedral B1 sites and “empty” Fe$^{3+}$ cations on the B2-sites has been reported in the refinement for the first time. This is consistent with a [001] nesting vector instability at the Fermi surface in the Fe$_B$ minority
Figure 3.15: Two possible models for charge-ordering on the $B$ sublattice in the full $\sqrt{2}a \times \sqrt{2}a \times 2a$ $Cc$ supercell of Fe$_3$O$_4$. The blue and red circle represent Fe$^{2+}$ and Fe$^{3+}$ sites, respectively. The left corresponds to the class-I, although the right is one of 32 possible class-II CO models. [001] charge density modulation is shown.
**Tab. 3.1**: The refined cation-anion distances found in Fe₃O₄ at 90 K; individual and mean distances to the coordinating oxygens (O₁–O₆), bond valence sums (BVS), and the renormalized valences \( V \) are presented.

<table>
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<th>Fe site</th>
<th>-O bonds</th>
<th>( d(\text{Fe-O})/\text{Å} )</th>
<th>( \langle d(\text{Fe-O}) \rangle/\text{Å} )</th>
<th>BVS</th>
<th>( V )</th>
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<tr>
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<td>2.019(3)</td>
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<tr>
<td>B4</td>
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<td>-O6</td>
<td>2.053(3)</td>
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</table>
3.4 Electronic properties of Fe₃O₄

In this section we carry out results of the band-structure calculations which have been performed for the low-temperature crystal structure of Fe₃O₄ recently refined at 90K (Wright et al. 2001, Wright et al. 2002). Although the superstructure peaks in this refinement were indexed on the monoclinic unit cell which has $Cc$ symmetry and axes;

$$a_m = - (a_c + b_c),$$
$$b_m = a_c - b_c,$$
$$c_m = 2c_c,$$

the reduced cell with $a = a_m/2$, $b = b_m/2$, and $c = c_m$ was able to account for all observed superstructure intensities except for three very weak reflections (Wright et al. 2001, Wright et al. 2002). The refined cell parameters determined by fitting the 90 K x-ray profile and used in the calculations are $a = 5.94437(1)$ Å, $b = 5.92471(2)$ Å, $c = 16.77512(4)$ Å, and $\beta = 90.236(1)^\circ$. The monoclinic $P2/c$ unit cell contains eight formula units. There are eight different types of iron atom sites: two tetrahedrally coordinated $A$-sites, and six $B$-sites, octahedrally coordinated by six O atoms.

The electronic structure of magnetite was calculated self-consistently using local-spin-density approximation LSDA/LSDA+$U$ in the tight-binding linear muffin tin orbital (TB-LMTO) calculation scheme (Andersen 1975, Anisimov et al. 1991, Liechtensten et al. 1995). In our calculations we neglect the small spin-orbit coupling for simplicity (from previous calculations for cubic Fe₃O₄ spin-orbital splitting of the $3d$-band was two order smaller then crystal field splitting (Antonov et al. 2001)). The radii of the muffin-tin spheres were taken as $R_{Fe} = 2.125$ a.u., and $R_{O} = 2.0$ a.u. Fifteen kinds of empty spheres were introduced to fill up the inter-atomic space.

3.4.1 Band structure calculations

In order to investigate electronic structure of the low-temperature Fe₃O₄ we perform spin-polarized local-density (LSDA) calculations. Figure 3.16 shows total
and partial density of states of Fe$_3$O$_4$ obtained by the LSDA. Interestingly, the crystal structure distortion taken explicitly in the monoclinic phase does not strongly affect on the electronic structure of Fe$_3$O$_4$. In particular, the calculation results agree well with previous band-structure calculations for the cubic phase (Zhang and Satpathy 1991, Yanase and Hamada 1999). Thus, the LSDA gives a uniform half-metallic ferrimagnetic solution with partially filled bands originating from the minority spin $t_{2g}$ orbitals of Fe$_B$ cations. The tetrahedral Fe$_A$ cations do not participate in the formation of bands near the Fermi level, since their minority and majority spin 3$d$ states are completely occupied and completely empty, respectively.

An energy gap of $\sim$1 eV opens in the majority spin channel between occupied Fe$_B$ $e_g$ and the top of empty Fe$_A$ states. The lower part of the valence band (below -3.5 eV) is mainly formed by O 2$p$ states with a bonding hybridization with Fe 3$d$ states, whereas bands near the Fermi level, between -3.5 eV and 2 eV, have predominant contribution of Fe 3$d$ states. The exchange splitting between the spin-up and spin-down Fe 3$d$ states is roughly 3 eV. Additionally, the five-fold 3$d$ levels are split by the crystal field into $t_{2g}$ and $e_g$ sub-bands. The oxygen octahedra in Fe$_3$O$_4$ are strongly distorted and the local symmetry of Fe sites is lower than cubic. Nevertheless, the cubic component of the ligand field, which is determined by the relative strength of Fe $d$–O $p$ hybridization of $\pi$- and $\sigma$-type, remains dominant, whereas the splitting within “$t_{2g}$” and “$e_g$” subbands is smaller than the corresponding bandwidth. This allows one to label the corresponding states as $t_{2g}$ and $e_g$. Note, however, that the $P2/c$ frame is rotated by $\sim \pi/4$ with respect to the $Fd3m$ one and the angular dependence of the $t_{2g}$ states is given by $d_{xz} \pm d_{yz}$ and $d_{x^2-y^2}$ combinations of cubic harmonics. The crystal field splitting is roughly 2 eV, which is less than the exchange splitting. This is consistent with the high-spin state of the Fe cations. The partially occupied bands originate from minority spin 3$d$ $t_{2g}$ orbitals of the octahedral Fe$_B$ sites. The empty minority spin $e_g$ states are situated between 2.0 and 3.0 eV. The occupied Fe$_A$ 3$d$ majority states form bands between 2.0 and 3.0 eV, whereas majority spin states are completely empty and are shifted to the higher energy interval between 3.0 and 5.0 eV.

In contrast to experimental data the LSDA calculations result in a half-metal solution without charge ordering. Apparently, the change of the LSDA electronic structure, produced by the crystal structure distortion from cubic to the monoclinic phase, is not sufficient to explain the charge-ordering and metal-insulator transition in Fe$_3$O$_4$. The electron-electron correlations, mainly in the 3$d$ shell of Fe cations, play a significant role.

In order to account for the strong electronic correlations in the Fe 3$d$ shell, at least on the static Hartree-Fock level, we calculate the electronic structure of the LT phase of Fe$_3$O$_4$ using the LSDA+$U$ method, which proved to be quite successful in treating transition metal oxides with strong electron-electron correlations as well
Figure 3.16: Total and partial density of states of the $P2_1/c$ phase of Fe$_3$O$_4$ self-consistently obtained by the LSDA. The top of valence band shown by dotted lines. Top and bottom panels correspond to the majority and minority spin state, respectively. The absolute values of magnetic moments are 3.14, 3.30, 3.44, 3.27, 3.38 $\mu_B$ for Fe$_A$ and Fe$_{B_1-B_4}$ cations, respectively. The total ferromagnetic moment per Fe$_3$O$_4$ formula unit is 4.0 $\mu_B$. 
Figure 3.17: Total DOS and corresponding band structure of the \(P2/c\) phase of \(\text{Fe}_3\text{O}_4\) self-consistently obtained by the LSDA. The Fermi level denoted by the horizontal line and is taken as the zero of energy. The energy bands predominantly originated from the \(\text{Fe}_B \ t_{2g}\) and \(e_g\) states are shown in red and blue colors, respectively. The green color corresponds to the \(\text{Fe}_A\) 3\(d\) bands. For majority spin an energy gap of \(\sim 0.7\) eV opens between occupied \(\text{Fe}_B \ e_g\) and empty \(\text{Fe}_A\) bands shown in blue and green color, respectively.
as systems with a long-range order (Anisimov et al. 1996, Antonov et al. 2001, Antonov et al. 2003, Liechtensten et al. 1995). The value of the \( U \) parameter for Fe cations estimated using different experimental and theoretical techniques lies in the range of 4.5-6 eV (Anisimov et al. 1996, Zuo et al. 1990, Chen, Huang, Tanaka, Chang, Chüng, Wu and Chen 2004). A reasonably good agreement of the calculated gap value of 0.18 eV with the experimental value of 0.14 eV at 10 K (Park, Ishikawa and Tokura 1998) was obtained using the \( U \) value of 5 eV (see Fig. 3.18). Note, however, that the charge and orbital order derived from the LSDA+\( U \) calculations does not depend on the exact \( U \) value when it is varied within the above mentioned limits. The value of the Hund’s coupling \( J=1 \) eV was estimated from the constrained LDA calculations (Pickett, Erwin and Ethridge 1998). All results presented in the following were obtained using the \( U \) value of 5 eV.

Figure 3.19 shows the LSDA+\( U \) band structure and the total DOS calculated self-consistently for the low-temperature phase of \( \text{Fe}_3\text{O}_4 \). The corresponding partial Fe\(_B\) 3\( d \) DOS are shown in Fig. 3.20. The LSDA+\( U \) calculations give qualitatively distinct to the LSDA results. An indirect energy gap of 0.18 eV opens in the minority spin channel between \( M \) and \( \Gamma \) symmetry points. The top of the valence band is formed by the occupied \( t_{2g1} \) states of B1 and B4 Fe\(^{2+} \) cations. The bottom of the conduction band is formed predominantly by the empty \( t_{2g1} \) states of B2 and B3 Fe\(^{3+} \) cations. The remaining unoccupied \( t_{2g} \) minority states of B1 and B4 Fe\(^{2+} \) cations are pushed by the strong Coulomb repulsion to the energies above 2.5 eV. Majority spin 3\( d \) Fe\(_B\) states are shifted below O 2\( p \) states, which form a wide band in the energy interval between -7 and -2 eV. This is in strong contrast to the uniform half-metallic solution obtained by the LSDA.

**Tab. 3.2:** Total and \( l \)-projected charges, magnetic moments, and occupation of the most populated \( t_{2g} \) minority orbitals calculated for inequivalent Fe\(_B\) ions in the low-temperature \( P2/c \) phase of \( \text{Fe}_3\text{O}_4 \).

<table>
<thead>
<tr>
<th>Fe(_B) ion</th>
<th>( q )</th>
<th>( q_s )</th>
<th>( q_p )</th>
<th>( q_d )</th>
<th>( M (\mu_B) )</th>
<th>( t_{2g1} ) orbital</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(_B1)</td>
<td>6.04</td>
<td>0.17</td>
<td>0.19</td>
<td>5.69</td>
<td>3.50</td>
<td>( d_{xz} \pm d_{yz} )</td>
<td>0.76</td>
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<tr>
<td>Fe(_B2)</td>
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<td>0.19</td>
<td>0.21</td>
<td>5.44</td>
<td>3.94</td>
<td>( d_{xy} )</td>
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<tr>
<td>Fe(_B3)</td>
<td>5.91</td>
<td>0.19</td>
<td>0.21</td>
<td>5.51</td>
<td>3.81</td>
<td>( d_{xy} )</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe(_B4)</td>
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<td>0.16</td>
<td>0.18</td>
<td>5.69</td>
<td>3.48</td>
<td>( d_{x^2-y^2} )</td>
<td>0.80</td>
</tr>
</tbody>
</table>

### 3.4.2 Charge ordering

An analysis of the 3\( d \) minority occupation matrices of Fe\(_B\) cations confirms very effective charge disproportionation within the Fe\(_B\) \( t_{2g} \) minority spin subshell. As
shown in Table 3.2, one of the $t_{2g1}$ states of Fe$_{B1}^{2+}$ and Fe$_{B4}^{2+}$ cations is almost completely filled with the occupation number $n \approx 0.8$. On the other hand, the remained two $t_{2g1}$ orbitals of the Fe$^{2+}$ cations have significantly smaller population of about 0.15. The occupation numbers of $t_{2g1}$ orbitals for Fe$_{B2}^{3+}$ and Fe$_{B3}^{3+}$ cations do not exceed 0.09, which gives a value of about 0.7 for the largest difference of Fe$_{B2}^{2+}$ and Fe$_{B3}^{3+}$ $t_{2g1}$ occupancies. The corresponding 3$d$ charges difference (0.23) and disproportionation of the total electron charges inside the atomic spheres of Fe$_{B2}^{2+}$ and Fe$_{B3}^{3+}$ ions (0.24) are in reasonably good agreement with a bond valence sum (BVS) analysis of the $P2/c$ structure (0.2). The change of $t_{2g1}$ occupations caused by the charge-ordering is very effectively screened by the rearrangement of the other Fe electrons. A significant contribution to the screening charge is provided by the Fe$_B$ $e_g$ states. Although the bands originating from these states are located well above the energy gap, the $e_g$ minority orbitals form relatively strong $\sigma$-bonds with 2$p$-states of the oxygen octahedron and, as a result, give an appreciable contribution to the occupied part of the valence band. The above-mentioned screening of the charge difference in the Fe$_B$ $t_{2g}$ minority occupations reduces the energy loss due to the development of the charge order incompatible with the Anderson criterion in the LT phase of Fe$_3$O$_4$. Hence, due to the strong screening effects, the order parameter introduced as the total 3$d$ charge
Figure 3.19: Total DOS and corresponding band structure of the $P2/c$ phase of Fe$_3$O$_4$ self-consistently obtained by the LSDA+$U$ with $U=5$ eV and $J=1$ eV. The Fermi level denoted by the horizontal line and is taken as the zero of energy. The calculated band gap value of 0.18 eV opens between $M$-$\Gamma$ symmetry points. The energy bands predominantly originated from the Fe$_B^{3+} t_{2g}$ and $e_g$ states are shown in red and green colors, respectively. The blue color corresponds to Fe$_B^{2+} t_{2g}$ bands. For majority spin an energy gap of $\sim$2 eV opens between Fe$_B^{2+} e_g$ and Fe$_A$ bands shown in blue and green color, respectively.
Figure 3.20: Partial DOS obtained from the LSDA+U calculations with $U=5$ eV and $J=1$ eV for the $P2_1/c$ phase of Fe$_3$O$_4$. The Fermi level shown by dotted lines. A charge ordered insulating solution with an energy gap of 0.18 eV is obtained. Fe 3$d$ minority states corresponding to B1 and B4 sites are occupied (Fe$^{2+}$) and located just below the Fermi level, whereas B2 and B3 are empty (Fe$^{3+}$). The charge difference between 2+ and 3+ Fe$_B$ cations is 0.23 $\bar{e}$. The value of magnetic moments are $\sim 3.74 \mu_B$ for Fe$_A$, whereas for Fe$_B$ they are presented in Table 3.2.
difference between 2+ and 3+ Fe\textsubscript{B} cations, is ill-defined. That explains why the BVS analysis does not give convincing prove of CO existence. Apparently, the well-defined order parameter is the difference of \(t_{2g}\) minority occupancies for Fe\textsuperscript{2+\textsubscript{B}} and Fe\textsuperscript{3+\textsubscript{B}} cations, which amounts to 70\% of the ideal ionic CO model and clearly pronounces the existence of charge ordering below the Verwey transition.

