Summary

An optical spectrometer may be a tool unfamiliar to an outsider of the optics community. It can be regarded as a natural evolution of the way we perceive the surrounding environment. Light coming from the sun is reflected or transmitted by objects. The human eye, by measuring this reflected or transmitted light, gains some information about the objects themselves, such as their color, brightness, and shape. Using the same principles, an optical spectrometer is designed to gain even more information. It has a source of light used to send light on some objects, and a hi-tech detector to measure the transmitted or reflected light.

After the material has been measured, a relation needs to be established between its optical response and its main physical properties. In this thesis we consider the case of solid state materials. These are materials where the atoms are in close proximity to each other, and arranged in repetitive patterns on macroscopic distances, to make a compact structures (a good example is NaCl, kitchen salt). To establish the above mentioned relation the following procedure is followed. First, the optical response (transmission, reflectivity, absorption, etc.) at each frequency in the incident light is measured. The result is quantified in terms of the so called dielectric constant of the bulk \( \varepsilon(\omega) \). In a second step, this function is related to the main physical properties of the measured solid state material, using the knowledge of its particular structure, determined before by different type of measurements, such as for instance X-ray diffraction. Today, optical spectroscopy has become one of the most important standard tools for investigating novel condensed matter materials.

Solid state materials containing transition and/or rare-earth metal oxides exhibit a large variety of physical properties, which are often very sensitive to small changes of parameters like chemical composition, temperature and pressure. Their conducting properties range from highly insulating to metallic and even superconducting. Also, their magnetic properties are extremely diverse, where in materials which show magnetic ordering the type of magnetic ordering may vary from ferro- or ferri- to antiferromagnetic. One other interesting aspect of the metal oxides is that some of the, in particular, transi-
tion metal oxides are found to be low dimensional in their physical properties. The high sensitivity of the physical properties to small changes is for instance found in the metal to insulator transition observed in $\beta$-$\text{Na}_{0.33}\text{V}_2\text{O}_5$. This transition rapidly disappears upon changing the sodium content by as little as 5%. Another example of sensitivity to chemical composition is the presence of a metal-insulator transition in nearly stoichiometric EuO thin films, but not in EuO with an exact stoichiometry. The wide range of properties in transition metal oxides compounds is primarily related to the localized nature of the $d$ electrons.

The aim of the work presented in this thesis is to investigate the low energy excitation spectra and the (induced) phase transitions in transition metal oxides:

Chapter 2 of this thesis concentrates on a four point resistivity investigation of the vanadium bronze $\beta$-$\text{Na}_{0.33}\text{V}_2\text{O}_5$. We have conducted the first detailed field dependent measurements of the non-linear conductivity of this vanadium bronze in the temperature range 30 K - 300 K. First, clear evidence for a metal to insulator transition is found at $T_{MI} = 136$ K. Below $T_{MI}$, in the charge ordered phase, the low field data has shown that two type of excitations contribute to the non-linear transport. While the first contribution arises from motion of the charge density modulation, with a quasiparticle gap of 700 - 800 K, the second contribution results from an excitation of which origin is not presently clear, with a quasiparticle gap about 500 K. This second excitation might happen within the domain walls between ordered charge density modulation domains or can be a bound state of collective charge density modulation excitation, like the phason. Two competing models reasonably describe the low field transport, although both have deviations from the data below 50 K: a thermally activated field transport and the variable range hopping (VRH) model. The field dependent data is very similar to the transport in known charge density modulation materials, like $\text{K}_{0.3}\text{MoO}_3$, and clearly shows the charge density modulation nature of the insulating phase. In order to describe the measured data, we introduced a new phenomenological domain model, which is believed to be applicable in other charge ordered materials as well. In materials with low carrier density like $\beta$-$\text{Na}_{0.33}\text{V}_2\text{O}_5$ and $\text{K}_{0.3}\text{MoO}_3$, we believe that most of the transport properties, including the observed decrease of threshold fields upon raising temperature, can be understood in terms of enhanced screening of pinning centers by thermally excited charge carriers.

