Chapter 5

Samples

The requirements for the studies of Ho and EuTe films are quite different. While for the experiments on thin holmium films, the in-situ film preparation demanded a rather complex sample holder and excellent vacuum conditions, the experimental challenge for the study of the ex-situ prepared EuTe samples was the very low transition temperature of less than 15 K. Consequently, the sample holders differ substantially. The following sections outline the experimental details of both experiments.

5.1 Thin Lanthanide Metal Films

As a first application of the new apparatus, we examined the magnetic properties of in-situ prepared thin holmium metal films in connection with the problem of finite-size scaling of magnetic ordering temperatures in helical antiferromagnets. In-situ preparation of the highly reactive lanthanide metals is rather demanding. It requires an experimental environment that enables to control, characterize and reproduce the sample growth but does not limit the subsequent magnetic scattering experiments. The highly reactive lanthanide metal films were prepared on a W(110) crystal by means of vapor deposition of high-purity lanthanide metals following a standard recipe developed in earlier work of our group [125].

5.1.1 Sample Preparation

In the experiments, a home-made evaporator was used. Its advanced design is based on evaporators already in use in our group since years, but modified to accomplish a higher reproducibility and mechanical stability. The sample-material is evaporated from a crucible by heating either radiatively or by means of electron bombardment. The main advantages of the novel evaporators are the small size of only 16 mm × 155 mm and the comparably low price of about 150 Euro per unit. This permits to mount seven evaporators, filled with different materials, at the same time on a single DN CF64 flange, which is beneficial in particular for the preparation of multilayer samples. But also the preparation of single films benefits, for it avoids time-consuming and vacuum-corrupting replacements in the case of malfunctions - a crucial advantage for the time-limited synchrotron experiments. The evaporators are characterized by a long-time stability of operation parameters, high reproducibility and stability of evaporation rates as well as by an achievable working pressure of the order of $1 \cdot 10^{-10}$ mbar. The general assembly is displayed in Fig. 5.1. The essential part of each evaporator is the crucible(1) of 20 mm length and 6 mm in outer diameter. With a central hole of 5 mm diameter and 13 mm length it carries about 1g of the sample material, which is sufficient for the preparation of several

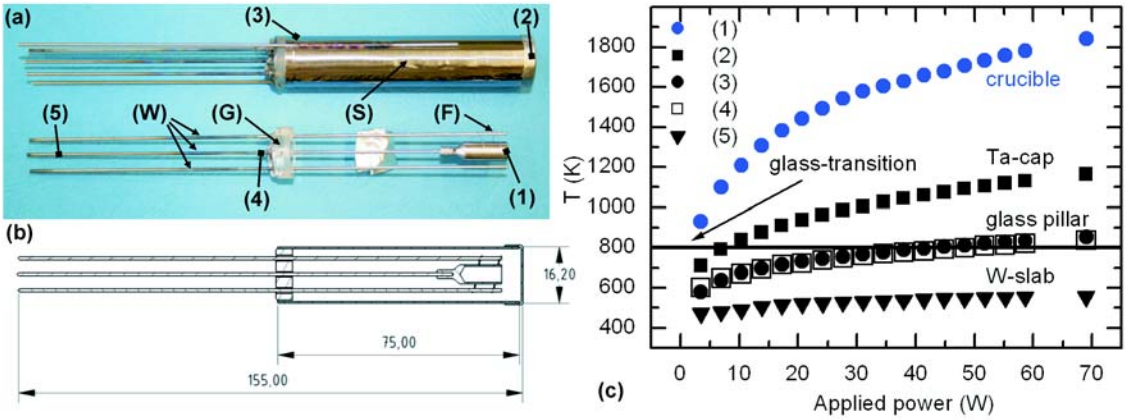

Figure 5.1: *(a): Photograph of the home-made evaporators: with mounted shield (top) and without shield (bottom). (b): Cross-sectional drawing (from Ref. [116]). (c) Temperature at different parts of the evaporator as a function of applied power. The solid line marks the glass-transition temperature of the used DURAN glass. The numbers correspond to positions marked in (a).*

