crystal growth and magnetostriction of high-temperature superconductors

Duijn, V.H.M.

Citation for published version (APA):
Duijn, V. H. M. (2000). crystal growth and magnetostriction of high-temperature superconductors

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
3 Techniques

3.1 Introduction

High-temperature superconductors exhibit a variety of interesting physical properties. These properties vary often strongly with experimental parameters, such as temperature, magnetic field and pressure but also with the orientation of the specimen in a magnetic field and its thermal and magnetic history. Moreover, in some cases a strong sample-dependence is observed, which is related to the experimental aspects of the sample preparation process like purity of the starting materials, crystal growth parameters and annealing temperature. For a profound experimental study of high-temperature superconductors it is important to have high-quality, well-defined samples and to perform the experiments in a well-defined way. The complex crystallographic structures of the compounds make the preparation of single-crystalline samples a difficult task. This chapter gives a description of the techniques that were used to prepare and to investigate some selected High-$T_c$ compounds. These techniques are presented in three sections. Section 3.2 describes the preparation techniques used to grow single-crystalline material and the ways to shape the grown crystals in a form suitable for the experiments. In section 3.3, the techniques used to characterize and orient the crystals are presented. Finally, section 3.4 describes the experimental techniques used to measure physical properties of the single-crystalline samples.

3.2 Preparation of single-crystalline samples

3.2.1 Mirror furnace

A NEC SC-N35HD (Nichiden Machinery Ltd.) image furnace is used for the crystal
Techniques

34
growth process. This is a double ellipsoid type mirror furnace with two halogen lamps as heat sources. A schematic outline of the equipment is given in figure 3.1.

The crystal growth in an image furnace is based upon the Travelling Floating Zone (TFZ) or the Travelling Solvent Floating Zone (TSFZ) technique. A rod of starting material is scanned through a heated zone. With the TFZ technique, the rod melts at one side of the zone and solidifies at the other side. With the TSFZ technique, the rod is dissolved in a molten solvent of different composition at one side of the heated zone and solidifies from the solvent at the other side. The molten zone is kept in place by its surface tension. In the image furnace the heating is performed by two halogen lamps placed in two parabolic gold-plated mirrors. The growth process takes place in the common focus of the mirrors. It is followed by a video camera. In order to follow the growth during several days, images can be recorded during certain intervals. The temperature of the molten zone is controlled by the DC voltage of the two halogen lamps. This power is regulated by a programmable controller. The temperature of the melt can not be measured directly. The growth process takes place in a quartz tube in which the atmosphere is regulated. The feed-rod and the seed

Figure 3.1  Outline of the NEC SC-N35HD image furnace.
are attached to rotatable shafts and rotate oppositely to obtain good mixing of the molten material and homogeneous heating of the melt. The mirrors, the shafts and the upper and lower parts of the quartz tube are kept at room temperature by means of water cooling. During the crystal growth there is no contact between sample and container. The feed-rod hangs on the upper shaft by a platinum wire. The growth process is stopped before the platinum reaches the melt. High-purity crystals can be obtained in this way. Parameters that can be varied during the growth process are the feed and seed translation speeds, feed and seed rotation speeds, the power of the lamps and the ambient atmosphere. Specifications of the image furnace are given in table 3.1.

Table 3.1 Specifications of the NEC SC-N35HD mirror furnace.

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Double ellipsoidal reflector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat source</td>
<td>Two halogen lamps of max. 3.5 kW</td>
</tr>
<tr>
<td>Temperature range</td>
<td>max. 2150 °C</td>
</tr>
<tr>
<td>Feed and Seed translation speed</td>
<td>0.2 - 75 mm/h for low-speed range 2 - 300 mm/h for high-middle-speed range</td>
</tr>
<tr>
<td>Feed and Seed rotation speed</td>
<td>3 - 150 rpm</td>
</tr>
<tr>
<td>Atmosphere pressure</td>
<td>10⁹ - 5 bar</td>
</tr>
<tr>
<td>Gas-flow rate</td>
<td>0 - 5 dm³/min</td>
</tr>
</tbody>
</table>

3.2.2 Weighing and mixing

The crystal-growth process makes use of polycrystalline feed-rods of 5 to 6 mm in diameter and 6 to 12 cm in length as starting material. These feed-rods were prepared from 3N5 or better quality starting materials in powder form. The materials were weighed on a METTLER AE240 balance connected to a computer. The computer program calculated the ratios and the amounts of material needed for a compound. Mixing of the weighed powders took place in an agate bowl with two small agate balls. The bowl was placed in a mechanical shaker. The weighed powders were mixed in acetone.