The LSDA+\(U\) calculations were also performed for the assumption of Verwey charge order in the \(P2/c\) structure. However, instead of the assumed Verwey CO model the same self-consistent solution as the one presented above was found. Therefore, the Verwey CO model is unstable in the distorted \(P2/c\) structure. It is well known that with increasing \(U\) value localization is effectively increased. Remarkably, even for a \(U\) value increased up to 7–8 eV no Verwey-like CO pattern was found self-consistently in the distorted \(P2/c\) structure. On the contrary, the LSDA+\(U\) calculations performed for an undistorted \(P2/c\) supercell of the \(Fd\text{3}m\) structure result in an insulating CO solution which is compatible with the Verwey CO model. It was also found that other CO solutions have larger value of the total energy but all of them obey the Anderson criterion. Estimation of the total energy for undistorted \(P2/c\) supercell of the \(Fd\text{3}m\) structure gave a larger value comparing with the distorted \(P2/c\) unit cell. Altogether this implies that the Verwey CO model is unstable under a structure transformation from the high-symmetry cubic into the low-symmetry \(P2/c\) phase.

Charge-ordering solution obtained by the LSDA+\(U\) is described by a dominant [001] charge density wave originated from the alternating chains of “occupied” Fe\textsuperscript{2+} cations on octahedral \(B1\) sites and “empty” Fe\textsuperscript{3+} cations on \(B2\) sites (see Fig. 3.22). The secondary [00\(\frac{1}{2}\)] modulation in the phase of CO, which is formed by the chain of alternately “occupied” Fe\textsuperscript{2+} ions on the \(B4\) sites and “empty” Fe\textsuperscript{3+} ions on \(B3\) sites, was found. This CO scheme of a dominant [001] charge density wave with a minor [00\(\frac{1}{2}\)] modulation in the CO phase coincides with the class-I CO model proposed by Wright et al. (2001). This is consistent with a [001] nesting vector instability at the Fermi surface found in the cubic phase (Yanase and Hamada 1999). The LSDA+\(U\) calculations confirm that the Anderson criterion is not fulfilled in the LT phase, i.e. tetrahedra formed by Fe\textsubscript{B} cations contain unequal numbers of 2+ and 3+ Fe cations. However, the Anderson criterion was introduced under the assumption of equal interatomic distances within each tetrahedron, whereas in the distorted LT structure the Fe-Fe distances varies from 2.86 to 3.05 Å. This is remarkably larger than the critical distance below which metal-metal bonding occurs in oxides as estimated by Goodenough (1973) to be 2.58 Å for Fe\textsuperscript{3+}-Fe\textsuperscript{3+} and 2.95 Å for Fe\textsuperscript{2+}-Fe\textsuperscript{2+}. Dimers in Fe\textsubscript{3}O\textsubscript{4} would formally be Fe\textsuperscript{2+}-Fe\textsuperscript{3+} bonds with a critical distance of \(~2.77\) Å, which is 0.1 Å below the shortest observed distance.

We also perform the LSDA+\(U\) calculations with certain \(U\) and \(J\) parameters (5 and 1 eV, respectively) for the assumption of one of the 32 class-II CO models
Tab. 3.3: 3d orbital contribution to the formation of Fe$_B$ minority states with occupancy $n$ evaluated by diagonalization of the corresponding occupation matrix. Although, one of the $t_{2g}$ state of B1 and B4 sites is almost occupied with $n$ larger than 0.7 $e$ the $t_{2g}$ minority spin occupancies of B2 and B3 Fe$^{3+}$ cations are less than 0.1 $e$. The occupied $t_{2g}$ state of B1 and B4 Fe$^{2+}$ cations is predominantly of $d_{xz}$ $\pm d_{yz}$ and $d_{x^2-y^2}$ character, respectively.

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<th>$yz$</th>
<th>$3z^2 - r^2$</th>
<th>$zx$</th>
<th>$x^2 - y^2$</th>
<th>$n$</th>
<th>$t_{2g}$</th>
</tr>
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<tbody>
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<td>Fe$_{B1(a)}$</td>
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<td>-0.47</td>
<td>0.00</td>
<td>-0.80</td>
<td>0.34</td>
<td><strong>0.81</strong></td>
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<td>0.06</td>
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<tr>
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<tr>
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<td>Fe$_{B4}$</td>
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<td>-0.02</td>
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<td><strong>0.80</strong></td>
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<td>-0.01</td>
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<td>-0.85</td>
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<td>0.04</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.66</td>
<td>-0.03</td>
<td>0.50</td>
<td>0.55</td>
<td>0.03</td>
<td>$t_{2g}$</td>
</tr>
</tbody>
</table>
within the $Cc$ supercell of $P2/c$, which is shown in Fig. 3.15. However, it was found that this kind of CO is unstable and the obtained self-consistent solution coincides with the stable one found previously, i.e., the obtained CO is almost defined by the local crystal structure distortion.

Comparing the LSDA+$U$ results for the undistorted and distorted $P2/c$ unit cells we can conclude that the charge-ordering pattern of $\text{Fe}_B^{2+}$ and $\text{Fe}_B^{3+}$ cations in the LT phase of Fe$_3$O$_4$, derived from the BVS analysis (Wright et al. 2001, Wright et al. 2002) and confirmed by our study, is mainly forced by the local distortions of the crystal structure. Obviously we did not manage to study all possible charge-ordering scenarios within $P2/c$ or $Cc$ supercell of $P2/c$. But our results consistently indicate the importance of the small amplitude of atom displacements (almost 0.07Å) recently resolved by x-ray and neutron powder diffraction (Wright et al. 2001, Wright et al. 2002).

The additional displacements leading to the $Cc$ supercell were estimated to be of $sim0.01\text{Å}$ but have not been fully resolved so far. They also may be important for full understanding of the CO in Fe$_3$O$_4$. In particular, in the $P2/c$ subcell the true atomic positions are averaged over the corresponding number of subsites in the $Cc$ cell. Therefore, the actual arrangement of the locally $\text{Fe}_B\text{O}_6$ octahedra in the true $Cc$ structure can be more complex, probably resulting in a more complicated charge and/or orbital order for the LT structure. The present calculations indicate that the competition of the “elastic” and electrostatic energy contributions in the total energy appears to be responsible for the CO, which is realized in the LT structure of Fe$_3$O$_4$ (Leonov et al. 2004). Because of this, the Verwey CO model, which has the lowest electrostatic but significant “elastic” energy contribution in the total energy, becomes less favorable than other arrangements.

### 3.4.3 Orbital ordering and octahedral distortion

The self-consistent solution obtained by the LSDA+$U$ is not only charge but also orbitally ordered. The occupied $t_{2g}$ state of $\text{Fe}_B^{2+}$ and $\text{Fe}_B^{3+}$ cations is predominantly of $d_{xz} \pm d_{yz}$ and $d_{x^2-y^2}$ character, respectively. This is shown in Table 3.3 which presents contribution of distinct 3$d$ cubic harmonics in formation of the most populated $\text{Fe}_B$ $t_{2g}$ orbitals. The relative orientation of occupied $t_{2g}$ orbital of $\text{Fe}_B$ cations corresponds to the anti-ferro-orbital order. Since all $\text{Fe}_B$ cations are ferromagnetically coupled, the obtained orbital order is consistent with the anti-ferro-orbital ferromagnetic state, which is the ground state of the degenerated Hubbard model according to the Kugel-Khomskii theory (Kugel and Khomskii 1975, Kugel and Khomskii 1982).

This orbital order leads to the corresponding distortions of $\text{FeO}_6$ octahedra. Each $t_{2g}$ orbital of $\text{Fe}_B$ form $\pi$-bonds with $p$-states of four oxygen ions lying in the
Tab. 3.4: The averaged Fe$_B$–O distances in the plane of $t_{2g}$ orbitals for Fe$^{2+}$ sites in the $P2/c$ structure. Here: $d_{xz} - d_{yz}$, $d_{xz} + d_{yz}$, and $d_{x^2-y^2}$ correspond to $d_x$, $d_y$, and $d_{xy}$ orbitals $t_{2g}$ in the local frame connected to an oxygen octahedron or in the $Fd3m$ frame.

<table>
<thead>
<tr>
<th>Fe$_B$ atom</th>
<th>orbital</th>
<th>$d_{orb.}$/Å</th>
<th>$d_{av.}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_{B1(a)}$</td>
<td>$d_{xz} + d_{yz}$</td>
<td>2.067</td>
<td>2.072</td>
</tr>
<tr>
<td></td>
<td>$d_{xz} - d_{yz}$</td>
<td>2.087</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{x^2-y^2}$</td>
<td>2.063</td>
<td></td>
</tr>
<tr>
<td>Fe$_{B1(b)}$</td>
<td>$d_{xz} + d_{yz}$</td>
<td>2.087</td>
<td>2.072</td>
</tr>
<tr>
<td></td>
<td>$d_{xz} - d_{yz}$</td>
<td>2.067</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$d_{x^2-y^2}$</td>
<td>2.063</td>
<td></td>
</tr>
<tr>
<td>Fe$_{B4}$</td>
<td>$d_{xz} \pm d_{yz}$</td>
<td>2.067</td>
<td>2.069</td>
</tr>
<tr>
<td></td>
<td>$d_{x^2-y^2}$</td>
<td>2.074</td>
<td></td>
</tr>
</tbody>
</table>

plane of the 3d orbital. If the oxygen octahedron is compressed along one of the diagonals the energy of the $t_{2g}$ state oriented perpendicular to the compression axis remains unchanged, whereas the energies of the other two states become higher because of the increased strength of the anti-bonding interaction with O $p$-states.

An analysis of interatomic distances in the monoclinic $P2/c$ structure presented in Table 3.4 shows that the average Fe$_{B1}$–O distance (2.087 Å) in a plane perpendicular to one of the diagonals of the distorted Fe$_{B1}$O$_6$ octahedron is sufficiently larger than average distances in the other two planes (2.063 and 2.067 Å). It turns out that the occupied Fe$_{B1}$ $t_{2g}$ minority orbital is the one oriented in the plane with the largest average Fe$_{B1}$–O distance. The same is also true for Fe$_{B4}$ ion but in this case the variation of the average Fe$_{B4}$–O distances is smaller (2.074 Å vs. 2× 2.067 Å) and, as a consequence, the out-of-plane rotation of the occupied $t_{2g}$ orbital is stronger (see Fig. 3.21). This simple consideration, which takes into account only the change of the Fe–O bond lengths and neglects the bending of the bonds, leads to conclusion that the calculated orbital order is mainly determined by the distortions of oxygen octahedra surrounding Fe$_B$ sites.

Also this simple analysis shows the remarkable difference between Fe$_{B1}$ and Fe$_{B4}$ cations. In particular, the average Fe$_{B1(a)}$–O distance in the plane of occupied $d_{xz} - d_{yz}$ orbital is 2.087 Å, whereas in the plane of other two $t_{2g}$ orbitals they are only 2.063 and 2.067 Å. This difference between the average cation-anion distance in the plane of occupied and unoccupied orbitals is remarkably larger for Fe$_{B1(a,b)}$ (more than 0.02 Å), although for Fe$_{B4}$ they are 2.074 and 2.067 Å for the occupied $d_{x^2-y^2}$ and unoccupied $d_{xz} \pm d_{yz}$ orbitals, respectively. Such a
Figure 3.21: Orbital order and corresponding distortions of oxygen octahedra for B1 (left) and B4 (right) Fe\textsuperscript{2+} cations.

A remarkably small difference (~0.007 Å) can be changed by applying the uniaxial stress to the P2/c unit cell. In particular, a few percents of magnitude elongation of the P2/c unit cell along c-axis with simultaneous, in order to preserve the same unit cell volume, compression in the ab-plane, gives rise to the orbital order crossover on the Fe\textsubscript{B4} site from d\textsubscript{x²−y²} to d\textsubscript{xy} occupied orbital, whereas the charge order and occupied orbitals on the Fe\textsubscript{B1(a,b)} sites remain the same. The pressure-induced spatial reorientation of the occupied Fe\textsubscript{B4} t\textsubscript{2g} orbital was proved by the LSDA+U calculations for the strained P2/c unit cell. Note, however, that this rough estimation does not take into account the elastic anisotropy in Fe\textsubscript{3}O\textsubscript{4}. However, they provide a new insight in the orbital-ordering phenomena behind the Verwey transition in magnetite as well as the problem of an external parameter controlled the electronic state (for example orbital ordering) in solids (Loa, Wang, Syassen, Roth, Lorenz, Hanfland and Mathis 2005).