thousands monolayers. In the experiments presented within this thesis, 99.95% pure tantalum was used as crucible material. The crucible is heated by means of a Ta filament(F) wound around the crucible in a distance of about 2.5 mm from the crucible. A current of about 6A through the filament heats the crucible up to 850 K. Higher temperatures are achieved by electron bombardment. The diameter of the filament wire was chosen to be 0.1 mm in order to have typical operation parameters (filament: 6 V × 5 A), that can be provided by standard low-voltage power supplies and feeded by standard electrical feedthroughs. Both, filament and crucible are held by three W rods(W) of 150 mm(2x) and 135 mm(1x) length, respectively. Mechanical stability and electric isolation, necessary to apply the high voltage, are realized by melting these three rods into a DURAN-glass pillar(G) of 16 mm outer diameter and 5 mm thickness. The heat transport to the glass pillar is effectively reduced by the small diameter of the W rods (1 mm). Additionally, it is necessary to reduce the heat radiated by the glowing crucible in order to minimize the heating-up of the environment of the evaporator which would cause substantial outgasing and pressure rise during operation. For this purpose and the protection of the crucible from external contaminations, the upper part of each evaporator is surrounded by a 75 mm long cylindrical shield (S) made of a 0.1 mm thin Ta foil. Additional W slabs on the outside of this shield enhance the mechanical stability of the shield position and enable to clean/degas the shield by electron bombardment heating. The top of the cylindrical shield is covered by a Ta cap(2) with a central hole of 5 mm diameter, leading to a well-defined evaporation beam profile (see Fig. 5.2). Since a controlled and high-quality sample preparation is one of the most crucial steps in the experiment, this construction was carefully characterized. Figure 5.1 displays the temperature at different parts of the evaporator for various heating powers, measured by a W/Re thermocouple spot-welded to the corresponding parts. The maximum temperature at the crucible is limited to about 1650 K by the temperature of the W slabs and of the Ta shield close to the glass pillar, which must not exceed the DURAN glass-point, where the glass starts to soften plastically. This maximum temperature enables to evaporate even the high-melting heavy rare-earth metals like gadolinium with evaporation rates of the order of several monolayers per minute as shown in the left panel of Fig. 5.2. The evaporation beam profile is shown in the right panel, revealing a constant rate on a length of about 10 mm, which is the size of the substrate crystal. Therefore, the growth of homogeneously thick films over the whole substrate crystal is warranted.

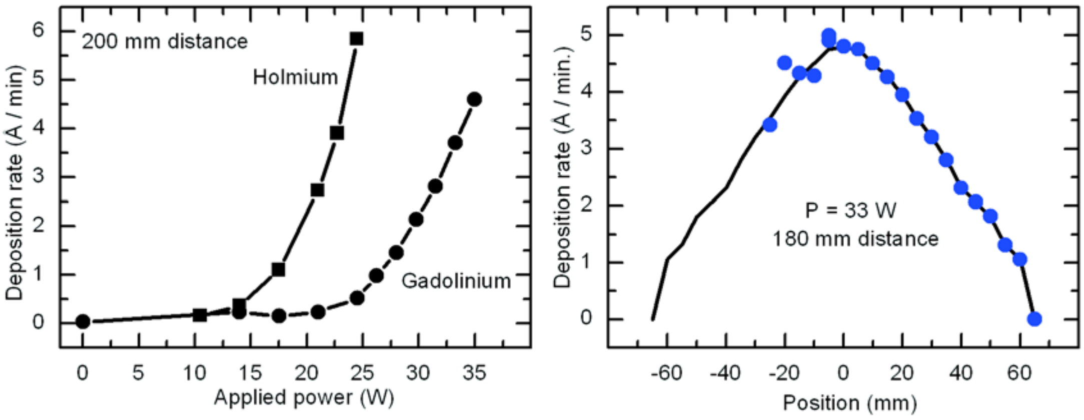

Figure 5.2: *Characterization of the evaporators. Left: Power-dependent deposition rate for a holmium and a gadolinium evaporator measured at a distance of 200 mm from the evaporator. Right: Position-dependent deposition rate of the gadolinium evaporator at a distance of 180 mm. The size of the used vacuum chamber limited the measurements essentially to one side. The solid line is a guide to the eyes. The position corresponds to a vertical shift of the thickness monitor.*