3.2.3 Cutting

The high-temperature superconductors are brittle ceramic materials. A round plate diamond
Techniques

saw with blade thickness 0.2 mm was used to cut the materials. During the cutting, alcohol was used as cooling, cleaning and lubrication liquid. After cutting, the samples were cleaned with alcohol or acetone in an ultrasound bath. A special holder was used to cut crystals which were oriented with an X-ray Laue apparatus. The cuts can be made parallel and perpendicular to each other with an accuracy of 3 degrees.

The spark-erosion technique was employed to wire-cut the doped (conducting) crystals of the high-temperature superconductors. The spark-erosion machine (AGIEPULS with a CNC-SP612 controller) is connected to a computer which enables one to program a sequence of cuts to be performed automatically. Besides the movement of the sample and the wire, one can control voltage, current, capacitance, amount of sparks per second and size of the sparks. A 50 μm copper wire was used. The wire can be positioned with an accuracy of 5 μm. The cutting took place in an oil bath. The oil was constantly filtered. During the spark-cutting, an ultrasound cleaning device, present in the oil bath, is activated. Samples were, after orientation with an X-ray Laue apparatus, glued to special holders for the spark erosion machine. The cuts can be made along any desired direction with an accuracy of one degree. Also, cylinders and spheres can be cut out of the sample. The large advantages of the spark-erosion technique are the high precision and during the cutting no force is applied on the sample. Disadvantages are the limitation of the technique to conducting materials and that the sample-surface is defected by the spark-erosion process.

3.2.4 Embedding and polishing

Polishing of the samples is necessary in order to study the surface. With a polarized light microscope the presence of grains with deviating orientations can be visualized. The microscope also enables one to make photographs of the surface. The Electron-Probe Micro Analysis (EPMA) also requires polished surfaces. Before polishing the samples, they are embedded in an epoxy to support them.

Two techniques were used to embed the samples in pills with a diameter of 25 mm and a height of 15 mm. The first method is by a PRIMOPRESS which uses pressure and heat to embed the sample in a (non-)conducting epoxy. Satisfactory results were obtained with a force of 20 kN at 150 °C for 10 minutes for the acrylic thermoplastic resin of RESIN-2 HQ containing copper or iron powder. The second technique makes use of a two component self hardening polymer (TECHNOVIT 5071). Once embedded, the samples can be recovered by dissolving the epoxy in acetone. The advantage of the self hardening epoxy is that the brittle samples can be embedded without heating and applying pressure. A disadvantage is that the self hardening epoxy is not conducting. Samples embedded in this way can not be used for the EPMA.

After embedding a sample it was rubbed manually for a few minutes with sandpaper
(grit 1200) to obtain a flat surface. Then, one of two techniques for polishing the very hard materials was used. The first technique is to polish with diamond spray on a soft cloth. A VIBROMET 2 Vibratory Polisher with BUEHLER Metadi Aerosol Spray Diamond Compound 1 µm served for this purpose. The polishing takes several hours. A black shiny surface is obtained. The second technique is lapping with Aluminium Oxide. In this case a LOGITECH PM4 Precision Lapping and Polishing Machine with Aluminium Oxide paste of 3 µm was used. The lapping takes 4 to 6 hours. The difficulty of polishing these hard and brittle materials is that small parts of the material tend to break from the surface. This causes holes while the broken pieces can produce scratches on the surface. With both procedures satisfactory results were obtained. Polishing with diamond spray is simpler and faster than the lapping technique.

3.3 Characterization of single-crystalline samples

3.3.1 Laue X-ray diffraction

The grown materials were examined crystallographically by means of X-ray Laue back-scattering diffraction. A Polaroid camera was used as detector. The camera is placed between the sample and the X-ray source. A single crystal of good quality is characterized by Laue photographs with well-defined reflection patterns and well-shaped single spots. A Laue photo gives information on the crystal quality of the surface over an area of about 1 mm$^2$. By taking several pictures at different positions information on mono-crystallinity can be obtained. X-ray Laue diffraction is also used to orient the samples. The best Laue-pictures are made on cleaved or polished surfaces, or on the shiny facets which are sometimes present on the crystals. A thin skin of Cu or CuO is often present on parts of the grown materials. This skin causes blurring of the Laue-picture. By cutting the samples with spark-erosion the surface is damaged in such a way that the Laue-pictures become diffuse. The size of the X-ray spot is 1 mm$^2$. The penetration in the crystal is about 20 µm. For all high-temperature superconductor compounds, CuKα radiation, generated with 40 mA at 20 kV for 3 minutes, was used.