3.5 Charge ordering model in Fe\textsubscript{3}O\textsubscript{4}: electronic repulsion vs. electron-lattice interaction

As was shown earlier, the Verwey CO model of the (001) planes alternately occupied by 2+ and 3+ Fe\textsubscript{B} cations possesses the minimum electrostatic repulsion energy among all possible CO models (Anderson 1956, Zuo et al. 1990). However, due to the existence of two perpendicular families of B-sites chains (for instance
[110] and [110]) correspondingly occupied by 2+ and 3+ Fe$_B$ cations the lattice “fills” significant stresses and tends to expand in the one ([110]) and to compress in the other ([110]) direction. Therefore, the Verwey CO gives a significant “elastic” energy contribution to the total energy, and in spite of the lowest electrostatic energy, becomes less favorable than other arrangements. The competition of these two (“elastic” and electrostatic) contributions in the total energy appears to be responsible for the charge order, which is realized in the experimentally observed low-temperature monoclinic structure. In this CO scheme the alternating (001) planes occupied by 2+ (“occupied” plane) and by 3+ (“empty” plane) Fe$_B$ cations are separated by the partially occupied plane. This (001) plane order makes the difference between [110] and [110] directions less pronounced and significantly reduce the lattice stress and, as a result, reduces the “lattice” energy contribution in the total energy. We proposed that this scenario is the primary cause for development of the class-I CO found below the Verwey transition.

This particular CO scenario was supported by our LSDA+$U$ study performed for the low-temperature $P2_1/c$ phase of Fe$_3$O$_4$. The LSDA+$U$ calculations result in a charge and orbitally ordered insulator with an energy gap of 0.18 eV. The obtained charge ordered ground-state is described by a dominant [001] charge density wave with a minor [00$\frac{1}{2}$] modulation. The calculations confirm a violation of the Anderson criterion. While the screening of the charge disproportion is so effective that the total 3$d$ charge disproportion is rather small (0.23), the charge order is well pronounced with an order parameter defined as a difference of $t_{2g1}$ occupancies of 2+ and 3+ Fe$_B$ cations (0.7). This agrees well with the result of BVS analysis for monoclinic structure (0.2). The anti-ferro-orbital order is in agreement with the Kugel-Khomskii theory and corresponds to the local distortions of oxygen octahedra surrounding Fe$_B$-sites.
**Figure 3.22:** The angular distribution of the minority spin 3$d$ electron density of the Fe$_B$ cations obtained from the LSDA+$U$ calculations with $U=5$ eV and $J=1$ eV for the $P2_1/c$ phase of Fe$_3$O$_4$. The angular distribution is calculated according to $\rho(\theta, \phi) = \sum_{m,m'} n_{m,m'} Y^*(m,\theta,\phi) Y_{m'}(\theta,\phi)$, where $n_{m,m'}$ is the occupation matrix of 3$d$ minority states for Fe$_B$ atoms. $Y_{m}(\theta, \phi)$ are corresponding spherical harmonics. Oxygen atoms are shown by small spheres.
4. Fe₂OBO₃ – A PROTOTYPE OF ELECTROSTATICALLY DRIVEN CHARGE ORDERED SYSTEM

The mutual Coulomb repulsion between the electrons plays a crucial role in the charge ordered systems. In particular, the so-called Anderson condition of minimum electrostatic repulsion is of fundamental importance in Fe₃O₄ (Anderson 1956). According to Anderson a short-range charge-ordering pattern is formed by the tetrahedron of Fe₆-sites with an equal number of 2⁺ and 3⁺ cations. However, a recent analysis of the charge and orbital order parameters in Fe₃O₄ inevitably results in a strong interplay between Jahn-Teller effect and electrostatic repulsion between electrons (Leonov et al. 2004). Therefore, an important issue, which is still unresolved is whether the charge-ordering in Fe₃O₄ is driven by Coulomb repulsion between the charges or by the strain arising from electron-lattice interactions. In this chapter we would like to address this problem and consider iron oxoborate (Fe₂OBO₃), which according to Attfield, Bell, Rodríguez-Martínez, Greneche, Cernik, Clarke and Perkins (1998) exhibits “electrostatically driven” charge-ordering.

4.1 Crystal structure of Fe₂OBO₃

Iron borate (Fe₂OBO₃) is a semi-valent oxide (Attfield, Clarke and Perkins 1992, Attfield, Bell, Rodríguez-Martínez, Greneche, Retoux, Leblanc, Cernik, Clarke and Perkins 1999). It belongs to the homometallic warwickite family with formal chemical formula MM'OBO₃, where M and M' are a divalent and trivalent metal ions, respectively. Surprisingly that the homometallic (M = M') warwickites are known only for Fe (Attfield et al. 1992, Attfield et al. 1999) and Mn (Goff, Williams and Attfield 2004, Norrestam, Kritikos and Sjödín 1995). In both compounds the metal have octahedral coordination. These octahedra share edges to form ribbons of four infinite along crystallographic a-direction chains of octahedra linked by corner sharing and the trigonal BO₃ groups (see Fig. 4.1).

There are two crystallographically inequivalent sites of the metal ions Fe(1) and Fe(2). Fe₂OBO₃ is L-type ferrimagnetic with drastically smaller in comparison to Fe₃O₄ critical temperature of $T_c \approx 155$ K, the Fe(1) magnetic moments being
Figure 4.1: The low-temperature crystal structure of Fe$_2$OBO$_3$ (space group $P2_1/c$). Infinite chains of edge-sharing FeO$_6$ octahedra along $a$-direction form four octahedron wide ribbons by sharing edges with neighboring chains. Two structurally distinct chains of Fe(1)O$_6$ and Fe(2)O$_6$ octahedra are indicated by red and blue color, respectively. Oxygen atoms are shown by small dark shading spheres. The boron-oxygen bonds corresponding to the trigonal BO$_3$ groups are shown by green lines.
Figure 4.2: Schematic representation of Fe$_2$OBO$_3$ structure projected on (100) plane ($b$ vertical, $c$ horizontal). Two structurally distinct Fe(1)O$_6$ and Fe(2)O$_6$ octahedra shown by light and dark sharing respectively. Plus and minus signs indicate the relative orientation of the moments within each Fe(1) and Fe(2) chains in the magnetically ordered phase.
aligned antiparallel to the Fe(2) moments (see Fig. 4.2). It is almost antiferromagnetic but a small ferrimagnetic moment of \(\sim 0.03 \mu_B\) per Fe atom was found in a 0.05 T field (Attfield et al. 1992, Attfield et al. 1998, Attfield et al. 1999, Continentino, Pedreira, Guimarães, Mir, Fernandes, Freitas and Ghivelder 2001). At room temperature \(\text{Fe}_2\text{OBO}_3\) is a semiconductor with a thermoactivated conductivity low \(e^{-E_a/kT}\) with \(E_a \approx 0.35\) eV (Attfield et al. 1998, Attfield et al. 1999). Upon farther heating a broad semiconductor-to-semiconductor transition occurs at \(T_{co} \approx 317\) K, where resistivity drops down by a factor of \(\sim 3\) (see Fig. 4.3), and, as a result, a small decreasing of the activated energy up to \(E_a \approx 0.31\) eV above 350 K is observed (Attfield et al. 1998, Attfield et al. 1999).

The 317 K transition is assigned to charge-ordering of 2+ and 3+ Fe cations on Fe(1) and Fe(2) sites, and accompanied by a structural transition from monoclinic \(P2_1/c\) to the orthorhombic \(Pmcn\) symmetry (with increasing temperature). This structural transition is attributed by modification of the \(\beta\) angle from \(\beta = 90.220(1)^\circ\) at 3 K to \(\beta = 90^\circ\) at 337 K (Attfield et al. 1998, Attfield et al. 1999, Attfield et al. 1992). The change in conductivity and structure are small. But the \(^{57}\text{Fe}\) Mössbauer spectra at around 317 K presented in Fig. 4.4 clearly result in the charge localization at the transition with an equal distribution of Fe\(^{2+}\) and Fe\(^{3+}\) cations over the two structurally distinct Fe(1) and Fe(2) sites with formal chemical formula \(\text{Fe}(1)_{0.5}^2\text{Fe}(1)_{0.5}^3,\text{Fe}(2)_{0.5}^2\text{Fe}(2)_{0.5}^3,\text{OBO}_3\) (Attfield et al. 1999, Attfield et al. 1998, Douvalis, Papaefthymiou, Moukarika, Bakas and Kallias 2000, Attfield et al. 1992, Douvalis, Papaefthymiou, Moukarika and Bakas 2000, Continentino et al. 2001, Suda, Kohn and Nakamura 2003).

Although, there are two types of distorted FeO\(_6\) octahedra with Fe-O bond length varying between 1.92 and 2.23 Å for 3 K (shown in Table 4.1), the average Fe(1)-O and Fe(2)-O distances are 2.085 and 2.082 Å, respectively, i.e., equal within experimental errors (Attfield et al. 1999). Such a small difference results in the extremely small value of deviation (\(\leq 0.01\)) from the average 2.5+ value of valence of Fe cations estimated by the bond valence sum method. While an electronic transition between charge ordered and disordered state occurs at around 317 K, as evidenced by Mössbauer spectroscopy and resistivity measurements, no long range Fe\(^{2+}\)/Fe\(^{3+}\) ordering is directly observed by x-ray, neutron or electron diffraction. Thus, a long range charge-ordering such as the simple alternating scheme proposed by Attfield et al. (1998) (shown in Fig. 4.5) destroys the mirror symmetry, which leads to a tilting of the Fe-ribbons, consistent with the observed enlargement of the \(\beta\) angle below the transition.

However, there is no observation of the increasing of \(a\)-axis periodicity (it should increase by a factor of two or another integer factor below \(T_{co}\)). Thus, below the transition, a charge-ordering is not implicit in the atom coordinates, although it is indirectly evidenced by other experiments. This ambiguity is resolved through the electronic structure study, which reveals an arrangement of Fe\(^{2+}\) and Fe\(^{3+}\)
4.1. Crystal structure of Fe₂OBO₃

Figure 4.3: Conductivity and structural anomalies at the charge-ordering transition in Fe₂OBO₃. (a) Log(resistivity) plotted against inverse temperature, with linear high and low temperature limits and the temperature of the structural transition at 317 K shown. (b) The structural transition was found from the thermal variation of the full width at half maximum of the 102/102 doublet, which collapses to a single peak at the transition, measured by synchrotron powder x-ray diffraction; according to Attfield et al. (1998).
Figure 4.4: Mössbauer spectra of Fe$_2$OBO$_3$ between 190 and 500 K. Below 270 K, these consist of two $2^+$ and two $3^+$ Fe doublets of equal intensity, but between 270 and 380 K the signals broaden and coalesce owing to the exchange of Fe$^{2+}$ and Fe$^{3+}$ environments through electron hopping. Well defined Mössbauer peaks above 380K are consistent with rapid electron hopping at two structurally distinct Fe$^{2.5+}$ sites; according to Douvalis, Papaefthymiou, Moukarika, Bakas and Kallias (2000) and Douvalis, Papaefthymiou, Moukarika and Bakas (2000).
Tab. 4.1: The refined cation-anion distances for \( P2_1/c \) phase of \( \text{Fe}_2\text{OBO}_3 \) from neutron powder diffraction measurements at 3 K; individual and mean distances to the coordinating oxygens (O1–O4) and the ionic valences \( V \) are presented.

<table>
<thead>
<tr>
<th>Cation site</th>
<th>-O bonds</th>
<th>( d(\text{cation-O})/\text{Å} )</th>
<th>( \langle d(\text{cation-O})/\text{Å} \rangle )</th>
<th>( V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)</td>
<td>-O1</td>
<td>2.074(6)</td>
<td>2.085(2)</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td></td>
</tr>
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<td>1.397(6)</td>
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</tr>
<tr>
<td></td>
<td>-O4</td>
<td>1.353(5)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

cations alternately ordered within the chains along the \( a \)-direction.

### 4.2 Electronic structure of \( \text{Fe}_2\text{OBO}_3 \)

In this section we present theoretical investigation of the electronic and magnetic properties of \( \text{Fe}_2\text{OBO}_3 \). The band-structure was calculated using the LSDA/LSDA+\( U \) approach in the tight-binding linear muffin-tin orbital (TB-LMTO) calculation scheme (Andersen 1975, Anisimov et al. 1991, Liechtenstein et al. 1995). The present calculations have been carried out for the low-temperature monoclinic structure of \( \text{Fe}_2\text{OBO}_3 \). The corresponding \( P2_1/c \) unit cell contains four \( \text{Fe}_2\text{OBO}_3 \) formula units. The calculations were performed for the recently refined at 3 K by Attfield et al. (1999) atom coordinates and the cell parameters \( a = 3.1688 \) Å, \( b = 9.3835 \) Å, \( c = 9.2503 \) Å, and \( \beta = 90.22^\circ \). The radii of muffin-tin spheres were taken as \( R_{\text{Fe}} = 2.5 \) a.u., \( R_{\text{B}} = 1.275 \) a.u., \( R_{\text{O1,O4}} = 1.7 \) a.u., and \( R_{\text{O2,O3}} = 1.8 \) a.u. Seven kinds of empty spheres were introduced to fill up the inter-atomic space. For simplicity we neglect the small spin-orbit cou-
Figure 4.5: Schematic representation of charge-disorder to charge-order transition in Fe₂OBO₃. (a) The arrangement of sites within ribbon of four Fe sites chains in orthorhombic Fe₂OBO₃ above T₊. (b) A possible ordering scheme of 2+ and 3+ Fe cations below T₊ also showing an antiphase boundary that preserves the sense of the monoclinic distortion.

pling (for instance, in other iron oxide, in Fe₃O₄, the spin-orbital interaction for 3d electrons was found to be negligibly small). We consider only a collinear spin case, in which the Fe magnetic moments are aligned along the a-direction, which is in reasonably good agreement with the experimental magnetic structure of Fe₂OBO₃ below Tₑ (Attfield et al. 1992). Motivated by our results, we propose an order parameter, defined as the difference between t₂g minority spin occupancies of Fe(1)²⁺ and Fe(1)³⁺ as well as the difference between t₂g majority spin occupancies of Fe(2)²⁺ and Fe(2)³⁺ cations. Like in Fe₃O₄ this order parameter is found to be quite large although the total 3d charge difference between 2+ and 3+ cations is small.