After the fabrication and subsequent cleaning by means of an ultra-sonic bath, the evaporators are cleaned by alternating annealing of shield and crucible in high-vacuum (10^{-6} mbar) for several hours at the maximum power. The evaporators are filled by repeated melting of metal pieces of the chosen material under the same high-vacuum conditions, which ensures a maximum filling of the crucible. An evaporator, which was exposed to atmosphere needs a short degassing procedure[1] (30 minutes) in order to operate in the 10^{-9} mbar range, which may be sufficient for the preparation of rather inert materials. However, an extended degassing procedure yields a pressure during operation even below $1 \cdot 10^{-10}$ mbar.

The holmium films were prepared by deposition of high-purity metal (99.99%) onto the (110) surface of a tungsten single crystal using the described evaporation sources. Tungsten is an ideal substrate for the preparation of lanthanide films. The (110) surface of the body-centered cubic structure of tungsten (W) is only weakly reactive and does not show any tendency to alloy with the lanthanide metals up to their desorption temperature. The absence of interdiffusion of holmium into the substrate leads to sharp interfaces between the films and the W substrate. The growth additionally benefits from the comparably high surface energy of the W(110)-surface that favors layer-by-layer growth. Since the hexagonal lanthanide metals grow along their (0001) direction their surface structure does not match that of the cubic tungsten. The lattice mismatch is in the order of 10%. This leads to various superstructures [126] in the submonolayer regime but earlier studies revealed that the lanthanide metal films adapt their intrinsic structure at a film thickness of only one monolayer as evident from the observation of hexagonal LEED patterns [39]. From a practical point of view, the easy procedure of removing the film sample from the tungsten surface by a short heating to about 2000 K (flash) makes the tungsten substrate further favorable. The whole sample holder has to be made from rather high melting materials, in the present case only tantalum, tungsten and molybdenum parts were applied. Figure 5.3 displays a typical sample holder. The substrate crystal is mounted on a tantalum or tungsten frame. This frame is screwed on a copper block with thin sapphire plates inbetween. The sapphire plates ensure the electrical isolation and protect the copper from the hot frame during the flash procedures. While sapphire, at high temperatures, shows a poor thermal conductivity, it is a

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[1] Operation at moderate deposition rates.

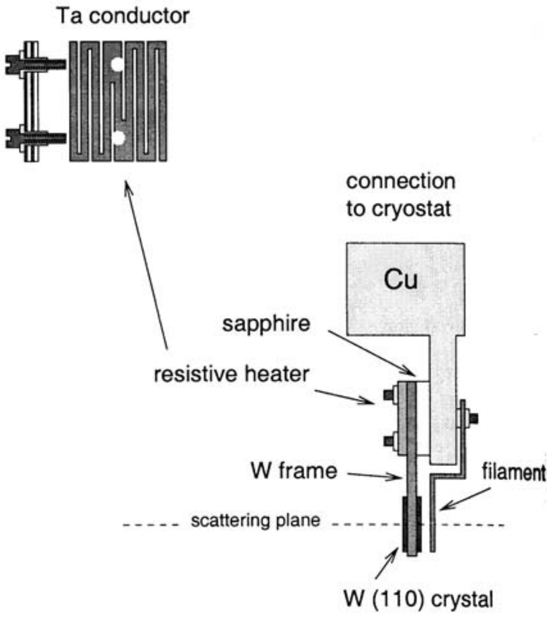

Figure 5.3: *Cross-sectional drawing of one of the applied sample holders for the in-situ preparation of thin lanthanide metal films. (from Ref. [54]).*