3.3.2 Powder X-ray diffraction

Powder X-ray diffraction gives information on the phases present in the sample and lattice parameters of the crystalline material. X-ray patterns were taken at room temperature by means of a Philips diffractometer with a vertical goniometer using CuKα radiation.
Analyses were done with a Philips APD 1700 Automatic diffraction program. For accurate measurements of the lattice parameters, silicon was used as a standard. Samples were powdered in a steel bowl, closed with a steel pin, by slamming with a hammer on the pin. No contamination with iron could be detected.

**3.3.3 Electron-probe micro analysis**

The Electron-probe micro analysis (EPMA) measurements provide information on chemical composition, homogeneity and single-crystallinity of the surface of the sample (See for instance Mackenzie [1993]). The measurements were performed at the FOM-ALMOS facility at the Kamerlingh Onnes Laboratory (KOL) in Leiden. The sample is exposed to an electron beam, with an acceleration voltage of 15 kV, which partly ionizes the different atoms of the compound, thus creating vacant energy levels. Electrons in higher energy levels fall back to the vacant levels, emitting photons. The photon-energy is characteristic for the energy level difference and hence for the atom. The number of photons with this characteristic energy counted per second is a measure for the amount of atoms of a certain type. At low concentrations of atoms the EPMA is limited, due to the low number of counts per second compared to the background. Also, when the two characteristic energy-peaks of different constituents overlap, the EPMA results should be interpreted with some care. For the EPMA measurements a flat surface is required and the sample should be conducting. Several different cross-sectional cuts were made across the sample. The cut samples were embedded in a conducting epoxy and polished. Electron microscopy was used to visualize the surface of the sample. Different phases show up as different colours. Then, at different places of one phase the exact composition of the sample is measured. In this way the homogeneity of the sample is determined. The EPMA is not sensitive for light elements such as oxygen, so little information on the oxygen content in the sample is obtained. Different orientations of different grains show up as different colour shadings.

**3.3.4 Density**

The porosity of the polycrystalline starting materials is an important parameter for the crystal-growth process (see chapter 4). A measure for the porosity is the density of the material, compared to the optimal density calculated from the crystal structure and the lattice parameters. The density of the grown crystals is, together with the lattice parameters and structure, a first check of the composition. Density measurements were performed at room temperature with an equipment based on Archimedes’ principle: the force of a
Techniques

A submerged body is equal to the weight of the displaced liquid. The weight of a sample is measured in air and in a liquid with a known density. The density of the sample can be determined from the weight difference. An extensive description of the used technique is given by Duijn [1999]. The measurements were performed with a Mettler AE 163 balance. Double demineralized water is used as liquid with known density. The temperature of this water is stabilized within 0.01 K with a Colora Messtechnik GMBH K3 temperature controller. The accuracy of the measurement is limited by this temperature stabilization. The relative accuracy is 0.1%. The absolute accuracy is 0.5%. The samples can be between 500 mg and 2 g in weight.

3.3.5 Ac-susceptibility and ac-resistivity

Ac-susceptibility and ac-resistivity measurements reflect the quality of the sample and give a first indication of superconductivity. The main purpose of these measurements is to get information about the onset of the superconducting transition $T_c$ and the transition width $\Delta T_c$, here defined as 90% of the transition centred around the midpoint of the transition. These data provide a measure of doping and homogeneity of the sample. The temperature dependence of the ac-susceptibility and ac-resistivity is followed from 4.2 K to room temperature with a computer controlled system.

The susceptibility is measured by sending an ac-signal through a primary coil which generates an ac-field. The sample is placed in one of two oppositely wound pick-up coils or secondary coils which are inside the primary coil. The generated inductance signal is a direct measure of the ac-susceptibility. The contribution of the empty holder is subtracted from the signal. A field of a few Gauss with a frequency of 90 Hz is used.