4.2.1 Band structure calculations

In order to study the ground state properties of Fe₂OBO₃ the LSDA method has been used. The LSDA calculations give only a metallic ferrimagnetic solution without charge separation (see Fig. 4.6) where partially filled bands at the Fermi level originate from the t₂g orbitals of Fe cations. As shown in Fig. 4.7 the lower part of the valence band (below -3.5 eV) is mainly formed by O 2p states with a bonding hybridization with Fe 3d states. Fe 3d states give predominant contribution to the bands at -3.5 eV below and up to 2.5 eV above the Fermi level. The exchange splitting between the spin-up and spin-down Fe 3d states is
Figure 4.6: Total density of states (DOS) obtained from the LSDA calculations for the low-temperature $P2_1/c$ phase of Fe$_2$OBO$_3$. The Fermi level is shown by dotted line. Top and bottom panels correspond to the majority and minority spin state, respectively. Metallic ferrimagnetic solution without charge separation is found. The symmetry inequivalence of Fe(1) and Fe(2) sites leads to the small ferrimagnetic moment of $\sim 0.31 \mu_B$ per f.u. The values of magnetic moments are -3.54 $\mu_B$ for Fe(1) and 3.81 $\mu_B$ for Fe(2) cations.
roughly 3 eV. Additionally, the five-fold 3d levels are split by the crystal field into \( t_{2g} \) and \( e_g \) subbands. The oxygen octahedra in Fe\(_2\)OBO\(_3\) are strongly distorted and the local symmetry of Fe sites is, of course, lower than cubic. Nevertheless, the cubic component of the ligand field, which is determined by the relative strength of Fe \( d - O \) \( p \) hybridization of \( \pi \)- and \( \sigma \)-type, remains dominant, whereas the splitting within “\( t_{2g} \)” and “\( e_g \)” subbands is smaller than the corresponding band width. This allows one to label the corresponding states as \( t_{2g} \) and \( e_g \). The crystal field splitting is roughly 2 eV, which is less than the exchange splitting. This is consistent with the high-spin state of Fe cations. The symmetry inequivalence of Fe(1) and Fe(2) sites leads to an inexact cancellation of magnetic moments and results in a small ferrimagnetic moment of \( \sim 0.31 \mu_B \) per formula unit. The absolute values of magnetic moments obtained by LSDA are 3.54 \( \mu_B \) and 3.81 \( \mu_B \) for Fe(1) and Fe(2) sites, respectively.

Fe(1) and Fe(2) \( t_{2g} \) and \( e_g \) states with the opposite spin projections share nearly the same energy intervals. Thus, Fe 3d states between -3.5 and -2.0 eV originate predominantly from majority spin Fe(1) and minority spin Fe(2) \( t_{2g} \) states whereas the states between -2.0 and -0.5 eV are mainly of \( e_g \) character (see Fig. 4.7). Partially occupied bands crossing the Fermi level are formed by minority spin Fe(1) and majority spin Fe(2) \( t_{2g} \) states. The nominal occupation of these bands is 1/6. In the majority spin channel, however, the Fe(2) \( t_{2g} \) state, that is oriented in the plane perpendicular to the shortest Fe(2)–O bond, forms quasi-one-dimensional bands with a strong dispersion along the \( a \)-direction. The one-dimensional character of the dispersion is explained by the fact that there are only two nearest neighbors of the same kind around each Fe(2) ion. The other two Fe(2) \( t_{2g} \) states are shifted to higher energy and the corresponding bands are completely unoccupied. As a result, the majority spin bands crossing the Fermi level turn out to be half-filled. An Fe(1) ion, in contrast to Fe(2) one, has four Fe(1) neighbors at close distances. Due to the hybridization between Fe(1) \( t_{2g} \) states the situation in the minority spin channel is more complicated. Twelve \( t_{2g} \) bands are split into three groups of 4 bands each. The Fermi level is crossed by lowest bands which show a rather strong dispersion along the \( a \) direction but with a period two times smaller than the quasi-one-dimensional Fe(2) bands.

However, in contrast to experimental data (Attfield et al. 1998, Douvalis, Papaefthymiou, Moukarika, Bakas and Kallias 2000, Douvalis, Papaefthymiou, Moukarika and Bakas 2000) the LSDA calculations predict Fe\(_2\)OBO\(_3\) to be metallic with substantial magnetic moment per unit cell. Apparently, the electron-electron correlations, mainly in the 3d shell of Fe cations, play a significant role.

To proceed further we take into account the strong electronic correlations in Fe 3d shell using the LSDA+\( U \) method. The calculations have been performed for the \( P2_1/c \) unit cell as well as for double (\( 2a \times b \times c \)) and triple (\( 3a \times b \times c \)) \( P2_1/c \) supercells of Fe\(_2\)OBO\(_3\) (without putting in any additional local displace-
Figure 4.7: Total DOS and corresponding band structure as obtained by the LSDA method for $P2_1/c\ Fe_2OBO_3$. The Fermi level is shown by dotted line. The energy bands predominantly originated from the Fe(1,2) $t_{2g}$ and $e_g$ states are shown in red and blue colors, respectively. The green color corresponds to the O 2$p$ bands. The octahedral crystal field splitting between the lower-energy triplet $t_{2g}$ and higher-energy doublet $e_g$ states which form two separated nonoverlapping bands is about 2 eV.
ments of oxygen atoms around of Fe\(^{2+}/Fe^{3+}\) sites). For the \(2a \times b \times c\) supercell the LSDA\(+U\) calculations using the value of Coulomb \(U = 5\,\text{eV}\) and exchange \(J = 1\,\text{eV}\) interaction parameters for Fe ion result in an insulating charge ordered (CO) solution with an energy gap of 0.13 eV. This is in a strong contrast to the metallic solution without CO obtained by the LSDA. The CO pattern obtained from the calculations is similar to the one proposed by Attfield et al. (1998) and shown in Fig. 4.5. This is a notable result because the CO is not implicit in the atomic coordinates, and it shows that LSDA\(+U\) calculations can assist experiments in revealing CO arrangements. To obtain a reasonably good agreement of the calculated gap of 0.39 eV with experimental value of 0.35 eV we increase the \(U\) value up to 5.5 eV (see Fig. 4.8). Note, however, that the CO obtained by LSDA\(+U\) within \(2a \times b \times c\) supercell does not depend on the \(U\) value of 5-5.5 eV. Here and in the following all results are presented for the double along \(a\)-direction \(P2_1/c\) supercell of Fe\(_2\)OBO\(_3\).

Tab. 4.2: Total and \(l\)-projected charges, magnetic moments, and occupation of the most populated \(t_{2g}\) orbitals calculated for inequivalent Fe atoms in the low-temperature \(P2_1/c\) phase of Fe\(_2\)OBO\(_3\).

<table>
<thead>
<tr>
<th>Fe ion</th>
<th>(q)</th>
<th>(q_s)</th>
<th>(q_p)</th>
<th>(q_d)</th>
<th>(M) ((\mu_B))</th>
<th>(t_{2g}) orbital</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe((1)^{3+})</td>
<td>6.90</td>
<td>0.40</td>
<td>0.55</td>
<td>5.95</td>
<td>-4.20</td>
<td>-</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe((1)^{2+})</td>
<td>7.12</td>
<td>0.35</td>
<td>0.50</td>
<td>6.27</td>
<td>-3.65</td>
<td>(d_{xy})</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe((2)^{3+})</td>
<td>6.79</td>
<td>0.38</td>
<td>0.54</td>
<td>5.86</td>
<td>4.33</td>
<td>-</td>
<td>0.09</td>
</tr>
<tr>
<td>Fe((2)^{2+})</td>
<td>7.04</td>
<td>0.34</td>
<td>0.50</td>
<td>6.21</td>
<td>3.69</td>
<td>(d_{yz})</td>
<td>0.89</td>
</tr>
</tbody>
</table>

As shown in Table 4.2, after self-consistency each of two groups of Fe\((1)\) and Fe\((2)\) atoms is split out in two subgroups of \(2^+\) and \(3^+\) Fe cations with equal number of \(2^+\) and \(3^+\) cations. Thus, one of \(t_{2g}\) majority/minority spin states of Fe\((2)\)/Fe\((1)\) ion becomes completely occupied, whereas all other \(t_{2g}\) states are pushed by the strong Coulomb interaction to the energies above 3 eV (see Fig. 4.9). The gap is opened between occupied and unoccupied \(t_{2g}\) states of Fe\((1)^{2+}\) and Fe\((1)^{3+}\) for spin-down and Fe\((2)^{2+}\) and Fe\((2)^{3+}\) for spin-up. As shown in Fig. 4.10, majority spin \(3d\) states of Fe\((1)^{3+}\) and minority spin states of Fe\((2)^{3+}\) cations are shifted below the O \(2p\) states, which form the band in the energy range of -8 and -2 eV. In contrast to Fe\(^{3+}\) states, the majority spin Fe\((1)^{2+}\) and minority spin Fe\((2)^{2+}\) \(3d\) states form the broad bands between -8 and -1 eV.

The obtained magnetic structure is almost antiferromagnetic (without spin moment per unit cell) with nearly the same spin moment per Fe\((1)^{3+}\) and Fe\((2)^{3+}\) as well as per Fe\((1)^{3+}\) and Fe\((2)^{3+}\) cations. Using the moment populations in Table 4.2, the calculated net moment is \(\sim 0.04\ \mu_B\) per Fe atom, in exact agreement with the experimental value (Attfield et al. 1998).
Figure 4.8: The total DOS for the low-temperature $P2_1/c$ phase of $\text{Fe}_2\text{OBO}_3$ obtained using the LSDA+$U$ with $U=5.5$ eV and $J=1$ eV. The top of the valence band is shown by dotted lines. Top and bottom panels correspond to the majority and minority spin state, respectively. Charge ordered insulating solution with an energy gap of 0.39 eV is obtained.
Figure 4.9: The partial DOS for different Fe cations are shown. The gap is opened between Fe(2)$^{2+}$ and Fe(2)$^{3+}$ for majority spin and Fe(1)$^{2+}$ and Fe(1)$^{3+}$ cations for minority spin states. The gap value of 0.39 eV was obtained by the LSDA+$U$ with $U=5.5$ eV and $J=1$ eV. The Fermi level is shown by dotted line. The total charge difference between 2+ and 3+ Fe cations is 0.24 $\bar{e}$. 

DOS (states/eV atom spin)

Energy (eV)
Figure 4.10: Total DOS and corresponding band structure self-consistently obtained by the LSDA+U with $U=5.5$ eV and $J=1$ eV for the $P2_1/c$ phase of Fe$_2$OBO$_3$. The Fermi level is denoted by the horizontal line and is taken as the zero of energy. The calculated energy gap of 0.39 eV opens between fully occupied band predominantly formed by Fe$^{2+}$ $d_{xy}$ (in local cubic frame) states and empty Fe$^{3+}$ $t_{2g}$ states. The energy bands predominantly originated from Fe$^{3+}$ $t_{2g}$ and $e_g$ states are shown in blue and green color, respectively. The red color corresponds to the occupied part of Fe$^{2+}$ $t_{2g}$ states.
The charge order obtained by LSDA+U in \(2a \times b \times c\) \(P_{21}/c\) supercell is consistent with observed enlargement of the \(\beta\) angle below the transition and coincides with charge-ordering scheme proposed earlier by Attfield et al. (1998). It is described by the sloping 2+ and 3+ Fe cation lines alternately stacked along \(a\)-direction, and could be considered as a quasi one dimensional analog of the Verwey CO model in the pyrochlore lattice of \(\text{Fe}_2\text{O}_4\). Using the same \(U\) and \(J\) values we perform additional self-consistent LSDA+U calculations for the \(P_{21}/c\) unit cell as well as for the double and triple along \(a\) direction \(P_{21}/c\) supercells. But only self-consistent solutions with larger value of the total energy or with substantial magnetic moment per unit cell, which contradicts to the experimental data, were found. Also we found that other charge arrangements in \(2a \times b \times c\) \(P_{21}/c\) supercell are unstable, and the stable one coincides with the CO found previously. Thus, the CO obtained for certain value of \(U\) and \(J\) does not depend on the initial charge arrangement. It is not possible to check all possible CO arrangements including more complex CO scenarios, but our results consistently indicate that the obtained CO solution is more favorable than other simple alternatives, and is the ground state of \(\text{Fe}_2\text{OBO}_3\) in the low-temperature phase.

Because of the small monoclinic distortion of the low temperature \(P_{21}/c\) structure the distances between the nearest Fe(1) cations become slightly different. It is important to note that in the calculated CO pattern the shortest (2.957 Å) is the distance between the pairs of equally charged Fe(1) cations whereas the distance between Fe(1)\(^{2+}\) and Fe(1)\(^{3+}\) cations turns out to be larger (2.961 Å). On the contrary, the pairs of Fe(1) and Fe(2) sites with the shortest distance between them are occupied by the cations with different valence. Thus, assuming a simple ionic model with the Coulomb interaction between Fe ions only the obtained CO pattern contradicts to the requirement of the minimal electrostatic energy. Indeed, the comparison of the Madelung energies shows that the energy lowers (about 0.07 eV per unit cell) if the nearest Fe(1) sites are occupied by Fe(1)\(^{2+}\) and Fe(1)\(^{3+}\) ions. This observation suggests that electron-lattice coupling rather than electrostatic repulsions drives the charge-ordering in \(\text{Fe}_2\text{OBO}_3\); the same conclusion was found for the charge order in \(\text{Fe}_3\text{O}_4\) (Wright et al. 2001, Wright et al. 2002, Leonov et al. 2004).

### 4.2.2 Charge ordering

Although the corresponding total 3\(d\) charges difference (0.34\(e\)) and disproportion of the total electron charges inside the atomic spheres of Fe\(^{2+}\) and Fe\(^{3+}\) cations (0.24\(e\)) is small, an analysis of occupation matrices of 3\(d\) Fe(1)/Fe(2) minority/majority spin states confirms substantial charge separation. Thus, as shown in Table 4.3, one of the \(t_{2g}\) states of Fe(1)\(^{2+}\) and Fe(2)\(^{2+}\) cations is almost completely filled with the occupation numbers \(n \approx 0.9\), whereas the remained two
Tab. 4.3: 3d orbital contribution to the formation of Fe(1)/Fe(2) minority/majority states with occupancy $n$ evaluated by diagonalization of the corresponding occupation matrix. Although, one of the $t_{2g}$ state of 2+ Fe sites is almost occupied with $n$ larger than 0.89 $\bar{e}$ the $t_{2g}$ occupancies of Fe$^{3+}$ cations are less than 0.1 $\bar{e}$. The occupied $t_{2g}$ state of Fe$^{2+}$ cations is predominantly of $d_{xy}$ character in the local cubic frame.

