Chapter 1

Introduction

The electronic properties of ordinary metals can be described using the free electron model, where the electrons in the material are thought to behave like independent particles with negligible interactions. The free-electron model can be modified with perturbation calculations, where additional interactions are used to alter the solutions of the free-electron picture to describe a larger number of materials. If the particle-particle interactions inside the material are too strong, the free-electron picture extended with perturbations fails to describe those systems. Such a material class is given by manganites, a subclass of the so called strongly correlated metal oxides.

Doped or mixed valence manganites are solids typically belonging to one of two structure families. One is called Ruddlesden-Popper series $(\mathrm{A,B})_{1+\mathrm{n}}\mathrm{Mn}_{\mathrm{n}}\mathrm{O}_{3\mathrm{n}+1}$, whereas the other is called perovskite manganites $(\mathrm{A,B})\mathrm{MnO}_3$. Normally, for A a trivalent element of the rare earth and for B a divalent alkali metal is chosen. Correspondingly, the oxidation state of the manganese ions is 3+ and 4+, respectively. In the case of a trivalent manganese ion, the important Jahn-Teller effect lowers the potential energy of the manganese ion by displacing the neighbor oxygens resulting in an orthorhombic lattice distortion. Thus, the occupied $3d_{3z^3-r^2}$ orbital has a preferred orientation due to the neighbor oxygens and, correspondingly, the electron is more localized.

Mixed valence manganites show a strong correlation between structural, electronic, orbital and spin degrees of freedom leading to a variety of magnetic and electronic properties. Mixed valence manganese oxides show for instance, a temperature dependent development of orbital ordering and charge ordered stripes at a commensurate ratio of trivalent and tetravalent manganese ions. Furthermore, mixed valence manganites like $\mathrm{La}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ feature the colossal magnetoresistance (CMR) effect close to the phase transition from the paramagnetic insulating to the ferromagnetic metallic state. These properties are of course sensitive to doping, either by changing cations with different valence, size, or magnetic moments, or by tuning the oxygen content. The strong correlation between the different degrees of freedom is reflected by a complex (x, B, T)-phase diagram exhibiting different ordering, structural and magnetic phases depending on the Hund's rule coupling between spins as well as the Jahn-Teller distortion.

This thesis is devoted to experimental studies on perovskite and naturally layered perovskite manganites using inelastic light scattering and spectroscopic ellipsometry. Raman spectroscopy is able to probe simultaneously vibrational, electronic and magnetic lattice excitations in a solid. It is also very sensitive to the local symmetry of the crystal lattice. A change in the lattice structure, which lowers the symmetry of the unit cell results in the activation of additional modes in the corresponding Raman spectrum.

Ellipsometry is a technique that measures the change in polarization of light upon reflection on a boundary between two media with a mismatch in the complex refractive index. Ellipsometry is a non-destructive and self-normalizing technique with high accuracy using very low intensities resulting in negligible influence on the sample. Another advantage of this technology is that the optical properties for a bulk system like the real part ϵ_1 and the imaginary part ϵ_2 of the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ can be determined simultaneously without using the Kramers-Kronig relations.

The first chapters introduce the spectroscopic ellipsometry technique (chapter 2) and Raman scattering (chapter 3). In the first section (4.1) of chapter 4, the physical properties and the structure of the manganites are introduced. In the following sections (4.2 and 4.3) the doped perovskite compound $La_{1-x}Ca_xMnO_3$ (LCMO) and the naturally layered $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (LSM327) are presented with a special focus on charge and orbital ordering phenomena. Afterwards, a closer look is taken on the insulating doped perovskite compound $Sr_{1-x}Ca_xMnO_3$ (SCMO) in section 4.4.

Chapter 2

Ellipsometry

Ellipsometry is a very powerful technique that measures the change in polarization of light upon reflection on a boundary between two media with a mismatch in the complex refractive index [8]. The change in polarization is due to the boundary conditions imposed by the Maxwell equations. Ellipsometry is a non-destructive and self-normalizing technique with high accuracy using very low intensities resulting in negligible influence on the sample. Another advantage of this technology is that the optical properties for a bulk system like the real part ϵ_1 and the imaginary part ϵ_2 of the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ or the refraction index n and the absorption coefficient k can be determined simultaneously without using the Kramers-Kronig relations [8].

2.1 Theory of Ellipsometry

2.1.1 Spectroscopic Ellipsometry Setup

A basic setup for a photometric ellipsometer is shown in Fig. 2.1. It consists of a light source, two linear polarizers and a photo detector.

