crystal growth and magnetostriction of high-temperature superconductors
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1 Introduction

1.1 Discovery of superconductivity

Superconductivity has proven to be an interesting and rich topic in solid state physics. It has inspired many researchers for a large part of the twentieth century. As a general introduction to this thesis a brief review of the history of superconductivity is presented (Lindenfeld [1996]).

Once Kamerlingh Onnes [1911] succeeded in liquefying helium, he set about measuring the electrical conduction of pure metals at low temperature. He discovered that the dc resistivity of mercury suddenly drops to zero at 4.2 K, the boiling point of liquid helium. This new phenomenon was first named supraconductivity and is nowadays known as superconductivity. A year later Kamerlingh Onnes discovered that, when a superconductor is placed in a strong magnetic field or when a large electrical current passes through the superconductor, the non-superconducting state is restored. In 1933, Meissner and Ochsenfeld [1933] found that below the superconducting transition temperature ($T_c$) the magnetic flux is always expelled from the interior of the superconductor. It makes no difference whether the sample is cooled in a magnetic field or is cooled first and then placed in a magnetic field. This expelling of the magnetic flux is called the Meissner effect and is the essential difference between a perfect conductor and a superconductor.

A significant step forward in describing the superconducting state was made in 1934 when London and London [1934] proposed a simple two-fluid model which yielded an explanation for the Meissner effect and a prediction of a characteristic length ($\lambda$) for the penetration of the magnetic flux in the superconductor. In 1950 Ginzburg and Landau [1950] proposed a phenomenological theory of superconductivity, describing most of the properties of superconductors. In the same year Maxwell [1950] and Reynolds et al. [1950] observed that $T_c$ varies with the isotopic mass. From this dependence, the involvement of lattice vibrations and hence electron-phonon interaction was concluded.

The understanding of the behaviour of superconductors in an external magnetic field...
was enhanced substantially by Abrikosov [1957], who discovered in 1957 the existence of two types of superconducting materials, named type-I and type-II superconductors. In the case of type-I, superconductors the magnetic field is completely expelled from the interior. In the case of type-II, superconductors the field is expelled at low fields, but partly penetrates the superconductor in higher fields. The formation of a so-called mixed state allows magnetic flux to penetrate the superconductor in the form of flux lines.

A comprehensive understanding of superconductivity came in 1957, when Bardeen, Cooper and Schrieffer [1957] published their microscopic theory of superconductivity, later named the BCS theory. Electrons repel each other through the Coulomb force. In the case of a superconductor a net attraction between two electrons, mediated by the lattice vibrations, leads to the formation of Cooper pairs. A Cooper pair consists of two electrons with opposite momentum and spin. All Cooper pairs move in a single coherent motion, so local perturbations cannot scatter an individual pair. Once this collective state of coherent electrons is set in motion, it flows without dissipation of energy.

In the sixties and seventies applications were developed, such as magnet coils and sensitive measuring equipment in the form of SQUID's (Superconducting Quantum Interference Device). Because their functioning is restricted to low temperatures, these devices could only be used in specialised laboratories.

Some textbooks, written in the seventies, claimed that superconductivity was a finished subject and no new developments were to be expected. The maximum value of $T_c$, calculated within the BCS theory, did not exceed 25 K. Consequently, there was great excitement when in 1986 Bednorz and Müller [1986] found superconductivity at 30 K in a compound of lanthanum, barium, copper and oxygen. A new group of materials with a $T_c$ value higher than expected from BCS-theory was discovered. This important discovery opened up a new area in the history of superconductivity, high-temperature superconductivity.

1.2 High-temperature superconductivity

After the discovery of high-temperature superconductivity many researchers started (or restarted) to work in the field of superconductivity. In February, 1987 Wu et al. [1987] discovered that the compound YBa$_2$Cu$_3$O$_7$ exhibits a $T_c$ value of 92 K. With this discovery, superconductivity could be reached in a simple and cheap way, i.e. by using liquid nitrogen as cryogenic fluid. The high superconducting transition temperatures make this new class of superconductors promising for applications. However, detailed studies showed that the crystallographic structure of these materials is rather complex. It exhibits a large anisotropy. Copper-oxygen layers and rare-earth-oxygen layers are stacked. The superconducting properties are largely anisotropic. Furthermore, the materials are brittle
and, consequently, difficult to process. For these reasons, applications of high-temperature superconductors, for instance in the form of a high-temperature SQUID, are difficult to realise. Nevertheless, progress is being made with the application of high-temperature superconductors. Recently a demonstration project started with power cables in a utility network (Garwin [1998]).