<table>
<thead>
<tr>
<th>Fe$^\text{B}$ ion</th>
<th>$xy$</th>
<th>$yz$</th>
<th>$3z^2-r^2$</th>
<th>$zx$</th>
<th>$x^2-y^2$</th>
<th>$n$</th>
<th>$t_{2g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)$^{2+}$</td>
<td>0.66</td>
<td>0.00</td>
<td>0.75</td>
<td>-0.01</td>
<td>0.06</td>
<td>0.91</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.67</td>
<td>-0.02</td>
<td>0.62</td>
<td>0.01</td>
<td>-0.41</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>-0.95</td>
<td>-0.01</td>
<td>0.31</td>
<td>0.01</td>
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<tr>
<td></td>
<td>-0.05</td>
<td>0.31</td>
<td>0.05</td>
<td>0.93</td>
<td>0.17</td>
<td>0.04</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.34</td>
<td>-0.06</td>
<td>0.23</td>
<td>-0.17</td>
<td>0.89</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Fe(1)$^{3+}$</td>
<td>0.71</td>
<td>0.18</td>
<td>-0.53</td>
<td>-0.06</td>
<td>0.44</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>-0.92</td>
<td>-0.09</td>
<td>0.36</td>
<td>0.09</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>-0.12</td>
<td>0.46</td>
<td>-0.35</td>
<td>-0.48</td>
<td>0.10</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.10</td>
<td>-0.19</td>
<td>0.44</td>
<td>-0.51</td>
<td>0.71</td>
<td>0.08</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.23</td>
<td>-0.28</td>
<td>-0.56</td>
<td>-0.70</td>
<td>-0.27</td>
<td>0.08</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td>Fe(2)$^{2+}$</td>
<td>-0.31</td>
<td>0.02</td>
<td>0.75</td>
<td>0.02</td>
<td>0.59</td>
<td>0.89</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.62</td>
<td>-0.10</td>
<td>-0.62</td>
<td>-0.04</td>
<td>0.46</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.06</td>
<td>-0.87</td>
<td>0.09</td>
<td>-0.48</td>
<td>-0.04</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.16</td>
<td>0.47</td>
<td>0.04</td>
<td>-0.86</td>
<td>-0.13</td>
<td>0.05</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.70</td>
<td>-0.10</td>
<td>0.22</td>
<td>0.19</td>
<td>-0.65</td>
<td>0.04</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td>Fe(2)$^{3+}$</td>
<td>-0.72</td>
<td>-0.07</td>
<td>-0.45</td>
<td>-0.05</td>
<td>0.52</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.08</td>
<td>-0.87</td>
<td>0.02</td>
<td>-0.49</td>
<td>-0.04</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.28</td>
<td>-0.44</td>
<td>-0.02</td>
<td>0.76</td>
<td>-0.40</td>
<td>0.09</td>
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</tr>
<tr>
<td></td>
<td>-0.47</td>
<td>0.24</td>
<td>-0.08</td>
<td>-0.43</td>
<td>-0.73</td>
<td>0.08</td>
<td>$t_{2g\perp}$</td>
</tr>
<tr>
<td></td>
<td>-0.41</td>
<td>0.00</td>
<td>0.89</td>
<td>-0.03</td>
<td>0.18</td>
<td>0.08</td>
<td>$t_{2g\perp}$</td>
</tr>
</tbody>
</table>

$t_{2g}$ orbitals of the Fe$^{2+}$ cations have significantly smaller population of about 0.1. Like in Fe$_3$O$_4$ we define an order parameter as the largest difference between Fe$^{2+}$ and Fe$^{3+}$ $t_{2g}$ populations. While due to strong static “screening” effects, the order parameter introduced as the total 3d charge difference between 2+ and 3+ Fe cations is ill-defined, the well-defined order parameter is the difference of $t_{2g}$ occupancies for Fe$^{3+}$ and Fe$^{2+}$ cations, which amounts to 80% of ideal ionic CO model and clearly pronounces the existence of CO below the transition. The occupation matrices analysis (see Table 4.3) shows that the change of the $t_{2g}$ occupations caused by the charge-ordering is very effectively screened by the rearrangement of the other Fe electrons. Thus, significant contribution to the charge-screening is provided by Fe $e_g$ states due to relatively strong $\sigma$ bonds with 2p O states and, as a result, appreciable contribution to the occupied part of the valence O band.
Figure 4.11: The angular distribution of the majority and minority spin $3d$ electron density of the Fe(2) and Fe(1) cations, respectively, within Fe-ribbon. The size of orbital corresponds to its occupancy. Oxygen atoms are shown by small spheres. X-Y-Z coordinate system corresponds to the local cubic frame.
Figure 4.12: The angular distribution of the majority and minority spin 3d electron density of the Fe(2) and Fe(1) cations, respectively, from different Fe-ribbons. The size of orbital corresponds to its occupancy. The frame of four Fe(1) atoms from the Fe-ribbon presented in Fig. 4.11 is shown by dashed lines.
The occupied \( t_{2g} \) states of \( Fe^{2+} \) cations are predominantly of \( d_{xy} \) character in the local cubic frame (according to that we later mark the orbital as \( d_{xy} \) orbital). This is illustrated in Fig. 4.11, which shows the angular distribution of the majority and minority spin 3\( d \) electron density of the Fe(2) and Fe(1) cations, respectively\(^1\). Thus, occupied Fe\(^{2+}\) and unoccupied Fe\(^{3+}\) cations are ordered alternately within the chain which is infinite along \( a \)-direction. The angular distribution of charge density of the Fe(1) and Fe(2) cations, which correspondingly belongs to different Fe-ribbons being formed a cross in the \( Fe_2OB_3 \) structure projected on (100) plane (see Fig. 4.1) is shown in Fig. 4.12.

**Tab. 4.4:** The averaged Fe–O distances in the plane of \( t_{2g} \) orbitals for \( P2_1/c \) structure of \( Fe_2OB_3 \). \( d_{xy} \) approximates to the doubly-occupied orbital of the 3\( d^6 \) Fe\(^{2+}\) states.

<table>
<thead>
<tr>
<th>Fe atom</th>
<th>orbital</th>
<th>( d_{orb.} ) (Å)</th>
<th>( d_{av.} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(1)</td>
<td>( d_{xy} )</td>
<td>2.111</td>
<td>2.085</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>2.076</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>2.069</td>
<td></td>
</tr>
<tr>
<td>Fe(2)</td>
<td>( d_{xy} )</td>
<td>2.109</td>
<td>2.082</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>2.083</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>2.055</td>
<td></td>
</tr>
</tbody>
</table>

An analysis of interatomic distances (Table 3.4) shows that the average Fe(2)-O distance (2.109 Å) in the plane perpendicular to one of the diagonals of the distorted Fe(2)O\(_6\) octahedron is considerably larger than average distances in the other two planes (2.055 and 2.083 Å). It turns out that the occupied Fe(2) \( t_{2g} \) majority spin orbital is the one oriented in the plane with the largest average Fe(2)-O distance. The same is also true for the Fe(1) ion but in this case the variation of the average Fe(1)-O distances is smaller (2.111 vs 2.069 and 2.076 Å) and, as a consequence, the out-of-plane rotation of the occupied \( t_{2g} \) minority spin orbital is stronger.

\(^1\) The distribution is calculated according to \( \rho(\theta, \phi) = \sum_{m,m'} n_{m,m'} Y_m^*(\theta, \phi) Y_{m'}(\theta, \phi) \), where \( n_{m,m'} \) is the occupation matrix of 3\( d \) minority states of Fe(1) and 3\( d \) majority states of Fe(2) cations. The occupation matrices were calculated by the LSDA+U with \( U=5.5 \) eV, \( J=1 \) eV for the low-temperature \( P2_1/c \) phase of \( Fe_2OB_3 \). \( Y_m(\theta, \phi) \) are corresponding spherical harmonics.
Tab. 4.5: Total and partial intraribbon exchange interaction parameters are shown. The values are given in Kelvin. The spatial representation of all these exchanges is schematically presented in Fig. 4.13.

<table>
<thead>
<tr>
<th>$J_i$</th>
<th>$t_{2g} - t_{2g}$</th>
<th>$t_{2g} - e_g$</th>
<th>$e_g - e_g$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>4</td>
<td>-22</td>
<td>-20</td>
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</tr>
<tr>
<td>$J_2$</td>
<td>-7</td>
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<tr>
<td>$J_3$</td>
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<td>-19</td>
<td>-16</td>
<td>-32</td>
</tr>
<tr>
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<td>-70</td>
</tr>
<tr>
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</table>

4.2.3 Magnetic structure and exchange couplings

Using the LSDA+$U$ method the exchange interaction parameters have been calculated via the variation of the ground state energy with respect to the magnetic-moment rotation angle (Lichtenstein et al. 1995, Anisimov, Aryasetiawan and Lichtenstein 1997). In Table 4.5 we have shown the total set of different intraribbon exchange parameters as well as a contribution of different subbands into exchange interactions. $J_i$ represents the effective pair exchange interaction between Fe atoms with Heisenberg Hamiltonian $H = -\sum_{i>j} J_{ij} e_i \cdot e_j$, where $e_i$ and $e_j$ are the magnetic moment unit vectors at site $i$ and $j$. Positive (negative) values of $J$ correspond to the ferromagnetic (antiferromagnetic) coupling between Fe sites. The spatial representation of all these exchanges is schematically presented in Fig. 4.13. Surprisingly, only the exchange interaction parameter between Fe(2)$^{2+}$ and Fe(2)$^{3+}$ cations is ferromagnetic with relatively small value of $J_6 = 6$ K. In contrast, the nearest sites in quasi-one-dimensional Fe(1) chain are coupled antiferromagnetically with noticeably larger exchange absolute value of $|J_5| = 69$ K. Furthermore, the exchange parameters between the nearest sites of two Fe(1) chains are relatively strong and antiferromagnetic (see $J_2$, $J_4$, and $J_8$ in Table 4.5). Therefore, the Fe(1) sublattice is highly frustrated, while the relatively weak frustrations in the Fe(2) sublattice considerably reduce ferromagnetic interaction within Fe(2) chain. Also it is interesting to note that relatively strong ferromagnetic intrachain interaction between $t_{2g}$ subbands of Fe(2)$^{2+}$ and Fe(2)$^{3+}$ cations (see $J_6$ in Table 4.5) is strongly suppressed by the substantial antiferromagnetic $t_{2g} - e_g$ and $e_g - e_g$ exchange.

On the other hand, the interribbon exchange interaction parameters between
**Figure 4.13:** The sketch of the arrangement of exchange interaction parameters within the ribbon of iron atoms. Open circles correspond to Fe$^{3+}$, while Fe$^{2+}$ cations are noted by the closed circles. The spin moment direction on each Fe site is shown by an arrow.

**Tab. 4.6:** Total and partial interribbon exchange interaction parameters are shown. The values are given in Kelvin. The spatial representation of all these exchanges is schematically presented in Fig. 4.14.

<table>
<thead>
<tr>
<th>$J_i$</th>
<th>$t_{2g} - t_{2g}$</th>
<th>$t_{2g} - e_g$</th>
<th>$e_g - e_g$</th>
<th>Total</th>
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<tr>
<td>$J_{10}$</td>
<td>-12</td>
<td>-114</td>
<td>-104</td>
<td>-229</td>
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<td>-16</td>
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<td>$J_{15}$</td>
<td>-12</td>
<td>-115</td>
<td>-19</td>
<td>-147</td>
</tr>
</tbody>
</table>
Figure 4.14: The sketch of the arrangement of interribbon exchange interaction parameters. Open circles correspond to Fe$^{3+}$, while Fe$^{2+}$ cations are noted by the closed circles. The spin moment direction on each Fe site is shown by arrow. Note that $J_{ij}$ exchange parameters presented here have the same total values as $J_{ii}$, while subband contributions are different.
Fe(1) and Fe(2) atoms are considerably larger. The values of these interactions are shown in Table 4.6, whereas the spatial representation is schematically presented in Fig. 4.14. Thus, the exchange parameters between Fe(1)$^{3+}$ and Fe(2)$^{2+}$ cations are antiferromagnetic with values of $J_{10} = -229$ K and $J_{14} = -207$ K (see Table 4.6). Such an appreciable difference between $J_{10}$ and $J_{14}$ arises from geometry since the former is due to the superexchange interaction between Fe ions linked by shortest bonds to a common O-ion. It seems that the geometrical reason is also responsible for decreasing of absolute value of the exchange interactions between Fe(1)$^{2+}$ and Fe(2)$^{3+}$ cations from $|J_{12}| = 209$ K to $|J_{15}| = 147$ K (see Table 4.6). Interestingly that the exchange interaction between Fe(1)$^{3+}$ and Fe(2)$^{3+}$ cations is considerably larger than between Fe(1)$^{2+}$ and Fe(2)$^{2+}$ ($J_{11}$ and $J_{13}$, respectively). We find that the interribbon exchange interactions play predominant role and determine the whole $L$-type ferrimagnetic spin structure below $T_c$ in contrast to the ferromagnetic intrachain order due to $d^5 - d^6$ superexchange (Attfield et al. 1998, Attfield et al. 1999).