good thermal conductor at low temperatures, which permits effective cooling down to 20 K with the copper block either mounted to a helium flow cryostat or to a closed-cycle helium refrigerator. The W crystal is heated either radiatively by a tantalum filament close to the backside of the crystal or by means of electron bombardment. This sample holder can achieve temperatures between 20 K and up to 2300 K. The high temperature limits the available temperature sensors. In the present case, a W/Re thermocouple ($W_{0.95}Re_{0.05}/W_{0.74}Re_{0,26}$) is applied. That sensor is characterized by a rather low differential thermo power, which leads to comparably large error bars below 50 K. The thermocouple wires (2) of 0.125 mm diameter each stick tightly in a bore of 0.3 mm, machined into the side of the tungsten crystal. Temperatures were measured with a Lakeshore 330 temperature controller. In the scattering experiment, the filament cannot be used to heat the sample because of the disturbing visible light. Therefore, a radiationless heater, designed in an earlier work [54] was applied. It is made of a 0.1 mm-thin tantalum foil cut from two sides to give a meandered conductor and is sandwiched between two sapphire plates.

Prior to the growth of the holmium films, the tungsten crystal has to be cleaned. While a short flash desorbs all residual lanthanide films or adsorbed gases, a carbon superstructure remains after several flashing procedures, caused by the segregation of carbon from the tungsten bulk to the surface. It can be removed by annealing the W crystal at about 1100 K for several minutes in an oxygen atmosphere of a oxygen partial pressure of $1 \cdot 10^{-6}$ mbar. That procedure oxidizes the carbon and desorbs it. The remaining tungsten oxide is removed by a subsequent short flash. The growth mode of the lanthanide metal films on W(100) depends on the substrate temperature. Growth with the substrate held at room temperature and subsequent annealing to 600 K results in high-quality homogeneous single-crystalline films, characterized by a RMS roughness less than one monolayer as inferred from reflectivity measurements. Lower substrate temperatures during the sample preparation, on the other hand, result in polycrystalline films [127].

5.2 Europium Telluride Thin Films

In contrast to the experiments on thin holmium metal films, the studied EuTe samples were prepared ex-situ by the group of Professor Springholz from the Johannes-Kepler-Institut für Halbleitertechnik at the university of Linz. The experimental challenge of this study was the very low ordering temperature of less than 15 K. Consequently, the applied sample holder completely differs from that used for in-situ preparation of holmium metal. The following pages describe this sample holder as well as the studied EuTe samples.

5.2.1 Sample Properties

The magnetic semiconductor EuTe crystallizes in the rock-salt structure with a bulk lattice constant at room temperature of 6.598 Å [128]. In this structure, the Eu^{2+} ions, responsible for the magnetism, form an fcc sublattice. Below the bulk ordering temperature of about 9.8 K a simple AFM structure is formed, characterized by ferromagnetically ordered (111) planes with alternating layer magnetization along the [111] direction. Consequently, the preferred sample for resonant magnetic scattering experiments, in particular in the soft x-ray range, are those with the [111] direction normal to the surface. Such samples are available for almost a decade, prepared by means of molecular-beam epitaxy and characterized by an extremely high crystalline quality. A number of experiments were performed in order to study the growth and structural properties of such epitaxial layers exploiting mainly conventional x-ray diffraction [129], RHEED [128] and STM techniques [130]. One key parameter of epitaxial growth is the chosen substrate. In the present case, a (111) PbTe buffer layer grown on BaF_2 is used. PbTe also crystallizes in the rock-salt structure with a room-temperature lattice constant of 6.462 Å [128], which results in a rather small lattice mismatch between the EuTe and the substrate of only 2.1%. This initially thick (several μm) and fully relaxed PbTe buffer layer is characterized by an extremely smooth unreconstructed surface. The only surface structure visible are growth spirals formed around the cores of dislocations originating from the 3D nucleation of PbTe on the BaF_2 substrate. The flat terraces are separated by steps of exactly 1 monolayer (1 ML PbTe = 3.73 Å) [130] in height with a mean distance of 150 nm. The absence of 2D islands nucleated on top of these terraces indicates a large PbTe surface diffusion length and step flow growth.