The electrical resistivity is measured by a four point method. An alternating current of 2 mA with a frequency of 90 Hz is sent through the current leads and the voltage over the sample is measured. The voltage is measured by a lock-in amplifier of EG&G Princeton Applied Research, type PAR 5208 two-phase lock-in amplifier.

The insert, with either the coils for susceptibility or the sample holder for resistivity, is put in a sample space which is surrounded by an exchange space filled with helium gas. Measurements are performed by cooling the sample at a rate of 5 to 10 mK/sec, while continuously monitoring the temperature and signal. The cooling rate is regulated by varying the helium pressure in the exchange space. The temperature is read with a Carbon Glass thermometer for temperatures below 77 K and a Platinum thermometer for temperatures above 50 K. The thermometer is positioned a few millimetres from the sample. To obtain good thermal contact between sample and thermometer the sample space is filled with half a bar of helium gas at room temperature.
3.3.6 Neutron diffraction

Several neutron-diffraction studies have been performed on the as-grown crystals. These studies were performed in cooperation with, or by, collaborative research groups. Besides, for characterization and orientation of the samples, neutron diffraction is used to study the crystal structure and the magnetic structure of the material. Characterization and orientation studies were performed at the Interfacultair Reactor Instituut (IRI) in Delft and at the Laboratoire Léon Brillouin (LLB) in Saclay. Neutron experiments for determining more complex physical properties of the materials were performed on the samples at IRI (Depolarisation study and flux profile study by Roest [1995]), LLB (Phonon study), Institut Laue-Langevin (ILL) in Grenoble and Hahn-Meitner Institut (HMI) in Berlin (both for magnetic study). In this work only the results of the crystallographic structures of the grown materials are described.

Most of the grown materials were checked for single-crystallinity by neutron diffraction. The principle of neutron diffraction is the same as the principle of X-ray diffraction. A monochromatic beam of neutrons is scattered from the sample in Bragg interference patterns. By scanning of the detector around the sample or by rotating the sample itself a rocking curve revealing the Bragg peaks is obtained. One of the advantages of neutron diffraction is the large penetration depth of the neutrons, making it possible to study the bulk of the sample. The measurements provide information on single-crystallinity of the whole sample (providing the sample is smaller than the size of the beam). The amount of grains in the grown boule and the relative size of the grains are revealed. The orientation and the position of the individual single-crystalline grains in the grown rod can also be detected.

3.4 Experimental setups

3.4.1 Specific heat

Specific heat measurements were performed by means of the adiabatic and the relaxation method. The adiabatic method is the most common method to measure specific heat. A thermometer and a heater are thermally connected to the sample but isolated from its surroundings. A certain amount of energy $\Delta Q$, is applied by the heater, which causes a temperature change $\Delta T$. The heat capacity, $c_p$, is given by:

$$
 c_p = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT}
$$

(3.1)
The difference between \( c_p \) and \( c_v \) is neglected. The advantage of the adiabatic method is that the absolute and relative accuracy can be very high. A disadvantage is that a heat-switch is needed to cool the sample to the lowest temperature.

With the relaxation method the sample, thermometer and heater are connected via a weak heatlink to its surroundings (the frame). The temperature of the frame is kept constant. When the temperature of the sample is stabilized at \( T_1 \), a constant power, \( P \), is supplied to the sample. After some time the sample will reach a constant temperature, \( T_2 \), since the heat per unit time that flows from the sample to the frame becomes equal to the power that is supplied to the sample. Then, the power is switched off and the temperature of the sample will relax to the temperature of the frame. The heat capacity of the sample plus addenda, i.e. support, heater and thermometer, can be determined from the temperature difference, \( \Delta T = T_2 - T_1 \), and the relaxation rate, \( \tau \). It is given by:

\[
C = \tau \kappa
\]

where the thermal conductivity of the heat link, \( \kappa = P \Delta T \). An advantage of the relaxation method is that no heat switch is needed. The sample cools via the heat link to the lowest temperature. A disadvantage is that the relaxation time changes with the heat capacity, since the heat link is fixed. This makes it difficult to measure large variations in the heat capacity.

An experimental setup was used which made it possible to measure either with the adiabatic method or with the relaxation method. A schematic picture of the specific heat support is given in figure 3.2.

