Chapter 1

Introduction

1.1 Transition-Metal Oxides

1.1.1 General Properties

Transition-metal oxides with partially filled *d*-electron bands exhibit a wide range of unusual and not yet sufficiently understood phenomena like dynamic lattice distortions, magnetic-, charge-, and orbital ordering. However, apart from the high- T_c superconductivity of the cuprates, the most outstanding and prominent properties of these materials are the Mott insulating phase, the anomalous metallic phase with poor conduction as well as the metal-insulator transition. The transition occurs on variation of chemical composition or external parameters like temperature, pressure, or magnetic field. This complex behaviour cannot be explained by the conventional one-electron band theory assuming non-interacting electrons subject to the periodic lattice potential of the solid. The electronic structure of transition-metal oxides with partially filled *d*-electron bands is rather believed to be determined by strong electronic correlation effects in combination with strong electron-lattice coupling.

1.1.2 Electronic States

Two fundamental models, the Hubbard and the double-exchange model, are introduced in order to provide an overview of the basic theoretical concepts used to explain the unusual properties of transition-metal oxides. In spite of their rigorous simplifications, neglecting orbital degeneracy, hybridisation, and inter-site correlations, they manage to qualitatively reproduce the Mott insulating state, the metal-insulator transition, as well as the ferromagnetic metallic phase.

The Hubbard model

An approach towards the theoretical understanding of the Mott insulating state and the metal-insulator transition was achieved by the Hubbard model. This takes into account

the electron kinetic energy as well as electronic on-site interactions in a nondegenerate tight-binding band. In the second quantised form, the Hubbard Hamiltonian is given by [1, 2, 3, 4]

$$H_H = H_t + H_U = -t \sum_{\langle ij \rangle} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \qquad (1.1)$$

where $c_{i\sigma}^{\dagger}$ and $c_{i\sigma}$ are the creation and annihilation operators of an electron with spin $\sigma \in \{\uparrow,\downarrow\}$ at site *i*. The symbols \uparrow and \downarrow denote spin-up and spin-down electrons, respectively. The occupation number operator writes $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$. The first term of the sum is the kinetic energy determined by the transfer integral *t*. This is obtained from the overlap of two orbital wave functions at adjacent sites quantifying the probability that an electron moves from site *i* to site *j*. The second item describes the Coulomb repulsion of two electrons at the same site via the coupling strength *U*. At half filling, $n = \sum_i n_{i\sigma} = 1$, and in the strong-coupling limit, $U \gg t$, the considered band separates into lower and upper Hubbard band producing the Mott insulator. Second-order perturbation in terms of t/U yields the Heisenberg model,

$$H_H = J \sum_{\langle ij \rangle} \mathbf{S}^i \mathbf{S}^j, \tag{1.2}$$

where $J = 4t^2/U$ denotes the superexchange coupling and \mathbf{S}^i , \mathbf{S}^j are spin operators of adjacent sites i, j. The Hubbard model reproduces the metal-insulator transition as electron correlation strength U/t or band filling are changed. Fillings n = 0 and n = 2 correspond to the conventional band insulator.

The double-exchange model

The double-exchange model describes the interplay of itinerant electrons in a partially filled band with magnetic moments localised at certain lattice sites. While accounting for an interband exchange interaction between the two subsystems, no direct exchange between the localised moments is regarded [5, 6, 7]. The model Hamiltonian consists of two components,

$$H_{DE} = H_t + H_{Hund}.$$
 (1.3)

While H_t represents the kinetic energy of the conduction electrons as in Eq. (1.1), H_{Hund} specifies Hund's exchange energy with coupling strength J_H . This corresponds to an intraionic interaction between the conduction-electron spin σ^i and the localised magnetic moment \mathbf{S}^i ,

$$H_{Hund} = -J_H \sum_{i} \boldsymbol{\sigma}^i \mathbf{S}^i. \tag{1.4}$$

The positive sign of J_H determines the preferred ferromagnetic alignment of itinerant and localised spins. The double-exchange model predicts the ferromagnetic metallic phase as

electron itineracy mediates ferromagnetic exchange within the spin system. Further, it qualitatively explains the increase in resistivity upon the transition from a ferromagnetic to a paramagnetic phase as the band structure is modified by the magnetic state of the spin system: At low temperatures the spins are ordered and do not scatter electrons, whereas at high temperatures spin scattering localises electrons. However, the spin scattering is not sufficient to reproduce the metal-insulator transition [8, 9]. There is substantial evidence that additional electron-lattice coupling is required to constitute the insulating state [10].