### 4.3 Conclusion

In the present LSDA+$U$ study of the low-temperature $P2_1/c$ phase of Fe$_2$OBO$_3$ we found a charge ordered insulator with an energy gap of 0.39 eV. While the screening of the charge disproportion is so effective that the total 3d charge separation is rather small (0.34), the charge order is well pronounced with an order parameter defined as a difference of $t_{2g}$ occupancies of 2+ and 3+ Fe cations (0.8). The occupied Fe$^{2+}$ and Fe$^{3+}$ cations are ordered alternately within infinite along $a$-axis chains of Fe atoms. This result is remarkable in view of the absence of directly observed CO atomic displacements in the experimental coordinates, and demonstrates the utility of the LSDA+$U$ method as an aide to experimental studies of CO structures. The charge order obtained by LSDA+$U$ is consistent with observed enlargement of the $\beta$ angle and coincides with the charge-ordering scheme proposed earlier by Attfield et al. (1998). It seems certain that Fe$_2$OBO$_3$ is charge ordered below $T_{co}$, and the absence of the long range charge-ordering from x-ray, neutron or electron diffraction arises from formation of charge order within small domains, which have been termed “Wigner nanocrystals” (Rozenberg, Hearne, Pasternak, Metcalf and Honig 1996). Thus, the superstructure peaks are too weak and broad to be observed against background in diffraction patterns, whereas the observed long range monoclinic lattice distortion can arise despite a large concentration of defects as these preserve the direction of the monoclinic distortion, but do not propagate the coherent doubling of the lattice periodicity. An analysis of the exchange interaction parameters obtained by LSDA+$U$ method inevitably results in predominance of the interribbon exchange interactions which determine the whole $L$-type ferrimagnetic spin struc-
ture below $T_c$, in contrast to the ferromagnetic intrachain order due to $d^5 - d^6$ superexchange proposed earlier by Attfield et al. (1998).
4. \( \text{Fe}_2\text{OBO}_3 \) – a prototype of electrostatically driven charge ordered system
5. CHARGE ORDER AND SPIN-SINGLET PAIR FORMATION IN Ti$_4$O$_7$

In the last decade mixed-valent Magnéli phases M$_n$O$_{2n-1}$ (M = Ti, V) have attracted much interest due to the peculiar resistivity properties – the sharp metal-insulator transitions associated with a charge and orbital ordering phenomena (Eyert, Schwingenschlögl and Eckern 2004, Schwingenschlögl and Eyert 2004, Schwingenschlögl 2004). The titanium Magnéli phases

$\text{Ti}_n\text{O}_{2n-1} = \text{Ti}_2\text{O}_3 + (n - 2)\text{TiO}_2$ where $3 \leq n \leq 10$

form a relatively large family of Ti-oxides. However, in this chapter we only consider Ti$_4$O$_7$ ($n$=4) which shows two steep first-order transitions associated with formation and consequent ordering of singlet Ti$^{3+}$-Ti$^{3+}$ pairs, the so-called bipolarons, at low temperature (Lakiss, Schlenker, Chakraverty, Buder and Marezio 1976). In this respect, Ti$_4$O$_7$ is a mixed-valent system with a predictable Peierls-like charge-ordering transition. This is in remarkable contrast to the previously discussed Fe$_3$O$_4$ and Fe$_2$OBO$_3$. In this chapter we would like to address the universalities found in the charge ordered systems with different crystal, magnetic, and chemical structures.

5.1 Crystal structure of Ti$_4$O$_7$

Titanium oxide, Ti$_4$O$_7$ is a mixed valent compound which has an even mixture of 3+ and 4+ Ti cations, corresponding to average 3$d$ occupation of 1/2 electron per Ti site, with stoichiometric formula Ti$_2^{3+}$Ti$_2^{4+}$O$_7$. Electrical resistivity (Bartholomew and Frankl 1969), specific heat, magnetic susceptibility (Lakiss et al. 1976), and x-ray diffraction (Marezio, McWhan, Dernier and Reméika 1972) data reveal two first-order transitions in the temperature range of 130-150 K. Thus, the heat capacity at constant pressure, $c_p$, shown as a function of temperature in Fig. 5.1, reveals two sharp transitions occurred at the temperature range of 130-150 K. The high temperature peak at 154 K is 3 K wide, the low-temperature one is about 10 K wide and shows 130-142 K hysteresis.

The resistivity data measurements presented in Fig. 5.2 reveal two first-order transitions. In particular, a metal-semiconductor transition at 154 K is followed
Figure 5.1: Molar heat capacity of Ti$_4$O$_7$. Inset shows the molar heat capacity of single crystals in the temperature range of the transitions with a large horizontal scale and a smaller vertical one than the main figure. Measurements are performed with increasing temperatures; according to Lakkis et al. (1976).

Figure 5.2: Conductivity of Ti$_4$O$_7$ single crystals. Measurements were performed along the [031] pseudorutile direction. Inset shows the magnetic susceptibility vs temperature; according to Lakkis et al. (1976).
Figure 5.3: The low-temperature crystal structure of Ti₄O₇. Chains of four Ti sites run parallel to the pseudo-rutile c-axis. Red and blue chains of four Ti atoms correspond to the (a) and (b) chains Ti atoms, respectively. Further gradation of red and blue on light and dark subsets indicates inequivalent Ti sites in (a) and (b) chains.
by the semiconductor-semiconductor transition at 130-140 K, which is characterized by almost two orders of magnitude abrupt increase in the electrical resistivity (Bartholomew and Frankl 1969, Lakkis et al. 1976). The magnetic susceptibility shows a sharp enhancement when heating through 150 K. However, it is small and temperature independent below this temperature and does not show any anomaly at 140 K (Lakkis et al. 1976).

**Figure 5.4:** Atomic and molecular levels scheme for the Ti\(^{3+}\) chains (left) and for the Ti\(^{4+}\) chains (right). The orthorhombic crystal field splitting of \(t_{2g}\) triplet denoted by \(\Delta_1\) and \(\Delta_2\), whereas \(2J\) is a bonding-antibonding splitting of \(d_{xy}\) orbital into low-energy singlet and high-energy triplet states.

The crystal structure of Ti\(_4\)O\(_7\) shown in Fig. 5.3 can be viewed as rutile-type slabs of infinite extension and four Ti sites thickness, separated by shear planes with a corundum-like atomic arrangement. Below 130 K it crystallizes in a triclinic crystal structure with two formula units per primitive unit cell (Marezio and Dernier 1971, Hodeau and Marezio 1979, LePage and Marezio 1984). Four crystallographically inequivalent Ti sites are found at the centers of distorted oxygen octahedra. They form two types of chains, namely, (a) 1-3-3-1 and (b) 2-4-4-2, which run parallel to the pseudo-rutile \(c\)-axis and are separated by the crystallographic shear planes. Although interatomic distances in the (b)-chain are almost uniform (3.01 and 3.07 Å between 4-4 and 2-4 Ti sites, respectively) they are remarkably different for the (a)-chain (3.11 and 2.79 Å between 3-3 and 1-3 Ti sites).

A cubic octahedral crystal field lifts the five fold degeneracy of 3\(d\) Ti states which split into lowest triplet \(t_{2g}\) and a highest doublet \(e_g\). Additionally, the orthorhom-
bic component of the crystal field considerably lowers energy of the $d_{xy}$ orbital which splits into a low-energy bonding spin singlet and high-energy antibonding spin triplet states due to $\text{Ti}^{3+}$-$\text{Ti}^{3+}$ dimerization. The singlet and triplet states correspond to molecular orbitals built with the $d_{xy}$ orbitals of two neighboring Ti(1) and Ti(3) sites. This state should be slightly lower for $\text{Ti}^{3+}$ ($A$ level) comparing to the $\text{Ti}^{4+}$ sites ($B$ level). The splitting $2J$ between these bonding and antibonding states could be estimated from the temperature behavior of the magnetic susceptibility. It is temperature independent below 150 K, there is no direct contribution coming from an increase of the population of the triplet state with temperature. A rough estimation of magnitude for the bonding-antibonding splitting via the Van Vleck matrix elements between the singlet and excited state, assumed to be the triplet state, could be obtained via $\chi_{VV} \sim N\mu_B^2/2J$, where $N$ is the number of electrons of the ground state. Thus, a value for $2J$ of 0.3 eV was deduced. The energy $\delta$ obtained from the Orbach process gives $\sim0.1$ eV for the splitting between the $A$ and $B$ levels, which are the ground states of the $\text{Ti}^{3+}$ and $\text{Ti}^{4+}$ cations in the low-temperature phase. The crystal field splitting values $\Delta_1$ and $\Delta_2$ ($\sim0.4$ eV) were extracted from the EPR experiment (Lakkis et al. 1976).

The electronic structure photoemission study of $\text{Ti}_2\text{O}_7$ across two transitions in 130-150 K temperature range has been performed by Abbate, Potze, Sawatzky, Schlenker, Teahan and Turner (1995) and Kobayashi, Susaki, Fujimori, Tonogai and Takagi (2002). Remarkably that like in $\text{Fe}_3\text{O}_4$ no indication of a quasiparticle feature was observed in the high-temperature phase, which is in notable contrast to the famous Mott transition in $\text{V}_2\text{O}_3$ (Mo et al. 2003). A broad incoherent spectral weight maximum is situated at $-0.75$ eV and spectral intensity is strongly suppressed towards the chemical potential. Below 154 K an insulating spectrum was clearly observed, whereas above it the spectral onset cross the chemical potential without formation of a quasiparticle peak. Thus, the 154 K transition is a semiconductor-to-metal phase transition with an activation energy of 0.15 eV (below 154 K), whereas the 137 K one is a semiconductor-to-semiconductor one. Further crystal structure investigations allowed to elucidate the nature of the three phases distinguished by the two first-order transitions (LePage and Marezio 1984, Marezio and Dernier 1971, Hodeau and Marezio 1979, Marezio et al. 1972). In particular, in the metallic phase the average Ti-O bond lengths for crystallographically inequivalent TiO$_6$ octahedra are very similar which results in the average valence state of 3.5+ per each Ti cation (Marezio and Dernier 1971, Hodeau and Marezio 1979). Below 130 K charge is transferred from the (b) to the (a)-chains resulting in substantial difference between the average cation-anion distances of Ti(1,3) and Ti(2,4) sites (see Table 5.1). In addition, Ti$^{3+}$ cations in the alternate (a)-chains are paired to form nonmagnetic metal-metal bonds, whereas in the intermediate phase pairing also persists but its long-range order calls for a fivefold supercell (Lakkis et al. 1976). Thus, the 130-140 K transition is associated with a transition to the phase with a
long-range order of Ti$^{3+}$-Ti$^{3+}$ pairs, whereas above 150 K 3$^+$ and 4$^+$ Ti cations are disordered. The presence of the Ti$^{3+}$-Ti$^{3+}$ pairs strongly differentiates Ti$_4$O$_7$ from Fe$_3$O$_4$ and results in two steep first-order transitions found in the electrical resistivity (Bartholomew and Frankl 1969, Lakkis et al. 1976).

**Tab. 5.1:** The refined cation-anion distances for P\overline{1} phase of Ti$_4$O$_7$ obtained at 115 K; individual and mean distances to the coordinating oxygens (O1–O6) and the ionic valences $V$ are presented (see Marezio et al. (1972)).

<table>
<thead>
<tr>
<th>Ti site</th>
<th>-O bonds</th>
<th>$d$(Ti-O)/Å</th>
<th>$\langle d$(Ti-O)$\rangle$/Å</th>
<th>$V$</th>
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<td>Ti(1)</td>
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<td></td>
<td>-O7</td>
<td>1.797</td>
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### 5.2 Electronic properties of Ti$_4$O$_7$

In the present section we discuss the electronic structure of the low-temperature phase obtained with the LDA/LDA+$U$ approach in the tight-binding linear
Figure 5.5: (a) Schematic crystal structures of Ti$_4$O$_7$ which show only the chains parallel to the pseudo-rutile $c$-axis truncated by shear planes indicated by thick lines. In the low-temperature insulating (LI) phase, Ti$^{3+}$-Ti$^{3+}$ pairs are ordered. In the metallic (M) phase, all the Ti sites have a uniform valence of 3.5+. (b) Photoemission (PES) spectra of Ti$_4$O$_7$ taken by varying the temperature from bottom to the top. (c) Integrated PES intensity within 0.5 eV of $E_F$ normalized to that from $E_F$ to 1 eV. The solid line is a guide to the eye. (d) The M, H1, and LI phase spectra around $E_F$ plotted on an expanded scale; according to Kobayashi et al. (2002).
muffin-tin orbital (TB-LMTO) calculation scheme (Andersen 1975, Anisimov et al. 1991, Liechtensten et al. 1995). LDA calculations of both high- and low-temperature phase of Ti₄O₇ results in significant t₂g charge separation between crystallographically independent 3+ and 4+ Ti sites in the low-temperature phase, although a rather isotropic occupation of the t₂g states has been found at room-temperature (Eyert et al. 2004). While, in addition, an orbital order at the Ti d¹ chains originating from the metal-metal dimerization was found, LDA gives only metallic solution with semimetallic-like band overlap instead of the semiconducting gap. This problem was overcome taking into account strong electronic correlations in the Ti 3d shell using the LDA+U method.

The present band-structure calculations have been performed for the low-temperature triclinic structure of Ti₄O₇ (LePage and Marezio 1984). The Pɪ unit cell used in the calculations was constructed from the translation vectors of the original Iɪ cell with \( a = 5.626 \) Å, \( b = 7.202 \) Å, \( c = 20.2608 \) Å, \( \alpha = 67.90^\circ \), \( \beta = 57.69^\circ \), and \( \gamma = 109.68^\circ \) found at 115 K. The radii of muffin-tin spheres were taken as \( R_{\text{Ti-4}} = 2.27 \) a.u., \( R_{\text{O1,03,04-6}} = 1.78 \) a.u., and \( R_{\text{O2,07}} = 1.66 \) a.u. Fifteen kinds of empty spheres were introduced to fill up the inter-atomic space. For simplicity we neglect the small spin-orbit coupling and consider only a collinear spin case.

The LDA+U calculations result in a charge and orbitally ordered insulator with an energy gap of 0.29 eV, which is in good agreement with experimental gap value of 0.25 eV (Kaplan, Schlenker and Since 1997). From our results, we propose an order parameter, defined as the difference between t₂g majority/minority spin occupancies of Ti(1)⁢3⁺/Ti(3)⁢3⁺ and Ti(2)⁢4⁺/Ti(4)⁢4⁺ cations, respectively. This order parameter is found to be quite large, although the total 3d charge difference between 3+ and 4+ cations, remains small. Also it is interesting to note that the total charge separation between 3+ and 4+ Ti cations is completely lost due to efficient screening caused by the rearrangement of the other Ti electrons. In addition, we find a strong antiferromagnetic coupling of \( J \approx 1700 \) K of the local moments within the dimerized Ti³⁺-Ti³⁺ pairs, whereas an inter-pair coupling is only of \( \approx 40 \) K. This is in good agreement with the small and temperature independent magnetic susceptibility in the low-temperature phase of Ti₄O₇.

