Construction of a setup for Ultrafast Electron Diffraction

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Chapter 5 Outlook: Superconducting properties of MgB$_2$ thin films grown on Mg(0001) studied by Ultrafast Electron Diffraction

One of the experiments that our Ultrafast Electron Diffraction (UED) setup is particularly equipped for is a study into the lattice changes upon the superconducting phase transition in MgB$_2$. Preparations of this experiment have been carried out but the experiment itself is something that is still to be done. This chapter introduces superconductivity in general and the very particular superconductor MgB$_2$ in more depth. The growth of thin films of MgB$_2$ is discussed, as well as the outcome of a complementary study with Angle Resolved Photoemission Spectroscopy (ARPES). Finally, a UED experiment on a superconducting cuprate is discussed to put this potential study in a context.

5.1 Introduction

In the 100 years since the discovery of superconductivity in mercury at temperatures below 4.2 K by Kamerlingh Onnes in 1911 [1-3], a lot of theoretical and experimental research has been carried out on this topic. A theoretical model of the phenomenon was proposed by Bardeen, Cooper and Schrieffer [4] in 1957 with their BCS-theory of superconductivity, in which so-called Cooper pairs consisting of two electrons (interacting through the exchange of phonons) can travel freely through materials at temperatures below the critical temperature ($T_c$). About half of the elements are superconducting and the typical $T_c$ values are in the liquid helium regime. To extent the use of this phenomenon for practical applications, a lot of effort has been devoted to achieving so-called high-temperature superconductivity, i.e. superconductivity at liquid nitrogen temperature (77 K) or higher. Most of the high-temperature superconductors are not simple metals (or conventional superconductors) but very special compounds (unconventional), among which cuprates are the category with the highest $T_c$ (see for example [5]), reaching above 150 K. The investigation of high temperature superconductivity is of great importance because superconductors make it possible to transport currents without heat loss. Applications are electromagnets in both scientific and medical (e.g. MRI) equipment but if the operational temperatures were higher, superconductors could find a plethora of uses such as
electric generators and motors, transformers, high power cables etc. To reach that goal it is crucial to fully understand this very non-intuitive state of matter from a fundamental point of view: why do very different materials show a resistance of exactly zero after going through a very sharp phase transition? Explaining superconductivity beyond BCS theory, which is now known to be valid only for a limited number of superconductors, is therefore one of the holy grails of contemporary condensed matter physics.

Until recently it was believed that all superconductors are of type 1 or type 2, depending on whether they exhibit a first order or second order phase transition from their normal phase to their superconducting phase. To understand this, it is important to know that besides being cooled below the critical temperature, there are two more conditions that have to be fulfilled for a material to exhibit superconductivity: the magnetic field to which the material is exposed must be below a characteristic value known as the critical magnetic field \(H_c\) and the current passing through a given cross-section of the material must be below a characteristic level known as the critical current density. The two types of superconductors differ in their magnetic properties. A type 1 superconductor has one critical point (temperature, applied magnetic field) below which it is in the superconducting state and completely expels low external magnetic fields. A typical phase diagram of such a superconductor is shown in Figure 5.1, left panel. A type 2 superconductor has two critical points, for the critical fields, \(H_{c1}\) and \(H_{c2}\). Below \(H_{c1}\) the material is just like a type 1 superconductor, while between \(H_{c1}\) and \(H_{c2}\) there exists another phase: the vortex state. In this state, an external magnetic field can produce quantum vortices, which can carry magnetic flux through the interior of the superconductor. A typical phase diagram of a type 2 superconductor is shown in Figure 5.1, right panel.

As of 2001, a lot of attention was drawn to the discovery of superconductivity in magnesium diboride (MgB\(_2\)), which turned out to have a critical temperature as high as 39 K [6], the highest so far for conventional superconductors and higher than expected from BCS-theory. The structure of MgB\(_2\) is shown in Figure 5.2.

The behaviour of MgB\(_2\) is anomalous in that one can distinguish two superconducting components associated with electrons belonging to different bands having different energy gaps but resulting in one single \(T_c\) due to finite
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coupling [7,8]. In fact, MgB$_2$ simultaneously has magnetic properties of type 1 and type 2 superconductors because of the interaction between the two bands and this is why Moshchalkov et al. [9] called this superconductivity type 1.5. In MgB$_2$ the pairing of electrons in the superconducting phase arises from attractive interactions between the electrons that are mediated by atomic vibrations as verified by isotopic replacement experiments and explained by several computational groups [10-12]. In this chapter we discuss two approaches of studying the electron phonon coupling in MgB$_2$ to get an understanding of the striking differences in transition temperature between cuprates, MgB$_2$ and conventional (metallic) superconductors.