The subsequent growth of EuTe onto this buffer layer strongly depends on the growth parameter. True 2D layer-by-layer growth occurs only in a very narrow parameter regime. The most sensitive parameters are the ratio of the Te_2 to Eu flux as well as the substrate temperature. At high Te_2 flux and high substrate temperatures, EuTe grows in the Stranski-Krastanov mode characterized by 3D nucleation of EuTe. That growth mode can be suppressed by choosing substrate temperatures below 300°C. On the other hand, below the Te_2 condensation temperature of about 220°C the growth is characterized by rapid surface roughening and subsequent polycrystalline EuTe overgrowth. The intermediate temperature regime shows at a Te_2 to Eu flux ratio of about 3:1 and a growth rate of 0.4 ML/s perfect 2D layer-by-layer growth with either a Te-stabilized (lower temperatures) or a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ reconstructed Eu-stabilized surface (higher temperatures). It turned out, that the maximum thickness of perfect 2D growth is obtained in the Eu-stabilized regime close to the Te-stabilized region at a temperature of about 260°C. In this regime, within the growth of the first 3 ML of EuTe, the change from the unreconstructed PbTe surface to the reconstructed EuTe surface is finished. As a consequence of the smaller PbTe lattice constant, the EuTe film is strained, which results in a decrease of the in-plane lattice constant by almost 2% accompanied by an increased monolayer distance of about 3.86 Å [129] (bulk value: 3.81 Å). RHEED studies [128] suggest pseudomorphic growth up to a critical layer thickness of about 45 ML, characterized by a constant in-plane lattice constant and a RMS roughness