### 5.2.1 Band structure calculations

In this section we carry out results of LSDA calculations for the low-temperature Pɪ phase of Ti₄O₇ (which well agree with the results of the previous work (Eyert et al. 2004, Schwingenschlögl 2004)). LSDA gives a nonmagnetic metallic solution with a substantial charge separation between the crystallographically independent Ti(1)/Ti(3) and Ti(2)/Ti(4) cations. The lower part of valence band below \( -3 \) eV is predominantly formed by O 2p states with a bonding hybridization with Ti 3d
states. Crystal field splitting of the latter is roughly of 2.5 eV. Ti $t_{2g}$ states form the group of bands between -1 eV below and 2 eV above the Fermi energy, whereas Ti $e_g$ states give a predominant contribution to the bands between 2.5 and 4.5 eV. Within the $t_{2g}$ group of bands the symmetry inequivalence of Ti(1)/Ti(3) and Ti(2)/Ti(4) sites leads to the substantial $t_{2g}$ charge separation between these two groups of Ti atoms. In addition, an analysis of the partial density of states reveals significant bonding-antibonding splitting of $d_{xy}$ (in local cubic frame) states of about 1.5 eV for Ti(1)/Ti(3) cations, whereas Ti(2)/Ti(4) cations show a relatively weak substructure. This substantial bonding-antibonding splitting of Ti(1)/Ti(3) $t_{2g}$ states agrees well with the concept of formation of Ti$^{3+}$-Ti$^{3+}$ spin-singlet pairs proposed earlier by Marezio, McWhan, Dernier and Remekia (1973). However, the LSDA calculations fail to reproduce the insulating spin-singlet ground state of the low-temperature phase of Ti$_4$O$_7$. Apparently, the electron-electron correlations, mainly in the 3$d$ shell of Ti cations, play a significant role.

In order to take into account the strong electronic correlations in Ti 3$d$ shell we perform the LDA+$U$ calculations for Ti$_4$O$_7$ in the low-temperature $P\bar{I}$ structure. In our calculations we use Coulomb interaction parameter $U = 3.0$ eV and exchange coupling $J = 0.8$ eV taken in agreement with previous constrained LDA calculations (Streltsov, Mylnikova, Shorikov, Pchelkina, Khomskii and Anisimov 2005, Solovyev, Hamada and Terakura 1996). The LDA+$U$ calculations result in a charge and orbitally ordered insulator with an energy gap of 0.29 eV (see Fig. 5.8). This is in strong contrast to the metallic solution with a substantial charge disproportionation between crystallographically inequivalent

\textbf{Figure 5.6:} Total DOS obtained from LDA calculations for the low-temperature $P\bar{I}$ phase of Ti$_4$O$_7$. The top of the valence band is shown by dotted lines.
Figure 5.7: Total DOS and corresponding band structure as obtained from LDA calculations for the low-temperature $P\bar{1}$ phase of Ti$_4$O$_7$. The Fermi level denoted by the horizontal line and is taken as the zero energy. The energy bands predominantly originated from the Ti $t_{2g}$ and $e_{g}$ states are shown in red and blue colors, respectively. The octahedral crystal field splitting is about 2.5 eV.

Figure 5.8: The total DOS obtained from LDA+$U$ calculations with $U=3.0$ eV and $J=0.8$ eV for the low-temperature $P\bar{1}$ phase of Ti$_4$O$_7$. The top of the valence band is shown by dotted lines. Top and bottom panels correspond to the majority and minority spin states, respectively.
5.2 Electronic properties of Ti$_4$O$_7$

Ti(1)/Ti(3) and Ti(2)/Ti(4) cations obtained by the LSDA and is in reasonably good agreement with an experimental gap value of 0.25 eV (Kaplan et al. 1997). Note, however, that the charge and orbital order pattern remains exactly the same for $U$ in the range of 2.5-4.5 eV, whereas the energy gap increases considerably up to 1.12 eV for $U=4.5$ eV. This remarkable increase of the gap value is accompanied by the enhancement of spin magnetic moment from 0.56 up to 0.8 $\mu_B$ per 3+ Ti(1)/Ti(3) cation as the $U$ value increased from 2.5 to 4.5 eV. In addition, we perform LDA+$U$ calculations for the high-temperature metallic phase of Ti$_4$O$_7$. In particular for $U$ of 2.5-3 eV a ferromagnetic metallic self-consistent solution with an average occupation 3.5+ for all Ti cations was obtained. Although, the calculations do not take into account possible short-range order of 3+ and 4+ Ti cations, this approximation seems to be justified by the small characteristic time scale usually observed in the charge-disordered state (see for instance García et al. (2000) where this time scale found to be less 10$^{-16}$ s in the charge-disordered phase of Fe$_3$O$_4$). With further increase of the $U$ value the metallic solution collapses into insulating one.

**Tab. 5.2**: Total $q$ and $l$-projected $q_{s,p,d}$ charges, magnetic moments $M$, and occupation of the most populated $t_{2g}$ orbitals $n$ calculated for inequivalent Ti atoms in the low-temperature $P\overline{1}$ phase of Ti$_4$O$_7$.

<table>
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<th>Ti ion</th>
<th>$q$</th>
<th>$q_s$</th>
<th>$q_p$</th>
<th>$q_d$</th>
<th>$M$ ($\mu_B$)</th>
<th>$t_{2g}$ orbital</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)$^{3+}$</td>
<td>2.27</td>
<td>0.18</td>
<td>0.27</td>
<td>1.83</td>
<td>0.66</td>
<td>$d_{xy}$</td>
<td>0.74</td>
</tr>
<tr>
<td>Ti(2)$^{4+}$</td>
<td>2.22</td>
<td>0.22</td>
<td>0.33</td>
<td>1.68</td>
<td>0.04</td>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td>Ti(3)$^{3+}$</td>
<td>2.16</td>
<td>0.18</td>
<td>0.25</td>
<td>1.74</td>
<td>-0.67</td>
<td>$d_{xy}$</td>
<td>0.73</td>
</tr>
<tr>
<td>Ti(4)$^{4+}$</td>
<td>2.16</td>
<td>0.21</td>
<td>0.33</td>
<td>1.62</td>
<td>-0.02</td>
<td></td>
<td>0.07</td>
</tr>
</tbody>
</table>

After self-consistency was achieved four crystallographically independent Ti atoms are split out in two subgroups with respect to the spin magnetic moment per Ti site: Ti(1)/Ti(3) with a moment of 0.66/-0.67 $\mu_B$, respectively, and Ti(2)/Ti(4) with 0.04/-0.02 $\mu_B$. This is shown in Table 5.2 which collects contribution of the orbital projected charges $q_{s,p,d}$, magnetic moments, and occupation of the most populated Ti $t_{2g}$ orbitals. In particular, one of the $t_{2g}$ majority/minority spin states of Ti(1)/Ti(3) becomes occupied ($d^1$), whereas all other $t_{2g}$ states are pushed by the strong Coulomb interaction above the Fermi level. In contrast, all $t_{2g}$ states of Ti(2) and Ti(4) are almost depopulated ($d^0$) and form bands up to 2.5 eV above the Fermi level. The occupied Ti(1)/Ti(3) states are strongly localized and form a prominent structure with a band width of 0.25 eV just below the Fermi level (see Fig. 5.9). The strong Coulomb interaction does not affect much the empty Ti $e_g$ states, which give predominant contribution between 2.5 and 4.5 eV. The obtained magnetic structure is almost
antiferromagnetic with the spin magnetic moments within Ti(1)$^{3+}$-Ti(3)$^{3+}$ as well as Ti(2)$^{4+}$-Ti(4)$^{4+}$ pairs being of the same magnitude with opposite sign.

5.2.2 Charge ordering

An analysis of occupation matrices of the Ti(1)$^{3+}$/Ti(3)$^{3+}$ majority/minority 3$d$ spin states confirms substantial charge disproportion within the Ti 3$d$ shell. As shown in Table 5.2, one of the $t_{2g}$ states of Ti$^{3+}$ cations ($d^1$) is occupied with the occupation number of 0.74, whereas the remaining two $t_{2g}$ orbitals have a significantly smaller population of about 0.08. Thus, we define an orbital order parameter as the largest difference between 3$+$ and 4$+$ Ti $t_{2g}$ populations which amounts to 66% of the ideal ionic charge ordering model. The orbital order parameter clearly shows the existence of substantial charge disproportionation in the Ti 3$d$ shell of Ti$_4$O$_7$ which is remarkable because of the complete lack of the total charge separation (see column $q$ in Table 5.2) between 3$+$ and 4$+$ Ti cations. The occupation matrices analysis shows that the change of the $t_{2g}$ occupations is very efficiently screened by the rearrangement of the other Ti electrons. A significant portion of the screening charge is provided by the Ti $e_g$ states due to the formation of relatively strong $\sigma$ bonds with O 2$p$ states, which results in appreciable contribution of the former to the occupied part of valence band. Ti 4$s$ and 4$p$ states give additional contributions to the screening of the difference in $t_{2g}$ occupations which leads to complete loss of the disproportionation between the charges at 3$+$ and 4$+$ Ti sites.

5.2.3 Orbital ordering, hoppings, and exchange couplings

The occupied $t_{2g}$ Ti$^{3+}$ states are predominantly of $d_{xy}$ character in the local cubic frame (according to that we later mark the orbital as $d_{xy}$ orbital). This is illustrated in Fig. 5.11, which shows the angular distribution of the majority and minority spin 3$d$ electron density of Ti cations, marked by red and cyan color, respectively. Since Ti(1)$^{3+}$ and Ti(3)$^{3+}$ cations are antiferromagnetically coupled, the obtained ferro-orbital order is consistent with the formation of a bonding spin-singlet state from the $d_{xy}$ orbitals of two neighboring Ti(1) and Ti(3) sites. The orientation of occupied Ti$^{3+}$ $t_{2g}$ orbitals is consistent with the largest average Ti-O distance in the plane of $t_{2g}$ orbitals. As shown in Table 5.4 the average Ti(1)-O distance (2.061 Å) in the plane of $d_{xy}$ orbital is considerably

\begin{footnote}
\textsuperscript{1}The distribution is calculated according to $\rho(\theta, \phi) = \sum_{m,m'} n_{m,m'} Y^*_m(\theta, \phi) Y_{m'}(\theta, \phi)$, where $n_{m,m'}$ is the occupation matrix of 3$d$ majority states of Ti(1) and 3$d$ minority states of Ti(3) cations. The occupation matrices were calculated by the LDA+$U$ with $U=3.0$ eV, $J=0.8$ eV for the low-temperature $P1\overline{1}$ phase of Ti$_4$O$_7$. $Y_m(\theta, \phi)$ denotes corresponding spherical harmonics.
\end{footnote}
Figure 5.9: The partial DOS for Ti$(1)^{3+}$ and Ti$(2)^{4+}$ cations are shown. The gap value of 0.29 eV was obtained by the LDA+$U$ with $U=3.0$ eV and $J=0.8$ eV. The Fermi level is shown by dotted line. The occupied Ti$(1)/$Ti$(3)$ states are strongly localized and located just below the Fermi level, whereas Ti$(2,4)$ $t_{2g}$ states are almost depopulated ($d^{5}$).
Figure 5.10: Total DOS and corresponding band structure self-consistently obtained by the LDA+U with $U=3.0$ eV and $J=0.8$ eV for the $P\bar{1}$ phase of Ti$_4$O$_7$. The Fermi level is denoted by the horizontal line and is taken as the zero energy. An energy gap of 0.29 eV is opened between B-F symmetry points. The energy bands predominantly originated from the Ti $t_{2g}$ and $e_g$ states are shown in red and blue colors, respectively.
Tab. 5.3: $3d$ orbital contribution to the formation of Ti(1), Ti(2) majority and Ti(3), Ti(4) minority states with occupancy $n$ evaluated by diagonalization of the corresponding occupation matrix. One of the $t_{2g}$ state of Ti$^{3+}$ cation is almost occupied with $n$ larger than 0.73 $\bar{e}$. The $t_{2g}$ occupancies of Ti$^{4+}$ cations are less than 0.15 $\bar{e}$. The occupied $t_{2g}$ state of Ti$^{3+}$ cations is predominantly of $d_{xy}$ character in the local cubic frame.