A particular case of optical spectroscopy is Terahertz Time-Domain Spectroscopy (THz TDS). This is in fact a relatively new spectroscopic tool in which the light source has a frequency in the order of $10^{12}$ Hz. In Chapter 3 we are revealing the physical principles used by a terahertz spectrometer. Then, we provide a detailed characterization of the spectrometer. An investigation about how the measured dynamics time scale can influence the way material parameters are extracted in an optical-pump terahertz-probe experiment, has been performed. When the measured dynamics are developing on a time
scale which is comparable or smaller than the THz pulse duration, a two dimensional
type of analysis needs to be employed. This analysis takes into account the fact that a
THz probe pulse 'feels' a different dynamic effect with the beginning of the pulse than
with the end of the pulse.

Chapter 4 reveals the first optical-pump terahertz-probe investigation presented in
this thesis. A detailed pump-probe investigation of the direct band-gap semiconductor
Cu$_2$O has been performed. The most intriguing experimental observation is a sharp rise
in sample absorption upon excitation with 800 nm light, at 18 K. Following the excita-
tion, two phenomena seem to take place: the creation of free carries via a two-photon excitation process and the creation of a second type of particle which is viewed as a reso-
nance absorption peak in the far-infrared region. The main difficulty is to understand the
origin of the induced absorption peak. In a few picoseconds after the excitation, the res-
oneance peak intensity is decreasing and shifts towards lower energies. The same type of
peak behavior (intensity decrease and shift towards lower frequencies) is displayed also
upon decreasing the pump excitation energy. Peak strength is increasing linearly with
pump pulse energy until 0.6 mJ/cm$^2$, displaying a saturation above this power density
value. Sample excitation with different wavelengths has been performed, the only one
who resulted in absorption rise being the excitation with 800 nm light. Repeating the
same type of excitation on two Cu$_2$O samples with different concentrations of impurity
indicated that the induced absorption peak might be V$_{O}^+$ impurity related. We have used
two types of mathematical descriptions which can describe equally well the observed
phenomena. The first one, "Drude+Lorentz", describes the free carries evolution with
a Drude response and the resonance absorption peak with a Lorentz oscillator response.
The second one, "Drude+Droplet", takes into account the possibility that the absorption
peak is the response of a "droplet", resulting from the concentration of induced charge
carriers around impurity centers. We also discuss different physical phenomena which
might lead to the observed resonance absorption peak. It cannot be the response of an
electron-hole droplet because with our setup we can induce a maximum exciton den-
sity of $10^{15}$ cm$^{-3}$ in Cu$_2$O while the electron-hole droplet phase is expected to exist for
densities above $10^{21}$ cm$^{-3}$ only. Another possibility would be that the resonance may
be the response of biexcitons induced by the optical excitation. Still, resonant excita-
tion experiments have shown that this phenomena does not have an excitonic origin. We
might also be directly exciting a weakly bound impurity state, which contains a resonant transition in the THz range. For example, the incident photons might excite electrons
to the V$_{O}^+$ impurity state, and create dipoles in the system, dipoles which can interact
through dipole-dipole interaction. For this possibility a number of at least $10^{18}$ cm$^{-3}$
oxygen vacancies are needed, which is higher than our sample vacancy concentration,$10^{15}$ cm$^{-3}$. 
At the moment there is no straightforward explanation for the observed effects and their time dynamics. Therefore, additional experiments are required to prove or disprove the discussed possibilities or to propose new ones.

In chapter 5 a terahertz time-domain spectroscopy and optical-pump terahertz-probe investigation of a EuO thin film is presented. One of the goals of these experiments was to find whether the EuO thin film sample undergoes a semiconductor-to-metal transition, i.e. whether the sample is stoichiometric. Our data have shown no indication of such phase transition, which indicates that the sample is nearly stoichiometric. During the optical-pump terahertz-probe investigation, we manage to optically induce a metallic phase in the EuO thin film. The life time of the metallic phase below 70 K is linearly decreasing with increasing temperature, being in the order of a few hundred picoseconds. Above 70 K, we are inducing the same excitation, but the recovery time (via phonon assisted electron-hole pair decay) becomes very fast, due to the presence of a large number of phonons. In other words, above 70 K, the metallic phase lifetime is very small, outside our experimental time resolution. Future experiments will have to prove the ferromagnetic nature of the metallic phase, as is the case for the thermal semi-conductor to metal transition in off-stoichiometric films.