Introduction

Why Charge-Carrier Dynamics Are so Interesting

Besides the fundamental significance, knowledge of the dynamics of charge carriers in matter is extremely important for technological applications. The manner in which electrons relax their energy and their average velocity by interaction with their surroundings crucially influences the performance of, for instance, electronic circuits [Int05], solar cells [Hen05], and insulating gases [Chr00].

Electronic devices, for example, have to become smaller, faster, and cheaper. Moore's law roughly predicts that the number of transistors on an integrated circuit chip doubles every 18 months. At present, this development has led to silicon-based field-effect transistors with linear dimensions of about 50 nm [Int05]. Further miniaturization requires a higher conductivity to reduce the size of the conducting channels and a higher electron density to keep the screening length of the gate electric fields below the transistor dimensions [Rot04]. In addition, a smaller size implies a lower capacitance and thus permits higher clock frequencies. Possible alternatives to traditional semiconductors like Si and Ge include carbon nanotubes [Rot04] and thin graphite films [Nov04] as base materials for smaller and faster electronic devices.

In view of their technological potential in future electronics and due to their close relationship to each other, the charge-carrier dynamics in carbon nanotubes and graphite are investigated in this work by time-resolved THz spectroscopy: The sample is excited by an ultrashort visible laser pulse and, after some temporal delay, probed by a THz pulse which is particularly sensitive to the charge carriers as detailed below.

Charge-carrier dynamics not only play a major role in solids; they are also important in gases, for example in insulating gases inside high-voltage equipment. Here, highly mobile electrons have to be quenched very efficiently before they start to generate sparks and short-circuits by avalanche ionization of gas molecules. SF_6 is used as an insulating gas in such facilities because of its large cross section for electron capture [Chr00].

In this work, THz pulses are used to probe the decay and the velocity relaxation of quasifree electrons in optically ionized gases such as O_2, Ar, and SF_6.

Why THz Radiation Is so Sensitive to Charge Carriers

The electronic conductivity of a material is dominated by the free and weakly bound electrons, that is, by charge carriers with low excitation energies. Therefore, THz radiation is particularly sensitive to these carriers because of its low photon energy $\hbar\omega$ of, for instance, 4.1 meV for a frequency of $\omega/2\pi = 1\,\mathrm{THz}$. In contrast, the response to visible light with photon energies of $\sim 1\,\mathrm{eV}$ is dominated by electronic transitions of higher energy. Thus, visible light mainly probes carriers which do *not* contribute to the transport properties in the steady state.

The sensitivity of THz radiation to low-energy excitations is illustrated by the following examples:

- In a single-particle picture, the conductivity of a solid is due to the "free" electrons and holes near the Fermi energy. THz radiation with its low photon energy probes electronic transitions close to this range, whereas visible light also accesses electrons much further below the Fermi edge, which are usually "frozen" [Bea02].
- Bound electron-hole pairs (excitons) in semiconductors like GaAs have binding energies from about 10 to 100 meV [Mad78]. THz radiation can probe the *internal* excitations of excitons and thus quantify their population [Hub05a]. Due to the discrete nature of the lower-lying excitonic states THz radiation can distinguish between the response of excitons and free charge carriers.

Other interesting excitations also lie in the THz-range, including molecular vibrations, phonons, and magnons.

THz Spectroscopy

Despite its importance, THz radiation was not easily available as a spectroscopic probe until 15 years ago due to a lack of powerful THz sources and suitable detectors [Bea02]. As a consequence of the low THz power, the probing THz radiation arriving at the He-cooled bolometer is completely overwhelmed by the black-body radiation of the surrounding. Note that at a temperature of 300 K and according to Wien's law, the black-body radiation has its intensity maximum at 17 THz.