Orbital degeneracy

The physical properties of transition-metal oxides are determined mainly by the transitionmetal 3d electrons. Atomic d orbitals have fivefold degeneracy, excluding spin. In the solid, the degeneracy is lifted by the crystal field. In the cubic perovskite lattice the transition-metal ions are surrounded by six ligand O^{2-} ions in octahedron configuration, see Fig. 1.1. Because of the negative valence of the ligand ions the d electrons are, in the direction towards adjacent oxygen ions, subject to a higher crystal field as compared to other directions. This yields a splitting of the d orbitals into two degenerate e_g orbitals $(d_{x^2-y^2}, d_{3z^2-r^2})$ and three degenerate t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) at lower energy.



Figure 1.1: Undistorted crystal structure of perovskite transition-metal oxides. T and A denote transition-metal ion and A-site cation. The dashed lines indicate an O₆ octahedron.

Electron-lattice coupling

Considering perovskite transition-metal oxides ATO_3 with cation A and transition-metal ion T, two types of electron-lattice coupling influence the electronic structure: First, the cation size and hence the tolerance factor of the lattice affects the T-O-T bond angle. Yet, the one-electron conduction-band width and the transfer amplitude t, thus the electron kinetic energy, are very sensitive of the bond angle [11]. This compositional effect arises from the static crystal structure. Second, dynamical electron-lattice coupling may localize carriers: The occupation of the $d_{3z^2-r^2}$ orbital causes the orthorhombic distortion of the respective TO_6 octahedron as compared to the ideal perovskite structure. This Jahn-Teller distortion lifts the e_g degeneracy by Δ_{JT} . It is associated with orthorhombic phonon modes. At sufficiently strong coupling the electron is trapped in the self-induced potential minimum leading to the formation of a bound state called polaron. In case of high e_g electron density coherent long-range Jahn-Teller distortions are observed along with insulating behaviour. In contrast, the presence of incoherent local lattice distortions of comparable size is characteristic of the insulating high-temperature phase of colossalmagnetoresistance compounds. On the transition to the ferromagnetic metallic phase, however, they gradually vanish [12].

Hybridisation

The orbital overlap of the *d*-wave functions of a given transition-metal ion and the *p*-wave functions of adjacent oxygen ions causes hybridisation. The hybridisation strength depends on the atomic number of the transition metal, as increasing nuclear charge decreases the chemical potential of the *d* electrons and thus the relative energetic difference of *d* and *p* bands. Consequently, the hybridisation of *d* and *p* bands is particularly strong in compounds with heavy transition metals like Ni or Cu. The relative energetic position of *d* and *p* bands and the corresponding hybridisation strength have important influence on the low-energy physics of the Mott insulator. If, on the one hand, the oxygen *p* level ϵ_p lies far below the transition-metal *d* level ϵ_d , so that the *d*-electron interaction *U* is smaller than the charge-transfer energy $\Delta = |\epsilon_d - \epsilon_p|$, the charge gap is determined by *U* and low-energy excitations have predominantly *d* character. This type of compound is referred to as *Mott-Hubbard insulator*. If, on the other hand, $U > \Delta$, low-energy excitations are of the charge-transfer insulator. In case of strong hybridisation low-energy excitations have mixed *d* and *p* character.

The perovskite manganites and cobaltites investigated in the present thesis are situated at the crossover from prototype Mott-Hubbard insulators as the vanadates to canonical charge-transfer insulators like nickelates or cuprates. Yet, the nature of the charge gap in manganites and cobaltites is currently a matter of vital debate. The motivation of this work is to contribute by means of optical spectroscopy experimental evidence to the subject.

