Superconductivity by Electrochemical Intercalation of Copper into Bi$_2$Se$_3$ Crystals

Berend Zwartsenber (5935644)

September 12, 2011

Abstract

In this research project a new method of preparation for the reported superconductor Cu$_x$Bi$_2$Se$_3$ is investigated. The technique used is electrochemical intercalation. A pure sample of the topological insulator Bi$_2$Se$_3$ is used as the starting material and copper is successfully integrated into the crystal. Samples are either annealed or studied directly after processing. Resistance and susceptibility are measured. Resistance measurements show a transition at temperatures ranging from 1.5 to 2.4 Kelvin, but the largest resistance drop is only 65%. Susceptibility measurements do not show any transition therefore the volume fraction that is superconducting should be very small. Furthermore, samples that were not annealed were never found to be superconducting. These results are discussed in the light of literature concerning this compound. Suggestions are made for an improvement of the process.

Supervisor: Dr Y. Huang

Second corrector: Prof. Dr M.S. Golden

Verslag van Bachelorproject Natuur- en Sterrenkunde, omvang 12 EC, uitgevoerd in de periode 09-05-2011 tot 13-07-2011
Contents

1 Introduction 3

2 Theory 3
   2.1 Topological insulators: Bi$_2$Se$_3$ ................................................. 3
      2.1.1 Insulators ................................................................. 3
      2.1.2 Topological insulators ............................................... 4
      2.1.3 Bi$_2$Se$_3$ and doping with copper .................................... 5
   2.2 Superconductors .............................................................. 5

3 Experimental techniques 6
   3.1 Growth of Bi$_2$Se$_3$ single crystals ........................................ 6
   3.2 Electrochemical intercalation ............................................... 6
   3.3 Determining Cu concentration ............................................. 8
   3.4 Preparation process .......................................................... 8
   3.5 Resistance and susceptibility measurements ............................ 9
   3.6 SEM and EPMA measurements ............................................... 9

4 Results 9
   4.1 Susceptibility ................................................................. 10
   4.2 Resistance ................................................................. 10
   4.3 SEM and EPMA ............................................................ 13

5 Discussion 15
   5.1 Comparison with original paper ......................................... 15
   5.2 Inhomogeneity of the sample .......................................... 15
   5.3 Annealing ................................................................. 15

6 Conclusion 17

7 Acknowledgements 17
1 Introduction

Bi$_2$Se$_3$ is one of the few known topological insulators today. At the moment, topological insulators are at the front line of research. Early 2010 Y. S. Hor et al. reported superconductivity in copper doped Bi$_2$Se$_3$ with an onset at 3.8 K [1]. The results however were not all that satisfying: resistivity measurements did show a relatively sharp drop, but zero resistivity was not reported. In March 2011 a group from Osaka did obtain zero resistance, a shielding fraction of more than 43% and convincing specific heat measurements[2], having synthesised the Cu$_x$Bi$_2$Se$_3$ using a different technique. Earlier research, including the research at the quantum electron matter group at the van der Waals-Zeeman institute, used crystals grown in a similar way as pure Bi$_2$Se$_3$, by just adding copper to the starting materials. The group from Osaka on the other hand used electrochemically intercalated single crystals of Bi$_2$Se$_3$. In this process copper ions enter the crystal due to the electric field applied. At the start of this project zero resistance could not be achieved using the regular technique, making the investigation of the electrochemical intercalation technique both timely and interesting.

2 Theory

2.1 Topological insulators: Bi$_2$Se$_3$

A topological insulator is -as the name suggests- an insulator. The difference is in the word topology, a term from mathematics which allows you to make a distinction between an orange and a donut. The difference being you can not deform an orange into a donut, since you would have to alter its surface by making the hole. In topological insulators this obviously manifests itself in a different way and to see this I’ll first tell a bit about insulators.

2.1.1 Insulators

(a) The band structure of a typical insulator. The valence band is in blue, the conduction band in red. The Fermi energy is indicated with a dashed black line.

(b) Band structure of a typical insulator including surface states. The surface states cross the Fermi level an even number of times.

(c) Band structure of a topological insulator including surface states related to the interface with a regular insulator. The surface states cross the Fermi level an odd number of times.