Well collimated light from the source is incident on the polarizer defining the electric field vector $\vec{E}$ of the beam by an angle α_1 with respect to the plane of incidence. After passing the polarizer the beam impinges on the sample surface under an angle ϕ_0. The polarization of the beam is changed due to the refraction index mismatch of the sample against its surrounding environment, e.g. air. The directly reflected beam is analyzed by a second polarizer (analyzer) and hits the photo detector, which detects the dependence of the resulting intensity on the analyzer angle α_2. From the ratio of the intensities for different analyzer angles α_2 the so called ellipsometric parameters Ψ and Δ are calculated. These ellipsometric parameters are connected by the fundamental equation of ellipsometry to the complex reflection coefficients [8]:

$$\rho = \tan \Psi e^{i\Delta} = \frac{R_p}{R_s} \quad . \tag{2.1}$$

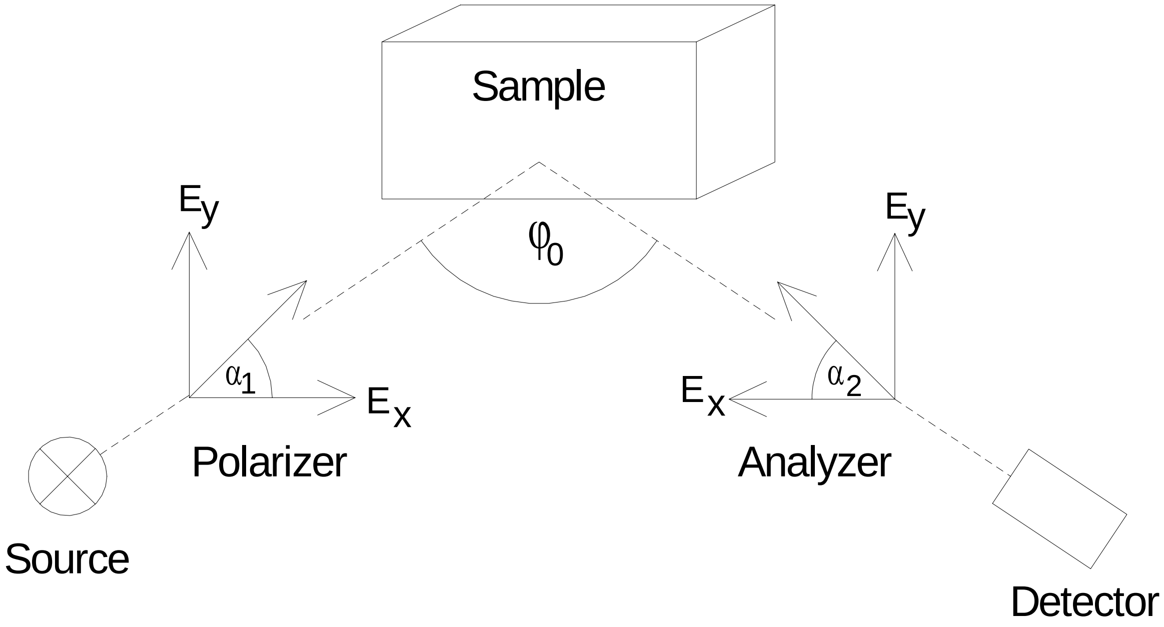

Figure 2.1: Basic setup for photometric ellipsometry

Preceding R_p and R_s are the complex reflection coefficients for the parallel and perpendicular component of the light beam with respect to the plane of incidence. For a bulk system these complex reflection coefficients are the Fresnel coefficients. The complex reflection coefficients $R_{p,s}$ can be written as a product of a phase and amplitude term

$$R_p = |r_p|\, e^{i\delta_p} \tag{2.2}$$

$$R_s = |r_s|\, e^{i\delta_s} \quad . \tag{2.3}$$

It can be easily seen, that the ellipsometric parameters are related to the relative change of the phase and amplitude by

$$\tan\Psi = \frac{|R_p|}{|R_s|} \tag{2.4}$$

$$\Delta = \delta_p - \delta_s \quad . \tag{2.5}$$

When considering the reflection of light at a surface, the theory of electrodynamics is used with the Maxwell equations and the associated material relations [33]

$$\begin{aligned}
&(2.6) \quad & \nabla \times \vec{H} &= \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{j} \quad , \qquad & (2.10) \quad & \vec{D} &= \vec{E} + 4\pi\vec{P} \\
&(2.7) \quad & \nabla \times \vec{E} &= \frac{1}{c}\frac{\partial \vec{B}}{\partial t} \quad , & (2.11) \quad & \vec{H} &= \vec{B} - 4\pi\vec{M} \quad , \\
&(2.8) \quad & \nabla \vec{D} &= 4\pi\rho \quad , & (2.12) \quad & \vec{j} &= \sigma\vec{E} \quad . \\
&(2.9) \quad & \nabla \vec{B} &= 0 \quad \text{with} & & &
\end{aligned}$$