1.2 Interaction of Light with Matter

1.2.1 The Dielectric Tensor

Linearly polarised light reflected by a semi-infinite planar surface becomes elliptically polarised with its major axis rotated from the original polarisation direction. In case of a magnetised ferromagnetic mirror components of rotation and ellipticity which are linear functions of the sample magnetisation are referred to as magneto-optic Kerr effect. The experimental observable, the electric displacement \mathbf{D} , is related to the electric field strength \mathbf{E} of the incident light by

$$\mathbf{D}(\omega, t) = \varepsilon(\omega) \,\mu(\omega) \,\mathbf{E}(\omega, t) \,, \tag{1.5}$$

where ε and μ are the dielectric and the magnetic-permeability tensors. At optical frequencies the magnetic susceptibility is usually neglected [13], hence in the following $\mu \equiv \mathbf{1}$. Consequently, the propagation of electromagnetic waves in a solid is characterised by its dielectric tensor ε . In case of cubic symmetry, with the magnetisation **M** parallel to the **z** direction and the coordinate axes pointing along the principal axes of the crystal, ε is of the form

$$\varepsilon = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & 0\\ -\varepsilon_{xy} & \varepsilon_{xx} & 0\\ 0 & 0 & \varepsilon_{zz} \end{pmatrix}.$$
 (1.6)

For an absorbing medium the tensor elements are complex, $\varepsilon_{ij} = \varepsilon_{1ij} + i \varepsilon_{2ij}$. Further, $\varepsilon_{zz} \approx \varepsilon_{xx}$. To first order, the diagonal elements ε_{xx} are independent of **M** describing the ordinary optical absorption. Ferromagnets exhibit off-diagonal components ε_{xy} , which are to second order proportinal to **M** and cause the magneto-optic Kerr effect [14]. In the visible and ultra-violet frequency range the ratio of ε_{xy} and ε_{xx} is of the order 10^{-3} to 10^{-2} .

In order to demonstrate the physical meaning of the dielectric tensor, the power P absorbed by the illuminated volume fraction V of the specimen is regarded [15]:

$$P(\omega, t) = -\int_{V} d^{3}r \, \frac{d}{dt} \mathbf{D}(\omega, t) \, \mathbf{E}(\omega, t).$$
(1.7)

Assuming harmonic time dependence of the field quantities and restricting the following considerations to the long-wavelength limit, that is neglecting the spatial variation of the electromagnetic field with respect to interatomic distances, the time-averaged power writes

$$P = \frac{\mathrm{i}\,\omega V}{2}\,\mathrm{Re}\left(\sum_{ij}\,\varepsilon_{ij}^*E_j^*E_i\right).\tag{1.8}$$

Imagine incident linearly polarised light as the proportional superposition of right- and left-circularly polarised (RCP and LCP) electromagnetic waves. Let the two senses of circular polarisation be defined as

$$\mathbf{E}^{\pm}(\omega, t) = E(\omega)(\mathbf{x} \pm \mathrm{i}\,\mathbf{y})e^{-\mathrm{i}\,\omega t},\tag{1.9}$$

x and **y** denoting coordinate unit vectors and the superscripts (+) and (-) referring to RCP and LCP light, respectively. In respect of the two senses of polarisation the power absorbed is given as

$$P^{\pm} = \omega V E^2 \left(\varepsilon_{2xx} \pm \varepsilon_{1xy} \right). \tag{1.10}$$

This result identifies ε_{2xx} and ε_{1xy} as the absorptive parts of the respective tensor elements. Further transformation yields

$$\varepsilon_{2xx} = \frac{P^+ + P^-}{2\omega V E^2},$$

$$\varepsilon_{1xy} = \frac{P^+ - P^-}{2\omega V E^2}.$$
(1.11)

To conclude, the absorptive part ε_{2xx} of the diagonal tensor element is proportional to the sum of absorption of LCP and RCP light. In contrast, the absorptive part ε_{1xy} of the off-diagonal element is proportional to their difference.

Assuming a sourceless medium and causality, i.e. that $\mathbf{E}(t)$ causes $\mathbf{D}(t)$, analytical considerations yield the Kramers-Kronig dispersion relations between real and imaginary parts of ε_{ij} [16]:

$$\varepsilon_{1ij}(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_{2ij}(\omega')}{\omega'^2 - \omega^2} d\omega',$$

$$\varepsilon_{2ij}(\omega) = \frac{-2\omega}{\pi} P \int_0^\infty \frac{\varepsilon_{1ij}(\omega')}{\omega'^2 - \omega^2} d\omega',$$
(1.12)

where P denotes the principal value of the integral.