![Figure 3.2 Specific heat support.](image)
The calorimeter consists of a sapphire-plate sample holder with dimensions $10 \times 10 \times 0.5 \text{ mm}^3$. As thermometer and heater two RuO$_2$ thick film resistors ($3.2 \times 1.6 \times 0.5 \text{ mm}^3$) are used, which are glued with GE-varnish onto the sapphire plate. The thermometer and the heater are connected by the four point method. An advantage of this sample holder is its very small heat capacity which does not depend on the magnetic field. The sample is glued with Apiezon N on the sapphire plate. The heat capacity of this grease is well known (Bunting 1969 and Bevolo 1974). The contribution of the empty holder and grease was subtracted from the total heat capacity. The sapphire plate is positioned adiabatically by four cotton wires. There is no heat switch. This implies that the lowest temperatures cannot be reached when measuring with the adiabatic method. For the relaxation measurements, a suitable heat link is prepared between the sapphire plate and the frame. Typically a copper wire 0.1 mm in diameter and 10 mm in length is used. Two inserts were used for the specific heat measurements. One for temperatures between 1.5 K and 300 K and one for temperatures between 300 mK and 5 K. Both inserts fit in a superconducting magnet of 8 T. The orientation of the sample in the magnetic field can be changed either by rotating the sample or by rotating the frame.

Additional measurements were performed at the Physikalisches Institut of the Universität zu Köln, Germany, with a continuous heating method. To apply this technique a thermometer is glued on one side of the sample and a carbon heater on the other side. The sample is suspended semi-adiabatically in the frame by superconducting leads to the thermometer and heater. A constant heat input is supplied to the sample, while its temperature is constantly monitored. From the temperature of the sample and the supplied power, the heat capacity of the sample is calculated. At intervals, the drift heating rate is measured by switching off the power. The calorimeter is mounted on an insert that fits into a $^4\text{He}$ cryostat with a 17 Tesla magnet. The temperature can be varied between 4.2 K and 200 K. An advantage of this method is the high density of data points that is obtained.

### 3.4.2 Thermal expansion and magnetostriction

The thermal expansion and the magnetostriction were measured by the parallel-plate capacitance method. The capacitance of a parallel-plate capacitor is given by:

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$

where $\varepsilon = \varepsilon_r \varepsilon_0$ is the dielectric constant of the medium between the plates, $A$ is the area of the plates and $d$ is the distance between the plates. If during the measurements one capacitance plate is fixed and the other attached to the sample, then the length change of the sample as a function of temperature or field is proportional to the capacitance change.
This change of the distance between the plates is given by:

$$\Delta d = -\frac{d^2}{\varepsilon A} \Delta C$$

or by:

$$\Delta d = -\frac{eA}{C^2} \Delta C$$

A schematic drawing of the parallel plate capacitance cell is shown in figure 3.3.

**Figure 3.3** Parallel-plate capacitance cell.

<table>
<thead>
<tr>
<th>1 upper plate</th>
<th>5 guard ring upper plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 lower plate</td>
<td>6 copper foil</td>
</tr>
<tr>
<td>3 sample</td>
<td>7 guard ring lower plate</td>
</tr>
<tr>
<td>4 screw and spring</td>
<td></td>
</tr>
</tbody>
</table>

The cell is made of Oxygen Free High Conductivity copper (OFHC copper) to guarantee good thermal conductivity and to avoid contributions to the empty cell from the paramagnetic oxygen atoms. The upper capacitance plate is fixed while the lower capacitance plate is connected to the sample. The lower plate is connected to a plateau below the cell by three rods (only one is shown) and positioned by a spring. The sample is clamped between the lower capacitance plate and the bottom of the cell by straining the
spring. The surfaces of the parallel capacitance plates are made flat within a few μm by means of spark erosion. Electrical isolation of the capacitance plates from the guard rings was accomplished by means of a thin sheet of kapton embedded in epoxy. The cell is made for samples with a length of 5.020 mm. The gap between the capacitance plates is determined by three copper foils (thickness 100 μm) placed between the guard rings of the lower and upper capacitance plates. The upper plate is somewhat larger than the lower plate. Therefore, the capacitance is not influenced by a tiny horizontal displacement of the plates. The effective area of the capacitance plates, $\varepsilon A = 9.47 \times 10^{-16} \text{Fm}$, is determined by measuring the proportionality constant for the capacitance as a function of the thickness of the foils. The uncertainty in the determination of this value gives an accuracy of 3% on the absolute value of the experimental data. The influence of a small amount of helium gas, present between the capacitance plates, on the dielectric constant can be neglected ($\varepsilon = \varepsilon_0$).