Figure 1

Insulators come in a variety of different flavours, one of which is the so called band insulator. Electrical conduction is related to the ability of electrons to move in a crystal and in a band insulator this is not
possible since there is an energy gap the electrons have to cross before they are able to reach unoccupied states. A typical band structure for an insulator can be seen in figure 1a. I assume the reader is familiar to these kind of images, otherwise the reader is referred to [3]. This band structure is a consequence of Bloch’s theorem for the periodic lattice potential of a crystal. One can intuitively see that at the boundaries of the crystal this model no longer holds, since the potential is no longer periodic in the same way as the rest of the crystal. This gives rise to a special kind of states called surface states which deviate from the normal band behaviour. In a regular insulator these surface states might look something like the green line in figure 1b. Important to note is that in systems that obey time reversal symmetry, Kramers theorem demands that the states at high symmetry points (i.e. $k = 0$ and $k = \frac{\pi}{a}$) are $2n$ degenerate, where $n$ is an integer. This means in such systems you could tune the Hamiltonian and by this change the energy of this points or the behaviour in between, but you can never lift the degeneracy and thereby “untie” this line.

2.1.2 Topological insulators

Topological insulators show very similar behaviour to regular insulators in the bulk but there is a major difference. Fu and Kane show that there is a topological parameter in every material which is defined by the parity of the states of all the bands at the high symmetry points (e.g. the $\Gamma$ point)[4]. This topological parameter is intrinsic to the bulk of the material and therefore cannot be changed by tuning the Hamiltonian (like the inability to make a donut out of an orange by just deforming - but not perforating - the surface). The phenomenon occurs for example in $\text{Bi}_2\text{Se}_3$ if a strong spin-orbit interaction is included in the calculation for the energy levels and this is shown in figure 2 [5]. In this image the energy states are calculated step by step and in the final step when the spin-orbit interaction is turned on two states cross the Fermi energy (dashed line). When this happens, both valence band (below the Fermi energy) and the conduction band (above the Fermi level) change parity which is called band inversion. This implies the material now is of a different topological order. If you now regard an interface between such a topological insulator and a regular insulator you will find surface states that relate the bulk of the regular insulator to the bulk of the topological insulator. These however, look a bit different from the surface states discussed for regular insulators and a typical example is shown in figure 1c. Note that states at the high symmetry points are still degenerate as Kramer’s theorem demands, but in this case the Fermi level is crossed only once. This means that although the Hamiltonian could be altered and therefore the in-gap bands could be deformed, Kramers theorem still has to be obeyed and the surface states cannot be shifted in such a way they don’t cross the Fermi level. In practise this means that
the interface between a topological insulator and a regular insulator is conducting and shows metallic behaviour. A deeper discussion on topological insulators is beyond the scope of this report but for those interested I suggest to read [4-6].

2.1.3 Bi$_2$Se$_3$ and doping with copper

Bi$_2$Se$_3$ is one of the materials that is of different topological order than regular insulators. As one would expect the material is made from elements with a high atomic number inducing a strong spin-orbit interaction (for a more detailed description see [7]). Bi$_2$Se$_3$ is a layered crystal and its structure can be seen in figure 4. The layers consist of Se-Bi-Se-Bi-Se quintuplets. The atoms in each plane have a hexagonal structure. Every layer of five is only bonded weakly to the other by the van der Waals interaction, making the crystal easy to cleave perpendicular to the c-axis. The material is a bulk insulator with a bandgap of $\sim 0.3$ eV [5], but since it is of different topological order, special states show up at the surface. Figure 3 shows a measurement of the similar compound Bi$_2$Te$_2$Se, compound taken with angle resolved photo-emission spectroscopy (ARPES). This material shows the same behaviour in the band structure as Bi$_2$Se$_3$. One can see the valence band at the bottom of the graph (white) and also the metallic surface states are visible (yellow-black cross).