1.2.2 Microscopic Theory

In this section a microscopic description of the origin of magneto-optical phenomena is presented relating the elements of the dielectric tensor to quantum-mechanical transition rates. From a microscopic perspective, the interaction of light with a solid is determined by multipole transitions from occupied electronic states $|\alpha\rangle$ with energy $\hbar\omega_{\alpha}$ to unoccupied states $|\beta\rangle$, $\hbar\omega_{\beta}$, upon absorption of a photon of energy $\hbar\omega_{\beta\alpha} = \hbar(\omega_{\beta} - \omega_{\alpha})$. Electric-dipole transitions are governed by the quantum-number selection rules $\Delta m_L = \pm 1$ and $\Delta m_S = 0$, corresponding to the change of z component of orbital angular momentum and spin. The (+) and (-) signs refer to transitions induced by RCP and LCP light, respectively. The contributions of further multipole-radiation processes are not considered because of their negligible orders of magnitude.

The quantum-mechanical transition rate $W_{\beta\alpha}$, i.e. the probability per unit time, of the corresponding transition is determined by time-dependent perturbation theory. The Hamiltonian of the radiated solid writes

$$H = H_0 + H_L = H_0 + \sum_i \frac{e}{m c} \pi_i \mathbf{A}_L(\mathbf{r}_i) + \frac{e^2}{2 m^2 c^2} \mathbf{A}_L^2(\mathbf{r}_i), \qquad (1.13)$$

where H_0 denotes the unperturbed Hamiltonian and H_L represents the interaction of the incident electromagnetic wave with the electrons of the solid at locations \mathbf{r}_i . e is the elementary charge, m the electron mass, c the vacuum velocity of light, and \mathbf{A}_L the vector potential of the electric field. Regarding elastic light scattering the expression of second order in \mathbf{A}_L is irrelevant. The kinetic momentum operator $\boldsymbol{\pi}_i$ including spin-orbit interaction is of the form

$$\boldsymbol{\pi}_{i} = \frac{\hbar}{\mathrm{i}} \nabla_{i} + \frac{e}{c} \mathbf{A}_{M}(\mathbf{r}_{i}) + \frac{\hbar}{4 \, m c^{2}} \, \boldsymbol{\sigma}_{i} \times \nabla_{i} V(\mathbf{r}_{i}), \qquad (1.14)$$

where \mathbf{A}_M and $\boldsymbol{\sigma}_i$ are the vector potential of the external magnetic field and the Pauli spin operator of the electron. The effective one-particle operator $V(\mathbf{r}_i)$ represents the potential energy of an electron in the absence of radiation, comprising the impact of both the periodic-lattice potential and the Coulomb electron-electron interaction on the electron under consideration. In the one-electron approximation H_0 writes

$$H_0 = \sum_i -\frac{\hbar^2 \nabla_i^2}{2m} + V(\mathbf{r}_i) + \frac{\hbar}{4m^2 c^2} \left(\frac{\hbar}{i} \nabla_i + \frac{e}{c} \mathbf{A}_M(\mathbf{r}_i)\right) \,\boldsymbol{\sigma}_i \times \nabla_i V(\mathbf{r}_i). \tag{1.15}$$

The last term describes the spin-orbit interaction. With respect to the vector potential of the electric field,

$$\mathbf{A}_{L}^{\pm} = c \, Re \left(\frac{E(\omega)}{\mathrm{i} \, \omega \sqrt{2}} \left(\mathbf{x} \pm \mathrm{i} \, \mathbf{y} \right) e^{-\mathrm{i} \, \omega t} \right), \tag{1.16}$$

 H_L is treated as a small periodic perturbation. Consider eigenfunctions $|\gamma\rangle = |\alpha\rangle, |\beta\rangle$ of $H_0, H_0 |\gamma\rangle = \hbar \omega_{\gamma} |\gamma\rangle$. Time-dependent perturbation theory yields the transition rates [17]

$$W_{\beta\alpha}^{\pm}(\omega) = \frac{2\pi}{\hbar} |\langle \beta | H_L^{\pm} | \alpha \rangle|^2 \,\delta(\omega_{\beta\alpha}^{\pm} - \omega).$$
(1.17)