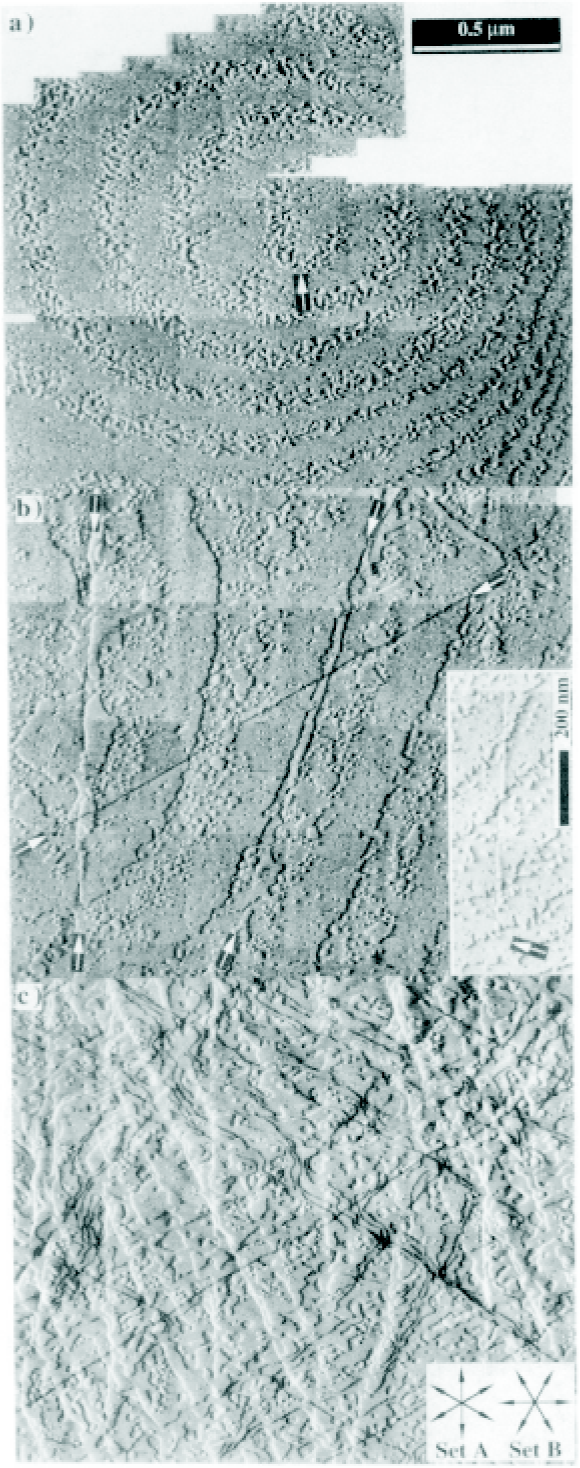

Figure 5.4: *STM images of EuTe epilayers of different thicknesses on PbTe(111) (from Ref. [130]). The surface morphology of the 20-ML film (a) still is dominated by the initial spiral structure of the PbTe buffer. At 30 ML (b) glide lines indicated by the arrows occur which completely dominate the surface of the 40-ML film (c).*

EuTe (ML)	PbTe Cap (Å)	PbTe buffer (μm)
2	200	2.20
3	200	1.80
4	200	1.80
5	200	1.64
6	400	2.35
7	200	1.64
14	400	3.00
20	800	1.60
40	800	1.60

Table 5.1: *Nominal thicknesses of the EuTe film, the PbTe cap, and the buffer layers of the studied samples.*

of about 1 ML. At higher coverages both, a sudden strong relaxation of the EuTe in-plane lattice constant and a surface roughening to values above 2 ML occurs within only a few monolayers. Origin of the limited thickness range of perfect 2D growth is the strain due to the lattice mismatch between EuTe and PbTe. In the absence of strain-induced formation of 3D islands, the criterion for mechanical stability of a strained layer is given by the Matthews-Blakeslee model from the competition between line tension and misfit strain force. Below the critical thickness the strain can be fully accommodated by biaxial elastic deformation of the lattice while for higher coverages the increasing misfit strain force results in segments of misfit dislocations at the layer-substrate interface. For the case of heteroepitaxial growth of EuTe on PbTe the Matthews-Blakeslee criterion suggests a critical thickness of only 14 ML, well below the observed value of 45 ML. However, later STM studies [131] revealed the presence of totally straight surface step lines, each corresponding to a misfit dislocation segment at the heterointerface, at EuTe coverage of only 15 ML. These glide lines cut through all other surface features and displace them exactly by 1 ML in height. These STM studies indeed suggest an onset of strain relaxation at about 15 ML, but with an extremely small area density of glide lines below a coverage of 25 ML (see Fig. 5.4). Up to this thickness, the surface morphology is dominated by the initial spiral structure of the PbTe buffer layer as can be seen from the top STM image shown in Fig. 5.4. 2D islands on top of the terraces indicate a comparable low surface diffusion length for the EuTe growth and 2D nucleation to be the responsible growth mechanism. The area density of the glide lines increases dramatically at about 35 ML. Consequently, STM images of 40-ML-thick films do no longer show the initial spiral structure (see bottom image of Fig. 5.4). At this coverage, the surface is fully dominated by the straight glide lines. The samples studied were prepared following the above described growth conditions. After the growth, they were captured by an additional PbTe cap layer to prevent oxidation of the highly reactive EuTe at ambient atmosphere which leads to symmetric interfaces on both sides of the EuTe films. Conventional x-ray diffraction experiments on EuTe/PbTe superlattices revealed the high crystalline quality even in the case of 400 superlattice periods each consisting of only a few monolayers of EuTe. However, indications for some interfacial disorder or the presence of interdiffusion at the heterointerface were found [89].

