Chapter 1
Electrical and Magnetic Behavior of GdOH Thin Films: A Search for Hydrogen Anion Superconductivity

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Abstract Anomalous resistive and magnetic behavior of GdOH thin films, which belong to the novel class of materials known as oxyhydrides, is reported. The oxyhydrides contain hydrogen in its rare negatively-charged anion state in combination with oxygen, which is also in the anion state. A range of GdOH films prepared on glass and single-crystalline substrates demonstrate a resistive transition from an insulating to conducting state with decrease of resistance starting as high as at about 200 K. At room temperature, the resistance per square area for the best GdOH films of the thickness of 200 nm is about 100 Ω, which is close to the resistance of the films of high-temperature superconductors of similar thickness. Apparent zero resistance is observed at about 40 K. Magneto-optical imaging registers effect of trapping magnetic flux typical for the superconducting state. The possible anion superconductivity is discussed in connection with recently published papers on near-room-temperature superconductivity in hydrides at high pressure and hydrogen-based superconductivity in biological systems.

1.1 Introduction

Superconductivity is a macroscopic quantum phenomenon of enormous importance. In theory, it represents quantum mechanics in most pure form while its applications range from magnets for Large Hadron Collider and International Thermonuclear Experimental Reactor to recently developed quantum computers. The material in the superconducting state can be compared with giant molecule, in which all electrons are paired and condensed in one state. Any attempt to change energy of one electron requires change in energy of all electrons. This leads to dissipation-free electrical current, ideal diamagnetism, quantization of magnetic flux, ability of current to flow

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without dissipation through a barrier and generation of coherent electromagnetic radiation in the presence of voltage on the barrier.

Such an ideal state of matter, however, is delicate, relatively rare and takes place mainly at low temperatures. There are several mechanisms able to combine electrons into pairs. Most known is electron-phonon interaction. It is, however, not able to provide high critical temperature (T_c), the temperature, below which material becomes superconducting. There are multiple attempts to extend T_c to room temperature involving exotic materials and different pairing mechanisms. A detailed account of these attempts is given in [1]. Most recently, these attempts resulted in the extension of T_c to nearly room temperature in the hydrides H_3S [2] and LaH_x [3, 4] at very high pressure. In these materials, electrons are paired through interaction with high-energy optical phonons.

It is interesting that superconductivity with T_c even higher than room temperature was predicted in hydrogen-based quasi-one-dimensional chains of organic molecules [5], and first experimental data start to appear confirming this prediction [6]. According to these data, superconductivity could be common in biological systems and most likely resides in microtubules filled with water, or rather tightly-confined hydrogen-oxygen chains [6]. If, like in other hydrides, hydrogen in these chains could be in anion form, it may allow, due to the presence of oxygen, its fluctuation between cation and anion states resulting in oscillations of charge and electron-electron interaction necessary for very high T_c, as in the model of Little [5]. From this point of view, investigation of materials with both oxygen and hydrogen in anion state is very important. Such materials are named oxyhydrides, and they are now a subject of very intensive research [7, 8]. They are, however, very delicate and difficult to study, as anion hydrogen is weakly bonded to the crystal lattice and easily lost being replaced by oxygen. GdOH is one of oxyhydrides. A range of GdOH thin films was prepared in this work, and their properties were investigated by electrical transport and magneto-optical measurements searching for the superconductivity in the material.

1.2 Experiment Details

1.2.1 Samples Preparation

GdHO films were prepared by a two-step process. In the first step, GdH_2 film was deposited by reactive sputtering in a chamber containing a mixture of argon and hydrogen using Leybold Optics A550V7 sputter unit. The deposition was done from a commercial Gd target of 99.9% purity. In the second step, GdH_2 film was taken from the chamber allowing for its natural oxidation for a certain period of time, after which it was sealed in nitrogen. Three types of substrates have been used for the deposition: borosilicate glass (Menzel–Gläser microscope slides) and two types of single-crystalline substrates—Si and $SrTiO_3$.

1.2.2 Measurements Techniques

The main measurement technique was a technique for electrical transport measurements allowing to record temperature dependence of the resistance of the samples. These measurements were performed in a protective nitrogen or helium atmosphere at a pressure close to ambient. The sample with a closely-spaced temperature sensor was mounted on an electrically-insulated rod inserted into liquid nitrogen or liquid helium dewar. The wires of the electrical circuit were attached to the sample with pressed indium contacts. The temperature was changed by slowly varying the position of the sample in the dewar. The measurement circuit consisted of power supply, temperature controller and two voltmeters to measure separately voltage and current through the sample. All devices were automatically controlled using a Matlab script with continuous record of a large number of data points in a designated time interval.

Before and between the measurements, the samples were outside of the protective atmosphere for a very short time only, which was necessary to attach contacts and wires. Typically, two current leads were permanently attached to the sample, while potential leads were frequently changed to explore different parts of the films.