Another scope of this project is to explore what happens when the dimensions of the crystal are shrunk to a level where two effects become important: quantum size effects and proximity effects. For lead, a conventional superconductor, it has recently been shown that superconductivity persists even in an only two-layer thick crystal [13] and quantum oscillations of $T_c$ were observed in samples with up to more than 10 layers. For MgB$_2$(0001) films grown on Mg(0001), the situation is more complicated due to stress in the sample, which is induced by a lattice parameter mismatch between the substrate and the thin film. Based on theoretical calculations [10] we expect that due to an increase of the lattice parameters, the density of electronic states and the electron phonon coupling will be enhanced. BCS model calculations in the tight binding approximation [14] predict that <4 layers thick MgB$_2$ films exhibit a severe decrease in $T_c$. $T_c$ oscillates sharply with thickness, shows a maximum at 5-6 layers, and at higher thickness
reaches the bulk value. Furthermore, it is well known that when a superconductor is placed in contact with an ordinary metal, like in our case, its superconductivity can be suppressed due to proximity effects, i.e. the Cooper pairs can diffuse into the metal. Several attempts have already been made in designing properties of \( \text{MgB}_2 \) using these effects, however, only few groups succeeded in modifying \( T_c \) in a \( \text{MgB}_2 \) film by changing the lattice parameters [15,16].

The research described in this outlook builds on the possibility to epitaxially grow very thin layers (down to 1 ML) of \( \text{MgB}_2 \) on \( \text{Mg}(0001) \) [17]. This allows us to investigate confinement and proximity effects in this material. ARPES experiments on thin \( \text{MgB}_2 \) films have been carried out and clarify the role of the film thickness and of the lattice parameters in driving the superconducting properties, of which the results are submitted for publication [18] and discussed below. Ultrafast Electron Diffraction (UED) can be used to complement the discussion of the electron-phonon coupling from the side of the lattice.

5.2 Preparation of \( \text{MgB}_2 \) thin films and Surface X-ray Diffraction
The \( \text{MgB}_2 \) films were grown in situ by molecular beam epitaxy (MBE) from pure Mg and B sources on a \( \text{Mg}(0001) \) single crystal, as reported earlier [19]. The \( \text{Mg}(0001) \) surface was prepared with cycles of sputtering and annealing at 493 K. For thin layers (thickness < 4 ML), deposition of B was sufficient, whereas for thicker layers co-deposition of Mg and B was necessary. The pressure was kept below \( 1\times10^{-9} \) mbar during the co-deposition, the substrate was held at 475±15 K and an atomic flux ratio Mg:B=3:2 was maintained. The evaporation rates were
calibrated from the attenuation of the substrate core level photoemission peaks when evaporating B on Mg(0001) and Mg on a copper plate at room temperature (RT). The MgB$_2$ ML is defined according to the standard used in previous works [17,19].

Surface X-ray diffraction (SXRD) experiments provided information about the crystalline structure of the grown films. The experiments were carried out at the ALOISA beamline [20] of the Elettra synchrotron, Trieste, Italy. The in-plane lattice parameter was determined by collecting radial scans across the substrate (110) reflection, while the inter-layer distance was obtained from the substrate (002) reflection. In both cases, line scans in the reciprocal space were obtained by scanning the photon energy at constant scattering geometry, in order to follow the thickness evolution of the film satellite peaks, hence the strain of the MgB$_2$ film with respect to the Mg(0001) substrate [17]. Figure 5.3 shows the recorded lattice parameters versus MgB$_2$ film thickness.

At low coverage the in-plane distance (upper panel) expanded and interlayer distance (lower panel) contracted to match the Mg(0001) substrate values. For the first monolayer the diffraction peaks of the MgB$_2$ film could not be

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**Figure 5.3:** In-plane lattice parameter (upper panel) and interlayer distance (lower) versus the MgB$_2$ films thickness (in ML), as obtained by means of surface x-ray diffraction. The dashed lines indicate the values for bulk Mg [19] and MgB$_2$ [20], respectively.
distinguished from those of the Mg(0001) substrate. By increasing the film thickness the lattice parameters were found to evolve towards those of bulk MgB\(_2\), which were reached for a thickness of about 8 ML for the interlayer distance and \(ca.\) 4 ML for the in-plane lattice parameter. For higher coverage the lattice parameters matched those of the bulk material.

5.3 Angle-resolved Photoelectron Spectroscopy

Angle-resolved Photoelectron Spectroscopy (ARPES) is a technique to study the band structure of crystals. When performing ARPES, samples are irradiated by photons, whose energy is used by valence band electrons to escape from the material (photoelectric effect) and these photoelectrons are collected under different angles of emission. Thus the special property of ARPES is that anisotropies in the occupied density of states can be detected in the experiments: under different angles, different values of the binding energy of electrons in a certain state can be found and in this way, the band structure of the material under investigation can be reconstructed.

Low-temperature (LT) ARPES measurements were performed with a photon energy of 9 eV in the region of the Brillouin zone where the surface state S and the \(\sigma\) band cross \[18\]. Specifically, we focused on the opening of a gap at the Fermi level for the surface state, S, which, as reported for bulk MgB\(_2\), has a width comparable to that of the gap of the \(\sigma\) band \[21\]. However, the determination of the gap opening for the S band is easier because of the higher photoemission intensity of this state as compared to the \(\sigma\) band. Spectra were acquired for 1, 4, 6 and 8 ML thick films, below and above the bulk \(T_c\) (39 K). The results are shown in Figure 5.4, together with the spectrum of the Fermi level region of the polycrystalline Ta foil measured at 10 K, which was used as a reference for the position of \(E_F\). A shift towards higher binding energy of the spectral leading edge from the position of the reference \(E_F\) is interpreted as the opening of a gap \(\Delta\) \[22\].