Alternative radiation sources to bridge the so-called "THz gap" in the electromagnetic spectrum are CO_2 and other molecule-based lasers which, however, lack frequency tunability [Bea02]. The quantum-cascade laser is still under development and does not produce short THz *pulses* which are required for a good temporal resolution in pump-probe experiments [Lab05]. Free-electron lasers (FEL) like FELBE located near Dresden (Germany) produce THz pulses with picosecond duration, but such devices are large and expensive. Moreover, the synchronization with pump pulses from a femtosecond laser is complicated due to a temporal jitter between the FEL and the visible femtosecond pulses [Ros05].

Fortunately, the availability of femtosecond laser pulses has led to the development of so-called THz time-domain spectroscopy or, shorter, THz spectroscopy (TS) which offers the following key features:

- Femtosecond laser pulses are employed to generate *short* THz pulses which extend over only a few oscillation cycles of the electric field. As a consequence, these pulses have an extremely *large bandwidth* comparable to the pulse center frequency. For example, the THz pulses used in this work are generated by 10-fs laser pulses, extend from about 10 to 30 THz, and have a duration as short as 100 fs. More "traditional" THz spectroscopy operates at around 1 THz with pulses of about 1 ps in duration.
- Femtosecond laser pulses are used as an ultrashort temporal gate to detect the *electric field* of the THz pulses rather than spectral intensities without phase information.

These features lead to important applications:

- The detection of the electric field enables the measurement of the complex dielectric function of a sample. Conventional spectroscopy detects only the spectral intensity and has to make problematic use of the Kramers-Kronig relations in order to extract the dielectric function. The knowledge of the dielectric function is, for example, crucial for the identification of the optical gap in the THz response of superconducting MgB_2 [Kai02].
- Moreover, the THz field *emitted* by an optically excited sample can be measured. Such THz emission spectroscopy has given important information on the acceleration of electrons in high electric fields [Lei99b] and the charge transfer in optically excited molecules [Bea02].
- Short THz pulses are useful probes in pump-probe experiments where the sample is excited by a visible pump pulse and probed by a temporally delayed THz pulse. By means of this time-resolved THz spectroscopy (TRTS), the temporal evolution of the dielectric function of the excited sample can be monitored. TRTS has been successfully employed to obtain new and important information on the charge dynamics in semiconductors [Hub01], insulators [Sha03], and nonpolar liquids [Kno01].

This Thesis

In this work, THz spectroscopy is the experimental method of choice to investigate the charge-carrier dynamics in optically excited graphite and carbon nanotubes, and in several optically ionized gases. This thesis will deal with the following issues:

- Graphite is the prototype of a semimetal and exhibits a very small Fermi surface compared to metals like Al. As a consequence, electrons can only be scattered by

phonons from a quite restricted subset of wavevectors. Does this imply a slow energy transfer from the optically excited electrons to the graphite lattice? Or is this restriction compensated for by the high quantum energies of the optical phonons? How do these phonons influence the Drude collision rate of the electrons?

- Carbon nanotubes are hollow cylinders made of carbon atoms. Depending on their geometrical structure, carbon nanotubes are purely metallic, or exhibit an electronic energy gap around 1 eV or 20 meV. Does the optical excitation generate excitons or free charge carriers in the tubes with the large energy gaps? How do the excited electrons relax in the tubes with the small energy gaps? Can THz radiation detect the spatial localization of charge carriers in the nanotubes?

- Gases become conducting upon optical ionization due to the generation of quasifree electrons. How "hot" are these electrons? How are they captured in a monatomic gas like Ar and a molecular gas like O_2? Does the electron scavenger SF_6 really accelerate the electron decay? Which mechanisms dominate the relaxation of an electronic current in these plasmas?

In order to obtain answers to these questions, certain experimental and analytical efforts were necessary. These include the construction of two THz spectrometers driven by either a femtosecond oscillator or by an amplified femtosecond laser system. The latter was imperative to optically ionize gases and probe the resulting plasma with THz pulses. Data analysis included a thorough description of the THz-wave propagation through the excited sample. Finally, in order to achieve a microscopic understanding of several experimental results, modeling based on linear-response theory and the 2-temperature model was required.