Another technique used in this work was magneto-optical imaging [9]. In this technique, the sample is mounted on a cold finger of a vacuum optical cryostat and covered by a transparent indicator film with a mirror between the film and the sample. The indicator film is illuminated with a beam of linear-polarized light, and it changes the polarization of the light in the presence of magnetic field. An analyzer outside the cryostat detects change in the polarization and maps distribution of magnetic field in the indicator, i.e. in the sample, which is close to it. It is important that the sample itself is not illuminated by the light, as it is behind the mirror. Therefore, it is not seen in magneto-optics if it is non-magnetic. This technique is based on the Faraday effect and it is widely used to investigate superconducting and magnetic materials [9].

1.3 Results and Discussion

The GdOH films deposited on borosilicate glass were the first, which were investigated in this paper. After the oxidation, they visually changed appearance indicating the development of an inhomogeneous polycrystalline structure with small grain size. The films showed an insulating behavior with a strong increase of resistance with a decrease in temperature, as it is shown in Fig. 1.1. However, in some areas, the decrease of resistance at temperature below 60 K has been observed. One could assume that high resistance is caused by either grain boundaries, or the regions of over-oxidation, in which anion hydrogen was removed from the structure. The decrease in resistance may indicate a phase transition, including development of local superconductivity with a large spread in T_c. To better isolate the phase responsible for

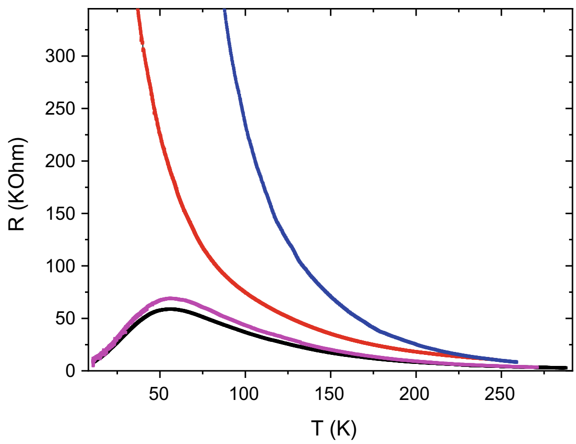

Fig. 1.1 Temperature dependence of resistance in different areas of GdOH films (shown in different color) deposited on borosilicate glass. A decrease in resistance at temperature below 60 K has been observed in some areas

the decrease in resistance, GdOH films were further prepared on single-crystalline $SrTiO_3$ and Si substrates.

An important result for GdOH films deposited on $SrTiO_3$ substrates was a very large drop in resistance compared with the films deposited on borosilicate glass. For the films of the thickness of 200 nm, resistance was about 100 Ω, which is close to the resistance of the films of high-temperature superconductors of similar thickness. Moreover, in spite of still present background increase of resistance at the reduction of temperature, its decrease is registered starting at temperatures as high as about 180 K (see Fig. 1.2). Such temperature is close to the superconducting transition temperature for hydrides at high pressure [2–4]. In this case, however, a decrease of resistance takes place at ambient pressure, but the transition is very wide, which is not characteristic for a homogeneous superconductor. In one of the curves in Fig. 1.2 plotted in black, resistance at low temperatures is close to zero.

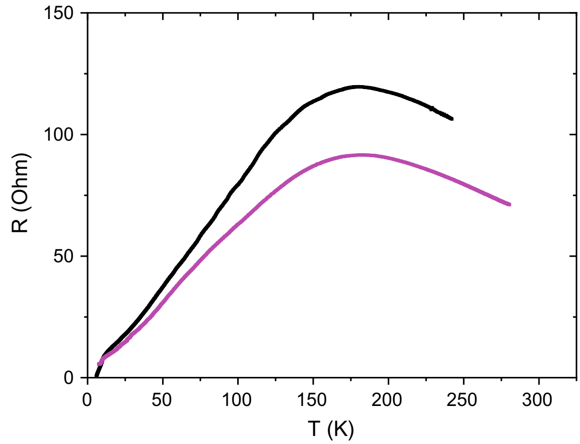

Fig. 1.2 Temperature dependence of resistance for different areas of GdOH films deposited on $SrTiO_3$ single-crystalline substrate shown in different color. A decrease in resistance has been observed at temperature below 180 K

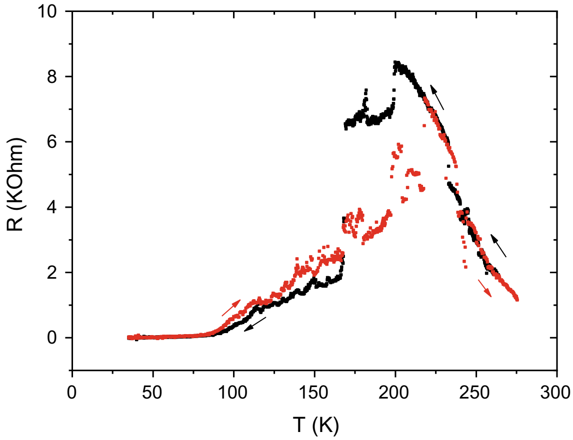

Fig. 1.3 Temperature dependence of resistance for GdOH film deposited on Si single-crystalline substrate. In spite of hysteresis and irreproducible jumps coming from the contacts, an apparent zero resistance is observed at temperatures below 40 K

The GdOH films deposited on single-crystalline Si substrates showed more peculiar behavior. Although their resistance was very high, similar to that observed in films deposited on borosilicate glass, decrease in resistance started at higher temperature than in other films, at about 200 K, and there was an apparent zero resistance at temperatures below 40 K. Such a temperature is close to T_c in other oxyhydrides reported recently [10, 11]. It was difficult to attach contacts to the films deposited on Si. Therefore, there were hysteresis and irreproducible jumps in the measurements, as it is seen in Fig. 1.3, in which points, recorded a decrease of temperature are shown in black and at increase—in red, with the arrows of the corresponding color.