The position of the spectral edge in the valence band spectra of the 1 and 4 ML thick films remained the same at all temperatures and the saddle point along the slope coincided with the \(E_F\) position of the Ta foil that served as a reference. In contrast, a change in the position of the spectral edge with temperature was observed for the 6 and 8 ML thick films. Moreover, this modification occurred only for spectra acquired below the bulk \(T_c\). We assign these changes to a
decrease of the density of states at the Fermi level and we conclude that this is compatible with the opening of a superconducting gap only in films of 6 MLs or thicker. Figure 5.5 (a) presents the detailed spectra of the Fermi level region acquired for the 6 and 8 ML thick films at 20 K. The fitting gave a value for the gap.
width $\Delta(20\,\text{K}) = 3.0 \pm 0.2$ meV for the 6 ML thick film and $\Delta(20\,\text{K}) = 3.4 \pm 0.2$ meV for the 8 ML thick film.

The gap width determined at different temperatures allowed for an estimate of the critical temperature of the film and of the value of the gap at $T=0$ K, according to the approach proposed in [11]. The values of the gap width vs. the temperature of the sample were fitted with the expression $\Delta(T) = \Delta(0)[1 - (T-T_c)^p^{1/2}]$, where $\Delta(0)$ is the gap at 0 K and $T_c$ is the critical temperature of the film. In Figure 5.5 (b) we show the result obtained for the 6 ML thick film. $T_c$ for this film was found to be $31 \pm 10$ K and the parameters $p = 2.4 \pm 0.9$ and $\Delta(0) = 3.6 \pm 1.5$ meV were extracted. For comparison, the curve obtained for the gap opening at the $\sigma$ band in bulk MgB$_2$ is shown, where $T_c = 39.1$ K, $p = 2.9$ and $\Delta(0) = 6.8$ meV [11] is also plotted [18].

We collaborated with the groups of Milorad Milosevic and François Peeters of the University of Antwerp, who performed theoretical calculations to interpret the experimental results [18]. From density functional theory (DFT) they could conclude that all samples with a few MLs of MgB$_2$ are Mg-terminated. They used density functional perturbation theory (DFPT) to calculate the phonon spectrum and electron phonon coupling. To unravel the origin of the measured superconductivity in the surface band, fully anisotropic Eliashberg theory was

Figure 5.5: (a) Detail of the ARPES spectra of the Fermi level region collected for 6 and 8 ML thick MgB$_2$ films at 20 K. The fit for the acquired data is reported as solid line. (b) Temperature dependence of the superconducting gap for a 6 ML thick MgB$_2$ film. The dashed line represents the fit to the data, while the solid line indicates the temperature dependence of the gap width for a band in bulk MgB$_2$ [11].
employed with the outcomes of the DFPT calculation as an input. From this calculation they concluded that the surface states indeed form a major contribution to the superconducting phase. In a thin film of 1 up to 4 MLs, the effect of the substrate is very large (e.g. a 1 ML film, a B layer is sandwiched between two Mg layers), whereas for 6 MLs or thicker samples there is a large similarity of the phonon spectrum with the bulk and the effect of the substrate is negligible. On the other hand, the situation of the electronic bands is still very different between a 6 ML thin film and the bulk. The surface contribution to the density of states (DOS) is pronounced in the thin film case, resulting in a profound influence on the multi-gap nature of the material. The role of the surface states is confirmed by the fact that the calculated $T_c = 33$ K of the surface band is in good agreement with the experimental value (31 K) and also the value for the calculated gap at 0 K (3.3 meV) is in good accordance with the experimental result (3.6 meV) [18].

5.4 Ultrafast Electron Diffraction and Superconductivity

UED has already proved to be a useful tool to study the mechanism behind superconductivity. Fabrizio Carbone et al. studied electron phonon coupling in superconducting cuprates from the Bi-Sr-Cu-Ca-O family [23]. They studied the role of doping and polarization of the excitation with respect to the sample orientation. From the experiment they concluded that simple 2D models are not sufficient to describe the whole phenomenon of superconductivity and that anisotropic carrier-phonon coupling must be taken into consideration.

Also for MgB$_2$ the significance of the interaction of the superfluid with the lattice is still debatable and there is still very little known. An experiment similar to the one performed by Carbone et al. would give insight into the role that the coupling to the lattice plays for superconducting properties in this material. Due to the advanced surface science preparation chamber and the UHV conditions, our UED setup would be very suitable to perform this experiment. The material would have to be grown in the way described earlier in this chapter and in situ characterised by XPS for the thicknesses of interest. The sample should then be cooled below the phase transition temperature and the UED data collected in reflection geometry, following the transient diffraction intensities corresponding to the MgB$_2$ thin film when the superconducting state is suppressed and subsequently recovered. This would provide essential information to complete
and confirm the insight in the role of the lattice and the surface state in the superconducting phase of MgB₂.

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