Here, $\vec{E}$ is the electrical field vector, $\vec{D}$ is the electric displacement, $\vec{B}$ is the magnetic field (also known as magnetic induction), $\vec{H}$ is the magnetic auxiliary field, $\vec{P}$ is the dipole moment and $\vec{M}$ is the magnetic dipole per unit volume, $\vec{j}$ is the current density, c is the speed of light, σ is called as conductivity, and ρ is the charge density. For a linear media the definitions for $\vec{D}$ and $\vec{H}$ can be written as

$$\vec{D} = \vec{E} + 4\pi\vec{P} \implies \vec{D} = \epsilon\vec{E} \quad \text{and} \tag{2.13}$$

$$\vec{H} = \vec{B} - 4\pi\vec{M} \implies \vec{H} = \frac{1}{\mu}\vec{B} \quad , \tag{2.14}$$

whereas ϵ is the electrical permittivity and μ the magnetic permeability. In the case of non magnetic materials the magnetic permeability $\mu = 1$. It is important to note that this theory describes only classical macroscopic parameters.

2.1.2 Polarization Ellipsoid

The term polarization refers to the time-dependence of the electric field vector at a fixed point in space. In the following it is assumed that the electromagnetic wave under consideration is a monochromatic plane wave with a direction $\vec{k}$ parallel to the z-axis of the coordinate system. Using the fact that a monochromatic plane wave can be written as the superposition of two linear polarized and to each other orthogonally waves

$$\vec{E}(\vec{r},t) = \begin{bmatrix} E_x(\vec{r},t) \\ E_y(\vec{r},t) \end{bmatrix} = \begin{bmatrix} |E_x| e^{-i(\vec{k}\vec{r}-\omega t-\delta_x)} \\ |E_y| e^{-i(\vec{k}\vec{r}-\omega t-\delta_y)} \end{bmatrix} \quad , \tag{2.15}$$

it can be shown that in the most general case the end point of the electric field vector $\vec{E}$ traces the outline of an ellipse. In this case the wave is elliptically polarized.

Elliptic polarization requires five parameters for complete determination of the time dependence of the electric field vector [8].The parameters, shown in figure 2.2, are the azimuth angle Θ, the ellipticity e, the handleness, the amplitude A and the absolute phase.

The azimuth angle Θ determines the orientation of the ellipse with respect to the xy-coordinate system as shown in Fig. 2.2. The ellipticity describes the appearance of the ellipse and is given by the ratio $e = b/a = \tan\gamma$, whereas a is the length of the major