Figure 5.5 visualizes the macroscopic structure of the studied samples: a single epilayer of EuTe embedded between two PbTe-layers on a BaF_2 substrate with the [111] direction perpendicular to the sample surface. During the experiments, samples of different EuTe thicknesses were studied. Table 5.1 summarizes the nominal thicknesses of the components of the studied samples according to the preparation process. The macroscopic size of all samples is about 5 mm × 5 mm. The ordering temperature of most of the studied samples is enhanced with respect to the bulk value as a consequence

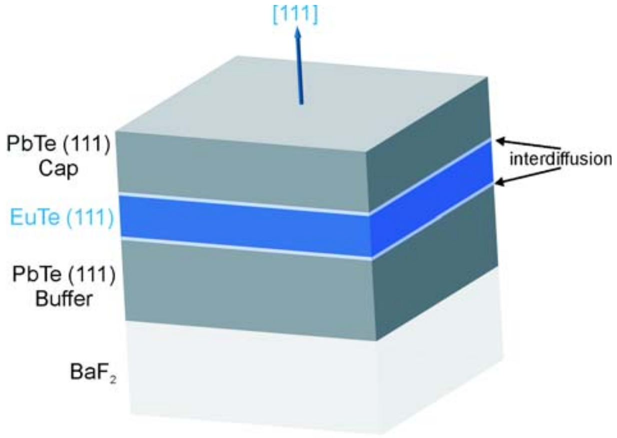

Figure 5.5: *Sandwich structure of the studied samples: epilayer of EuTe(111) (blue) embedded between two PbTe films (dark gray) on a BaF$_2$ substrate. The light blue regions at both EuTe/PbTe interfaces indicate weak interdiffusion/disorder at the heterointerface.*

of the epitaxial strain. However, the highest obtained ordering temperature is about 13 K, which still poses the main experimental challenge.

5.2.2 Sample Holder

As a consequence of the low ordering temperatures, the sample holder was optimized for effective cooling. Thus, the sample holder used to study the EuTe samples is far simpler than the complex sample holder applied in the lanthanide metal film experiments. Figure 5.6 displays the chosen solution: The samples are glued directly on a small hat-shaped copper disc of 10 mm diameter. These discs are mounted in a copper block in such a way that the surface of the disc matches that of the copper block at the front side, but sticks out by about 0.2 mm at the backside. The disc is fixed by a small copper plate mounted to the backside with four M 2.5 screws. With these four screws tightened, the disc is in sufficient thermal contact with the copper block. This design permits an easy and reproducible replacement of different samples and in addition permits to change the azimuthal orientation of the sample surface in-situ via an in-vacuum screw driver. The copper block can carry three copper discs simultaneously. The whole block was soldered to a Konti helium flow cryostat specified to reach 4.2 K. The cryostat was mounted on the top flange of the diffractometer, resulting in a vertical arrangement of the mounted samples with respect to the horizontal scattering plane. Optimized shielding against heat radiation turned out to be the key of reaching low temperatures as expected from the T^4 dependence of radiated power (Stefan-Boltzmann). Consequently, the whole copper block was surrounded by an aluminum shield connected to the heat shield of the cryostat, leaving only three small horizontal slits in front of the samples in order to perform the scattering experiment. The lowest achievable temperature with this construction at the sample position is 5.2 K. The temperature is measured by a DT470 silicon diode, with an accuracy of 0.05 K. The diode was electrically contacted by four 0.1 mm-thin copper wires. The silicon diode was mounted directly on the top copper disc of the sample holder, at a place equivalent to that of the samples in order to reduce systematic errors in the temperature measurement. The silicon diode was calibrated by measurements within LN$_2$ and LHe, yielding a systematic uncertainty of 0.1 K of the temperature measurement. A possible temperature gradient along the copper block can be ruled out from the measured equal ordering temperature of the 20-ML EuTe sample, mounted at two different sample positions at the block.

Figure 5.6: *Photograph of the used sample holder. Top: Copper disc with glued EuTe sample. Bottom: Copper block connected to the cryostat with two mounted EuTe samples (left and center slit) and the silicon diode temperature sensor (right slit). The whole sample holder is shielded by an aluminum tube with only three horizontal slits to perform the scattering experiment.*