The observations above suggest local superconductivity in GdOH films. However, an additional study is necessary to confirm this result. A robust technique for detecting superconductivity is magneto-optical imaging (MOI) described in the experimental part.

MOI allows observing the screening of the magnetic field by superconductor or trapped in its magnetic flux. It only works when superconducting current is of considerable magnitude. Here this technique is used on one of the GdOH films deposited on $SrTiO_3$. In the experiment, magnetic field of 18.7 mT was applied perpendicular to the film at temperature of 5.9 K. After that, it was reduced to zero allowing trap of magnetic field and the development of persisting supercurrent in the case the film is superconducting. This was followed by the increase of temperature and record of MOI images at selected temperatures. Since sensitivity of MOI indicator films is limited, differential imaging was used subtracting MOI images recorded at different temperatures.

In Fig. 1.4, two differential images are shown. The top image shows MOI map recorded at 5.9 K, from which the MOI map recorded at 20 K was subtracted, and the bottom image shows MOI map recorded at 16 K, from which the same 20 K MOI map was subtracted too. The outline of the square sample behind the indicator film is clearly seen on the top image (pointed by white arrow), while it is not seen on the bottom image. The form of the outline is typical for a superconducting film with a

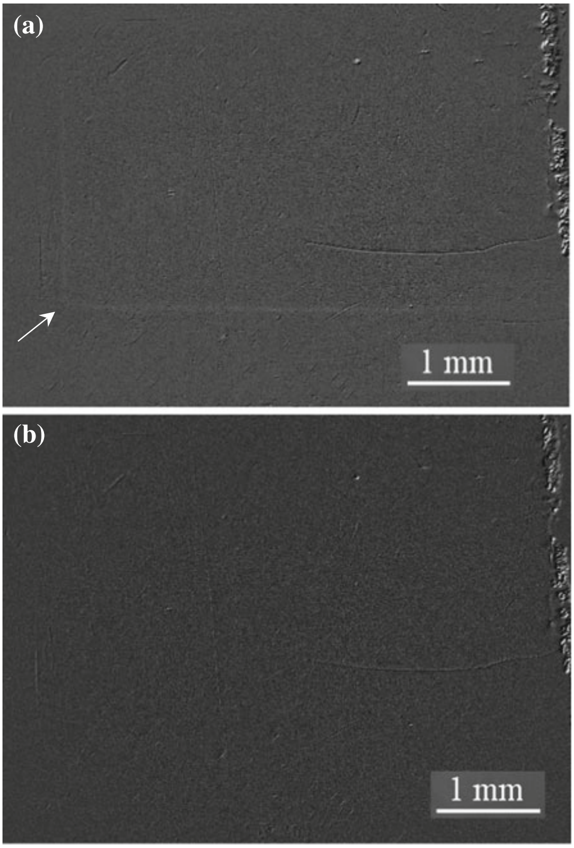

Fig. 1.4 Differential images for a GdOH film deposited on $SrTiO_3$ single-crystalline substrate. **a** MOI map recorded at 5.9 K, from which the map recorded at 20 K was subtracted. **b** MOI map recorded at 16 K, from which MOI map recorded at 20 K was subtracted too

trapped magnetic field. Two images are shown to ensure that there is no instrumental artifact, in which case the outline of the sample would be present on the bottom image too.

The recorded MOI signal in the top image is not strong. It is much weaker than, for example, in epitaxial films of high-temperature superconductors. In spite of that, this is an important result as GdOH might be the first oxyhydride with reasonably high T_c, superconductivity in which is confirmed by MOI. The weakness of the signal, however, indicates that conditions of GdOH film preparation and oxidation still need to be improved.

It is currently not clear what critical temperature of the optimally prepared GdOH would be. A double transition typical to superconducting granular systems is observed in Figs. 1.1, 1.2 and 1.3, but the top transition at a temperature of about 200 K could not be related to superconductivity. In the MOI, the trapped magnetic field effect disappears at temperatures about 16 K, but this technique is not very sensitive. This suggests a necessity for a more extensive experimental study of GdOH films with better control over preparation and handling, and perhaps with the deposition of protective layer, to not allow over-oxidation and loss of hydrogen.

In conclusion, electrical transport and magneto-optical measurements on hydride films of GdOH reveal interesting features that could be related to anion superconductivity in a novel class of superconducting materials from the family of oxyhydrides with suggested dominant electron-electron interaction providing the formation of Cooper pairs.

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