Besides the great effort in the search for new materials and applications, many experiments were performed aiming at understanding the basic properties of these high-temperature superconductors. Due to their complex, anisotropic structure, the need for single-crystalline samples to carry out this study was clear from the very beginning. However, the complex structure made it also difficult to grow single-crystalline material. The preparation and characterization of high-temperature superconductors became, just as the search for new materials, a large and important discipline within the research on high-temperature superconductors. Two main streams for growing single-crystalline materials can be distinguished. One approach focuses on single-crystalline samples in the form of thin films, while the other one aims at preparing bulk single crystals. Both kinds of approaches have advantages and disadvantages. The single-crystalline materials in the form of thin films can be made precisely, by building the crystal layer by layer. In this way, one can obtain high-quality well-defined films. An important motive for making thin films of high-temperature superconductors is the link with possible applications in chip technology. Bulk single crystals offer different advantages such as permitting other measuring techniques, like neutron diffraction. At present, crystals in both forms are available due to well-developed crystal-growth techniques. Most fundamental studies on high-temperature superconductors are performed on either thin films or bulk single crystals.

The BCS-theory proved not to be valid for the high-temperature superconductors and new theories had to be developed. The phenomenological theories remain valid, but lack in explaining the fundamental features. At present, still no satisfactory microscopic theory is available. The most important aspect of the high-temperature superconductors with respect to applications is the pinning of flux lines. At passing an electrical current through a type-II superconductor, a Lorentz force acts on the flux lines, which causes them to move in the absence of pinning. Movement of the flux lines causes dissipation of energy and, therefore, disappearance of the zero-resistivity state. A large pinning force allows large electrical currents to pass through the sample without dissipation of energy. Many experiments are being performed to study these pinning phenomena and to improve the flux pinning.

The discovery of High-Temperature Superconductivity (HTC) renewed the interest in Low-Temperature Superconductivity (LTC) or Low-Transition-Temperature (LTT) Superconductors. The LTC superconductors are often used as reference materials for studies on HTC superconductors. Several interesting physical properties of these materials like the peak effect and the de Haas van Alphen oscillations in the superconducting state were rediscovered and are being further investigated.
1.3 Outline of this thesis

The work presented in this thesis is a study of the growth and characterization of bulk single crystals of selected high-temperature superconductors. In addition a collection of physical properties of the prepared single-crystalline samples is presented. In order to better understand the HTC compounds, an extensive study of the thermodynamic properties of one of the LTC compounds is reported.

In the first part of this thesis, some important features of the theory of superconductivity are summarized. This summary is followed by a calculation of the magnetostriction of a superconductor, following the Bean model. Next, the equipment and the methods used for growing the single-crystalline samples, for characterization and shaping these samples and for measuring the physical properties are described. It turns out that the results of experiments performed on high-temperature superconductors can be extremely dependent on the experimental conditions. Therefore, the description of the measuring techniques is extensive where needed.

In the second part, the growth of single-crystalline \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) by means of the Travelling Solvent Floating Zone (TSFZ) method is described. The complex properties of the high-temperature superconductors create a large demand for single-crystalline samples. However, these properties also make the crystal growth process a complex and time consuming task. The grown crystals have been used by several research groups and were used for several measurements described in this thesis. An extensive characterization of the single-crystalline materials is reported as well.

The third and last part describes some of the physical properties of superconducting single crystals of both LTC and HTC superconductors. Special interest is given to magnetostriction measurements on the superconducting compounds. One LTC compound and two HTC compounds were studied extensively.

A thermodynamic study on the LTC compound \( \text{V}_3\text{Si} \) is reported. The original aim of this work was to have magnetostriction measurements on a reference material, which could be used to compare with the magnetostriction results on HTC materials. In addition, several other physical properties were measured, including an effort to observe dHvA oscillations in the superconducting state. The important aspect of this work on \( \text{V}_3\text{Si} \) is that all experiments have been performed on samples from the same single-crystalline batch. This allows for a direct comparison of the results of the different measurements.

The first HTC compound studied is \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \). Some of the physical properties of this compound are discussed. The large single-crystalline samples obtained in the growth experiments allowed for a profound study of this material. Special interest is given to the magnetization and magnetostriction measurements.

As the second HTC compound, the very anisotropic system \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) was
selected. The crystal growth process of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ and some of its physical properties are presented. Again special interest is given to the magnetization and the magnetostriction measurements.