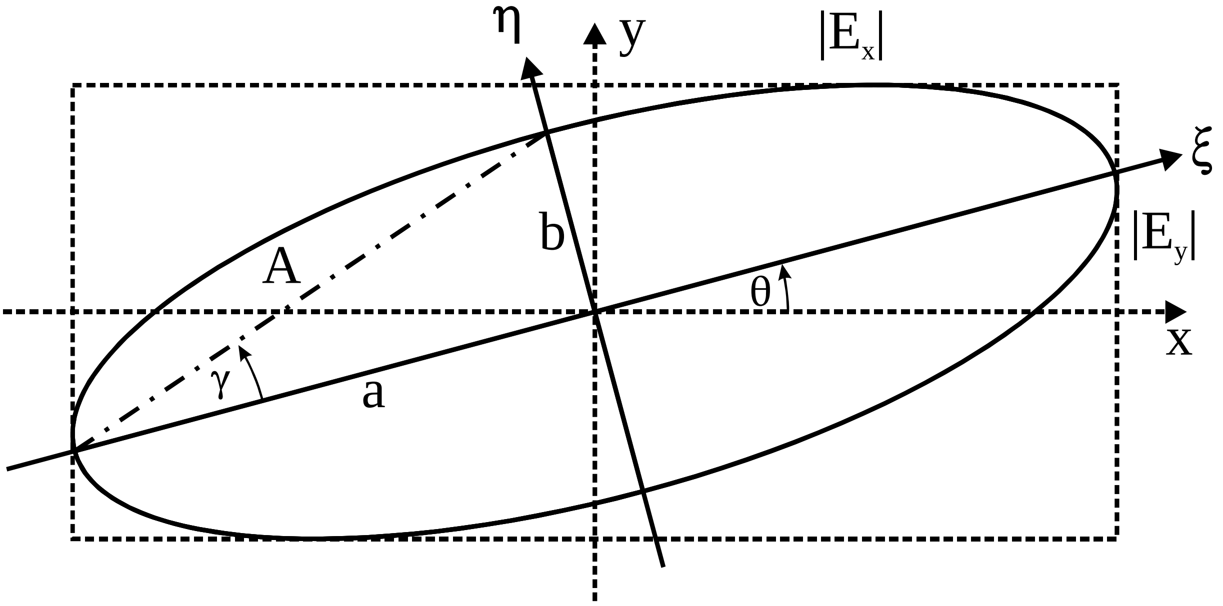

Figure 2.2: Parameters determining the polarization ellipse: Azimuth angle θ, amplitude A and the ellipticity $e = \tan\gamma$.

axis and b the length of the minor axis of the polarization ellipse. It can be seen that the special cases of linear and circular polarized light can be obtained from the general definition of elliptic polarization by setting the ellipticity to 0 and 1, respectively. The chirality is defined with respect to the viewer looking against the direction of propagation given by $\vec{k}$. Usually it is included into the ellipticity by determining its sign. The positive sign refers to clockwise tracing of the outline of the ellipse, while the negative sign refers to counterclockwise tracing. Hence, the ellipticity e is confined to the range

$$-1 \leq e \leq 1 \quad . \tag{2.16}$$

The amplitude $A = a^2 + b^2$ determines the size of the polarization ellipse and is usually also used to define the intensity of the wave. The last parameter, the absolute phase, is the position of the electric field vector with respect to a special moment in time (normally for t = 0 s).

2.1.3 Jones Vector Formalism

The Jones vector formalism is a useful representation for the behavior of an electromagnetic wave as it propagates through optical components [8]. The underlying principle of the Jones vector formalism is the representation of polarization by the superposition of two mathematically orthogonal basis states. A good choice for such basic polarization states are the two linear orthogonal polarizations as described in 2.1.2. In ellipsometry only the polarization properties are of interest. Therefore information about the absolute time dependence may be suppressed without loss of information. In this case the complete representation can be reduced to

$$\vec{E} = \begin{bmatrix} E_x \\ E_y \end{bmatrix} \quad \text{with} \quad E_x = |E_x| e^{i\delta_x} \quad \text{and} \quad E_y = |E_y| e^{i\delta_y} \quad . \tag{2.17}$$

The two components are complex numbers, also called phasors. They describe the amplitude of the two basis vectors and their phase difference. The superposition of these two components restores the polarization ellipse. In the Jones formalism, optical components are described by 2×2 matrices. For example, the effect of a linear polarizer with an azimuth angle α respective to the xy-coordinate system on a linearly polarized wave with Jones vector $\vec{E}_i$ is analogous to pre multiplying this Jones vector by a matrix given by

$$\vec{E}_o = \begin{bmatrix} \cos\alpha & 0 \\ 0 & \sin\alpha \end{bmatrix} \vec{E}_i \quad . \tag{2.18}$$

Starting with an input Jones vector $\vec{E}_i$, the resulting output Jones vector $\vec{E}_o$ after a sequence of optical elements can be obtained by subsequently multiplying the input Jones vector $\vec{E}_i$ with the Jones matrices representing the different optical elements.

2.1.4 Stokes Vector Formalism

An alternative way to represent the polarization of an electromagnetic wave is the so called Stokes vector formalism [15, 80]. The components of this four dimensional vector $\vec{S} = \{S_0, S_1, S_2, S_3\}$ are defined as

$$S_0 = |E_x|^2 + |E_y|^2 \tag{2.19}$$

$$S_1 = |E_x|^2 - |E_y|^2 \tag{2.20}$$

$$S_2 = 2|E_x||E_y|\cos(\delta_y - \delta_x) = 2|E_x||E_y|\cos\Delta \tag{2.21}$$

$$S_3 = 2|E_x||E_y|\sin(\delta_y - \delta_x) = 2|E_x||E_y|\sin\Delta \quad . \tag{2.22}$$

The components of the Stokes vector S_i have all dimensions of intensity. It is evident that S_0 gives the total intensity of the light wave and S_1 gives the difference between the intensities of the x and y components. S_2 represents the preference of the wave to either the $+\frac{\pi}{4}$ or the $-\frac{\pi}{4}$ linearly polarized component and S_3 represents the preference of the wave to either the right-handed or to the left-handed circularly polarized component [8]. The Stokes parameters of a totally polarized wave satisfy the condition

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 \quad , \tag{2.23}$$