<table>
<thead>
<tr>
<th>Ti ion $^+$</th>
<th>$xy$</th>
<th>$yz$</th>
<th>$3z^2 - r^2$</th>
<th>$zx$</th>
<th>$x^2 - y^2$</th>
<th>$n$</th>
<th>$t_{2g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)$^{3+}$</td>
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<td>-0.07</td>
<td>0.82</td>
<td>0.01</td>
<td>0.19</td>
<td><strong>0.74</strong></td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>-0.84</td>
<td>0.10</td>
<td>-0.50</td>
<td>-0.01</td>
<td>-0.18</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.03</td>
<td>-0.53</td>
<td>-0.06</td>
<td>-0.85</td>
<td>0.06</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.04</td>
<td>0.22</td>
<td>-0.23</td>
<td>-0.06</td>
<td>0.95</td>
<td><strong>0.08</strong></td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>-0.81</td>
<td>-0.15</td>
<td>0.53</td>
<td>0.18</td>
<td>0.07</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>Ti(2)$^{4+}$</td>
<td>-0.31</td>
<td>0.42</td>
<td>0.15</td>
<td>-0.80</td>
<td>0.26</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>0.38</td>
<td>-0.48</td>
<td>-0.23</td>
<td>-0.18</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.14</td>
<td>0.50</td>
<td>0.39</td>
<td>0.15</td>
<td>-0.74</td>
<td>0.15</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>-0.59</td>
<td>0.10</td>
<td>-0.77</td>
<td>0.07</td>
<td>-0.21</td>
<td>0.12</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>-0.65</td>
<td>0.00</td>
<td>-0.53</td>
<td>-0.55</td>
<td>0.10</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>Ti(3)$^{4+}$</td>
<td>0.41</td>
<td>-0.26</td>
<td>-0.81</td>
<td>0.25</td>
<td>0.22</td>
<td><strong>0.73</strong></td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>-0.84</td>
<td>0.10</td>
<td>-0.49</td>
<td>0.07</td>
<td>-0.20</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.02</td>
<td>-0.57</td>
<td>-0.12</td>
<td>-0.79</td>
<td>-0.18</td>
<td>0.17</td>
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</tr>
<tr>
<td></td>
<td>-0.32</td>
<td>-0.70</td>
<td>0.29</td>
<td>0.38</td>
<td>0.42</td>
<td>0.07</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>-0.32</td>
<td>0.07</td>
<td>0.40</td>
<td>-0.84</td>
<td>0.06</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td>Ti(4)$^{4+}$</td>
<td>-0.83</td>
<td>-0.08</td>
<td>0.53</td>
<td>0.03</td>
<td>0.18</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>-0.61</td>
<td>-0.09</td>
<td>0.78</td>
<td>-0.05</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.29</td>
<td>-0.33</td>
<td>0.12</td>
<td>-0.20</td>
<td>0.87</td>
<td><strong>0.12</strong></td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>0.71</td>
<td>0.09</td>
<td>0.59</td>
<td>0.36</td>
<td>0.10</td>
<td>$t_{2g}$</td>
</tr>
<tr>
<td></td>
<td>-0.48</td>
<td>0.05</td>
<td>-0.83</td>
<td>-0.03</td>
<td>0.28</td>
<td>0.08</td>
<td>$t_{2g}$</td>
</tr>
</tbody>
</table>

larger than average distances in the other two $yz$ and $zx$ planes (2.032 and 2.045 Å, respectively). The same is also true for Ti(3) cation but in this case the variation of the average Ti(3)-O distances is much smaller (2.047 vs 2.041 and 2.042 Å) and, as a consequence, the out-of-plane rotation of the occupied $t_{2g}$ minority spin orbital is stronger.

In addition, hopping matrix elements were evaluated via Fourier transformation from reciprocal to the real space of the Ti $t_{2g}$ LDA Wannier Hamiltonian (Anisimov, Kondakov, Kochevnikov, Nekrasov, Pchelkina, Allen, Mo, Kim, Metcalf, Suga, Sekiya, Keller, Leonov, Ren and Vollhardt 2005). Remarkably, for the low-temperature phase the Ti(1)-Ti(3) intra-pair $d_{xy}$-$d_{xy}$ hopping matrix element is found to be of 0.61 eV, whereas all other hoppings are 3-4 times smaller.
Figure 5.11: Structure of Ti$_4$O$_7$ showing the angular distribution of the majority and minority spin 3$d$ electron density of Ti cations. Red and cyan (light and dark, respectively, on the black and white image) orbitals correspond to the majority and minority 3$d$ spin states, respectively. Oxygen atoms are shown by small spheres. The size of orbital corresponds to its occupancy. X-Y-Z coordinate system corresponds to the local cubic frame.
Tab. 5.4: The averaged Ti-O distances in the plane of \( t_{2g} \) orbitals \( (d_{\text{orb}}) \) and in the oxygen octahedra \( (d_{\text{av}}) \) for the \( P\bar{1} \) structure of \( \text{Ti}_4\text{O}_7 \). The occupied orbital of the \( 3d^1 \) Ti(1) and Ti(3) \( 3+ \) cations is predominantly of \( d_{xy} \) character in the local cubic frame.

<table>
<thead>
<tr>
<th>Ti atom</th>
<th>orbital</th>
<th>( d_{\text{orb}} ) (Å)</th>
<th>( d_{\text{av}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(1)</td>
<td>( d_{xy} )</td>
<td>2.061</td>
<td>2.046</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>2.032</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>2.045</td>
<td></td>
</tr>
<tr>
<td>Ti(2)</td>
<td>( d_{xy} )</td>
<td>2.012</td>
<td>2.000</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>1.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>2.013</td>
<td></td>
</tr>
<tr>
<td>Ti(3)</td>
<td>( d_{xy} )</td>
<td>2.047</td>
<td>2.043</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>2.041</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>2.042</td>
<td></td>
</tr>
<tr>
<td>Ti(4)</td>
<td>( d_{xy} )</td>
<td>1.973</td>
<td>1.977</td>
</tr>
<tr>
<td></td>
<td>( d_{yz} )</td>
<td>1.976</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( d_{zx} )</td>
<td>1.981</td>
<td></td>
</tr>
</tbody>
</table>

This strong inhomogeneity of the hopping matrix elements disappears in the high-temperature phase. Thus, according to our calculations hopping elements in the high-temperature phase are 0.23, 0.21, 0.39, and 0.33 eV between 1-3, 2-4, 3-3, and 4-4 Ti sites, respectively.

Estimation of exchange interaction parameters via the variation of the ground state energy with respect to the magnetic moment rotation angle (Liechtensten et al. 1995, Anisimov, Aryasetiawan and Lichtenstein 1997) results in a strong antiferromagnetic coupling of -1.696 K between Ti(1)\(^{3+} \) and Ti(3)\(^{3+} \) cations\(^2 \). All other couplings are (almost) two orders of magnitudes smaller. This indicates a possible formation of the spin-singlet pairs via a direct antiferromagnetic exchange between neighboring Ti(1) and Ti(3) sites. The contribution of the superexchange via O \( p \) orbitals to the Ti(1)-Ti(3) exchange coupling is found to be negligible. This was verified by calculating the exchange coupling constants with the sub-blocks of the LMTO Hamiltonian responsible for the Ti-O hybridization.

\(^2\) The exchange coupling parameter \( J \) represents the effective pair exchange interaction between Ti atoms with effective Heisenberg Hamiltonian \( H = - \sum_{i>j} J_{ij} S_i \cdot S_j \), where \( S_i \) and \( S_j \) are spin magnetic moment vectors at site \( i \) and \( j \). Positive (negative) values of \( J \) correspond to the ferromagnetic (antiferromagnetic) coupling between sites.
being set to zero. This calculation gave the qualitatively same results for exchange constants although the possibility for superexchange via O p orbitals was eliminated.

5.3 Conclusion

In the present electronic structure study of the low-temperature P1 phase of Ti$_4$O$_7$ we found a charge ordered insulating solution with an energy gap of 0.29 eV. The total 3d charge separation is small (less than 0.14), whereas an orbital order parameter defined as a difference between $t_{2g}$ occupancies of Ti$^{3+}$ and Ti$^{4+}$ cations is large and gives direct evidence for charge ordering. Ti 4s and 4p states give a strong contribution to the static “screening” of the total 3d charge separation. This effective charge screening leads to complete loss of the disproportionation between the charges at 3+ and 4+ Ti sites. The occupied $t_{2g}$ states of Ti$^{3+}$ cations are predominantly of $d_{xy}$ character (in the local cubic frame) and form a spin-singlet molecular orbital via the strong direct antiferromagnetic exchange coupling between neighboring Ti(1) and Ti(3) sites of $J \approx 1700$ K, whereas the role of superexchange is found to be negligible. This is in good agreement with the small and temperature independent magnetic susceptibility in the low-temperature phase of Ti$_4$O$_7$. Finally, we have to point out quite remarkable similarity found between Ti$_4$O$_7$ and a recently proposed orbital-assisted metal-insulator transition in VO$_2$ (Haverkort, Hu, Tanaka, Reichelt, Streltsov, Korotin, Anisimov, Hsieh, Lin, Chen, Khomskii and Tjeng 2005). Like in VO$_2$, an orbital “switching” in the V 3d state across the metal-insulator transition (in low-temperature and high-temperature phases) was found. The system becomes more one-dimensional and more susceptible to a Peierls-like charge ordering transition. Furthermore, our calculations also proved that the system is close to a Mott-insulating regime.
6. CONCLUSIONS AND PERSPECTIVES

The present work was devoted to the systematic first principle theoretical investigation of the charge-ordering phenomena in mixed-valent transition metal oxides (TMOs). Particularly, we have focused on a specific subclass of mixed-valent TMOs – the strongly correlated electron systems with partially filled \( t_{2g} \) orbitals. We considered magnetite, \( \text{Fe}_3\text{O}_4 \), a prototype of CO system whose low-temperature properties have been a subject of strong recent debates (Wright et al. 2001, García et al. 2001). According to the results presented in Chapter 3 (“Charge order in \( \text{Fe}_3\text{O}_4 \)”), \( \text{Fe}_3\text{O}_4 \) is a long-range charge ordered insulator below the Verwey transition temperature. This is in strong contrast to the intermediate valence regime proposed by García et al. (2001). The total charge disproportion (in other words, charge order parameter) is rather small (0.23) which well agrees with experimental estimations (0.2). Charge and orbital order is well pronounced with an orbital order parameter (0.7) defined as a difference of \( t_{2g1} \) occupancies of 2+ and 3+ Fe\(_B\) cations. The charge order has a pronounced [001] charge density wave with a minor [00\( \frac{1}{2} \)] modulation and does not obey the Anderson criterion of minimum electrostatic repulsion energy (Anderson 1956). The competition of electrostatic and “elastic” energy contributions in the total energy appears to be responsible for development of the charge and orbital order found below the Verwey transition (Leonov et al. 2004).

To proceed further we have considered another iron oxide – iron oxoborate, \( \text{Fe}_2\text{OBO}_3 \), a prototype of “electrostatically driven” charge ordered system, whose low-temperature properties are not yet completely understood. \( \text{Fe}_2\text{OBO}_3 \) has, compared to \( \text{Fe}_3\text{O}_4 \) completely different warwickite-type crystal structure and physical properties (Attfield et al. 1992, Attfield et al. 1998). Similar to \( \text{Fe}_3\text{O}_4 \), it undergoes a structural phase transition (at 317 K) which is accompanied by a broad semiconductor-to-semiconductor transition, where resistivity drops down by a factor of \(~3\) upon heating. Although \(^{57}\text{Fe}\) Mössbauer spectra clearly show that the charge localization occurs at the transition, no long-range \( \text{Fe}^{2+}/\text{Fe}^{3+} \) ordering has been directly observed by x-ray, neutron or electron diffraction. Moreover, the average Fe-O distances are equal within experimental errors (Attfield et al. 1992, Attfield et al. 1998). The long-range alternating scheme proposed by Attfield et al. (1998) destroys the mirror symmetry, which leads to a tilting of the Fe-ribbons. This is consistent with the observed enlargement of the \( \beta \) angle below the transition, and increasing of the \( \alpha \)-axis periodicity. The latter, however, con-
tradricts to the present experiments (Attfield et al. 1998). Below the transition a charge-ordering is not implicit in the atomic coordinates, although it is indirectly evidenced by the other experiments. The Wigner crystallization scenario was proposed as a driving force for charge-ordering, whereas the magnetic structure below 150 K was explained in terms of the ferromagnetic intrachain order due to $d^5-d^6$ superexchange. The calculations presented in Chapter 4 ("Fe$_2$OBO$_3$ – a prototype of electrostatically driven charge ordered system") have been performed without putting in any additional local displacements of oxygen atoms around Fe$^{2+}$/Fe$^{3+}$ cations. The present study confirmed the existence of the charge-ordering below 317 K but questioned the pure electrostatic nature of the transition (see also Leonov, Yaresko, Antonov, Attfield and Anisimov (2005)). The CO pattern obtained from the calculations is consistent with observed enlargement of the $\beta$ angle and coincides with the charge-ordering scheme proposed before by Attfield et al. (1998). An analysis of the Fe 3$d$ charges shows that similar to Fe$_3$O$_4$ the total 3$d$ charge separation (0.34) is small, whereas an orbital order parameter is large (0.8). We have also shown that the interplay of inter- and intra-ribbon exchange couplings rather then $d^5-d^6$ superexchange is responsible for the whole $L$-type ferrimagnetic spin structure below 150 K.

Finally, the same tool (the LDA+$U$ approach) was applied for investigation of the charge order in titanium oxide, Ti$_4$O$_7$, a prototype of a spin-Peierls-like charge-ordering system (Lakkis et al. 1976, Eyert et al. 2004). The result of these investigations have been presented in Chapter 5 ("Charge order and spin-singlet pair formation in Ti$_4$O$_7"."). In particular, the calculations resulted in a large value of the orbital order parameter, whereas the effective charge screening leads to complete loss of the disproportion between the charges at 3+ and 4+ Ti sites (Leonov, Yaresko, Antonov, Schwingenschlögl, Eyert and Anisimov 2005). The occupied $t_{2g}$ states of Ti$^{3+}$ cations form a spin-singlet molecular orbital via the strong direct antiferromagnetic exchange coupling of $\sim$1700 K between neighboring sites. Furthermore, the calculations also proved that the system is close to a Mott-insulating regime.

Summing up all main results presented in this thesis we have to point out that the resulting charge disproportion is considerably less (or completely absent) comparing to the ideal ionic CO model. The charge order is evidenced through the strong "orbital order" parameter introduced as a difference of $t_{2g}$ orbital occupancies between charge-rich and charge-poor cations. At least for Fe$_3$O$_4$ and Fe$_2$OBO$_3$ the charge ordered self-consistent solution obtained by the LDA+$U$ violates criterion of minimum electrostatic repulsion. A smallness of the total charge disproportion has been ascribed to the "charge screening" phenomenon which reduces the total energy loss due to the development of the charge order incompatible with the minimum electrostatic repulsion. Particularly, the electron-lattice interaction tends to localize electron on a specific orbital which increases charge disproportionation between the charge-reach and charge-poor sites. In contrast to that, in order
to reduce the strong mutual Coulomb repulsion between electrons (and to gain in the kinetic energy) the system tends to be more charge-homogeneous. These findings can have a general character because of completely different crystal and chemical structures of the systems under investigation.

Charge-ordering is a complicated physical phenomenon originating from an intimate interplay of charge and orbital degrees of freedom. At present, we focus on the LDA+$U$ investigations of the ground state properties of the ordered insulators, whereas the outstanding challenge for further theoretical research will be a study of the charge-ordering transition itself, combining together the density-functional and dynamical-mean-field theories (Anisimov, Poteryaev, Korotin, Anokhin and Kotliar 1997, Kotliar and Vollhardt 2004, Georges et al. 1996, Maier et al. 2005).
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