The absolute values squared of the transition matrix elements write

$$|\langle\beta|H_L^{\pm}|\alpha\rangle|^2 = \frac{E^* E e^2}{8 \, m^2 \omega^2} \, |\langle\beta|\pi^{\pm}|\alpha\rangle|^2, \tag{1.18}$$

where $|\langle \beta | \pi^{\pm} | \alpha \rangle|^2 \equiv \Pi_{\beta\alpha}^{\pm}$ are the absolute values squared of the electric-dipole matrix elements and the operators $\pi^{\pm} = \pi_x \pm i \pi_y$ are linear combinations of components of π . The radiation power absorbed by the solid is

$$P(\omega) = \hbar \omega \sum_{\alpha,\beta} W^{\pm}_{\beta\alpha}(\omega), \qquad (1.19)$$

the sum extending over all occupied states $|\alpha\rangle$ and all unoccupied states $|\beta\rangle$. Hence, according to Eq. (1.11) the absorptive parts of the tensor elements ε_{ij} write

$$\varepsilon_{2xx}(\omega) \propto \frac{1}{\omega^2} \sum_{\alpha,\beta} \left(\Pi_{\beta\alpha}^+ + \Pi_{\beta\alpha}^- \right) \, \delta(\omega_{\beta\alpha} - \omega),$$

$$\varepsilon_{1xy}(\omega) \propto \frac{1}{\omega^2} \sum_{\alpha,\beta} \left(\Pi_{\beta\alpha}^+ - \Pi_{\beta\alpha}^- \right) \, \delta(\omega_{\beta\alpha} - \omega).$$
(1.20)

Application of the dispersion relations, Eq. (1.12), provides the dispersive parts of ε_{ij} :

$$\varepsilon_{1xx}(\omega) \propto -\sum_{\alpha,\beta} \frac{\Pi_{\beta\alpha}^{+} + \Pi_{\beta\alpha}^{-}}{\omega_{\beta\alpha} (\omega_{\beta\alpha}^{2} - \omega^{2})},$$

$$\varepsilon_{2xy}(\omega) \propto \frac{1}{\omega} \sum_{\alpha,\beta} \frac{\Pi_{\beta\alpha}^{+} - \Pi_{\beta\alpha}^{-}}{\omega_{\beta\alpha}^{2} - \omega^{2}}.$$
(1.21)

Instead of the dielectric tensor ε the physically equivalent optical-conductivity tensor σ is frequently referred to. The elements transform as

$$\sigma_{ij}(\omega) = -i\,\varepsilon_0\,\omega\,\varepsilon(\omega) - \delta_{ij},\tag{1.22}$$

where ε_0 denotes the dielectric constant of vacuum and δ is the Kronecker symbol. The optical conductivity is restricted by the f-sum rule:

$$\int_0^\infty \sigma_{1xx}(\omega) \, d\omega = \frac{\pi n e^2}{2m} \tag{1.23}$$

with electron density n of the specimen, elementary charge e, and free-electron mass m. The partial spectral-weight integral W of the frequency range from ω_1 to ω_2 defined as

$$W = \int_{\omega_1}^{\omega_2} \sigma_{1xx}(\omega) \, d\omega \tag{1.24}$$

is thus proportional to the effective number of electrons excited by photons of respective energy. According to f-sum rule and charge conservation the spectral weight integral, evaluated from zero to infinity, is constant.

Equations (1.20) and (1.21) illustrate that magneto-optical effects ($\varepsilon_{xy} \neq 0$) occur if the terms substracted do not cancel. This requires a difference in absorption of LCP and RCP light, that may be evoked by an external magnetic field and (or) spin-orbit coupling. Bennet and Stern calculate the off-diagonal tensor elements ε_{xy} to first order in the external magnetic field [14]. In order to evaluate $\Pi_{\beta\alpha}^{\pm}$ they apply the effective-mass approximation. Including the spin-orbit interaction to first order results in a contribution proportional to the average value of spin, i.e. linear in the magnetisation M. In ferromagnets the spinorbit contribution dominates over the magnetic-field contribution by orders of magnitude [18]. Consequently, the direct influence of the external magnetic field is neglected in the