The capacitance cell can be mounted in different inserts. The thermal expansion is measured between 1.5 K and 200 K in a normal $^4\text{He}$ insert. Between 0.3 K and 6 K a $^3\text{He}$ insert is used. Magnetostriction is measured in fields up to 8 Tesla with the two different inserts. During the magnetostriction measurements the temperature is regulated with a capacitance thermometer.

A new capacitance cell with a new insert has been designed for magnetostriction of small, thin samples. This cell fits in a rotatable magnet, which allows an angle dependent study of the magnetostriction. A schematic figure of the cell is shown in figure 3.4. A figure of the insert is presented in figure 3.5.

**Figure 3.4** One of the two capacitance plates of the small-sample parallel-plate capacitance cell (■ = copper).
The cell is made of two pieces of print-board that are covered on both sides with conducting copper. For each piece of print-board, one side serves as capacitance plate and the other as guard-ring. The samples are placed on insulated islands of copper. Insulation was obtained by removing the surrounding copper using an etching procedure. The cell is designed for three 100 μm thick samples of maximum size 2 × 3 mm². The measured magnetostriction is the average of the three samples. The samples are clamped between the plates by straining the spring with a screw. A Carbon Glass thermometer is placed close to the samples to monitor the temperature during the measurements. With the small-sample capacitance cell, magnetostriction measurements can be performed between 4.2 K and room temperature in fields up to 5 Tesla. The field can rotate over 330 degrees. The cell has an effective area εA of 1.26 × 10¹⁵ Fm.

For both cells the capacitance was measured with a sensitive three-terminal method to reduce the noise level. The measurements were performed using an Andeen-Hagerling capacitance bridge (type 2500A with option E) with an internal oven for temperature stabilisation of the reference capacitors in order to prevent thermal drift. With this apparatus, capacitance changes of 10⁻⁶ pF can be readily obtained. The relative length
Techniques

change is:

\[
\frac{\Delta L}{L} = \pm \epsilon A \frac{\Delta C}{LC_0^2}
\]  

(3.6)

The + sign applies when \( \Delta C \) is measured with the large-sample capacitance cell \((\Delta L = -\Delta d)\), while the - sign applies in case \( \Delta C \) is measured with the small-sample capacitance cell \((\Delta L = \Delta d)\). \( L \) is the length of the sample at room temperature. The resolution of the measuring method is high. Filling in equation 3.6 some typical values for \( \epsilon A \) \((= 9.47 \times 10^{-16} \text{ Fm})\), \( L \) \((= 1 \times 10^4 \text{ m})\) and \( C_0 \) \((= 1 \times 10^{-11} \text{ F})\) and the smallest measurable value for \( \Delta C \) \((= 1 \times 10^{-18} \text{ F})\) the accuracy with which \( \Delta L/L \) can be measured, can be determined. This accuracy is about \( 1 \times 10^{-7} \), which means that \( \Delta L \) can be measured with an accuracy of \( 1 \times 10^{-11} \text{ m} \).

3.4.3 Magnetization

Magnetization measurements were performed using a SQUID magnetometer and by a moving-sample magnetometer. The SQUID magnetometer is an MPMS-5 of Quantum Design. Measurements can be performed from 1.5 K to 350 K in fields up to 5 T. A rotatable insert can be used to measure angle dependence of the magnetization. The equipment can measure magnetization values in the range from \( 10^{-12} \) to \( 10^3 \text{ Am}^2 \) with an accuracy of 0.1%. The sample size is limited to \( 3 \times 3 \times 3 \text{ mm}^3 \). The moving-sample magnetometer is home made. Measurements can be performed at temperatures between 4.2 K and 300 K. The maximum field which can be applied is 8 T. The magnetization is measured by moving the sample between the centres of two oppositely wound pick-up coils. The integrated induced voltage is a direct measure for the magnetization of the sample and the holder. For accurate measurements the empty-holder contribution is subtracted from the measured signal. The magnetic moment of the sample can be determined with a sensitivity of \( 10^{-5} \text{ Am}^2 \). Samples up to \( 1 \times 1 \times 1 \text{ cm}^3 \) in size can be measured.