In prepared crystals of Bi$_2$Se$_3$, selenium is usually present in a lower concentration than the nominal “3”. Research has shown this is due to selenium vacancies in the crystal [8]. As shown in figure 4, selenium is present in the minus two oxidation state and if there is a vacancy, the bismuth atoms have spare electrons since there is no selenium to take them. Therefore the pure material with selenium vacancies is n-type with a carrier concentration of $2.2 \times 10^{19}$ cm$^{-3}$ [8]. The material can be doped with copper to tune the carrier concentration. Two possibilities are to substitute copper for bismuth (Cu$_x$Bi$_{2-x}$Se$_3$) or put copper in between the quintuplet layers (Cu$_x$Bi$_2$Se$_3$). The structure of the latter is shown in figure 4. It is believed that copper in this crystal is in the Cu$^+$ oxidation state [8]. If copper is singly oxidised and takes the bismuth sites, the doping should be p-type, since the formal charge goes from +3 to +1. If copper goes on an interstitial site (i.e. in between the layers), it donates an extra electron to the lattice and therefore the doping should be n-type. These effects are both experimentally confirmed in [8].

2.2 Superconductors

Electrical conductivity is made possible by the free movement of electrons and with this, the conductivity is inhibited if electrons are scattered. This scattering can be due to lattice defects or impurities in the crystal or due to the electron-phonon interaction. If a material is cooled down, the phonon contribution to scattering reduces and the resistance will go down to the point where there is only a contribution from crystal defects. This is not the case in a superconductor. As the name suggests a superconductor has zero resistance despite the defects in the crystal. A typical resistance versus temperature for a superconductor can be seen in figure 5. The resistance first goes down gradually to the point where phononic contribution to scattering is negligible. But then at a certain temperature called the “critical temperature” or $T_c$ the resistance suddenly vanishes.

In the superconducting state, electrons form so called Cooper pairs by which they lower their energy. Electrons in Cooper pairs couple through exchange of virtual phonon excitations, mediated by the electron-phonon interaction. For a more detailed description of this process and more on superconductors please refer to [3].

A superconductor also has some special magnetic properties: the material pushes all of the flux lines of
an external applied magnetic field out, reducing the field in the superconductor to zero. This is called the Meissner effect, and in this state $B = 0$. Assuming $H = \chi_m M$ gives $0 = \mu H = \mu_0 (1 + \chi_m) H$, and therefore $\chi_m = -1$. In other words, the susceptibility is minus one making the material a perfect diamagnet. On the transition to superconductivity therefore the susceptibility should drop sharply like the resistance.

3 Experimental techniques

3.1 Growth of Bi$_2$Se$_3$ single crystals

Single crystals of Bi$_2$Se$_3$ are grown using a modified Bridgman technique. This is a technique where the starting materials are melted together and then slowly cooled down in the presence of a temperature gradient. In this case the starting materials Bi (99.999% pure) and Se (99.9999% pure) are weighed to the right molar ratio and then sealed in a quartz tube under vacuum ($3 \times 10^{-7}$ mbar). Typically the total weight of the starting materials is about 5 grams. The quartz tube has a conical shape at one end where the crystal can start to nucleate. In the ideal case the crystal will grow from a point producing a single crystal. The quartz tube is placed inside a furnace and is heated to 850 °C, above the melting point for the material. The materials are allowed to mix for 12 hours after which the melt is slowly cooled down to 600 °C at a rate of 3 °C per hour. The system is then kept at 600 °C for 40 hours, after which the crystal is allowed to cool down. Large pieces of single crystals are collected. An example of a prepared batch of Bi$_2$Se$_3$ can be seen in figure 6. Samples are easily cleaved along the a-b plane, and the material is soft enough to cut perpendicular to the layers using a regular knife. The pure Bi$_2$Se$_3$ crystals are stored in a vacuum desiccator. However, over time samples do become more brittle, indicating deterioration possibly due to exposure to air during handling. The crystals used in this study were prepared earlier and at time of intercalation the samples were around 3 months old. Cu$_x$Bi$_2$Se$_3$ crystals are usually grown in the same way: a certain amount of copper (99.999% pure) is simply added to the starting materials. These types of crystals are generally heat treated before measurements are performed. In heat treatment, the samples are heated to a certain temperature, kept at that temperature for a certain time and then either cooled down slowly (annealed), or cooled down rapidly (quenched). Annealing is used among other things to redistribute atoms or get rid of unwanted substances with a low vapour pressure. Samples in this study were annealed for various times and temperatures. Annealing was performed in evacuated glass or quartz tubes. For diffusing the copper 550 °C was used, which is just under the melting point of the crystals. To remove contaminations, a lower temperature (200 °C) was used.

3.2 Electrochemical intercalation

Intercalation is the name of the process in which a substance is added in between layers of another substance. For example the layered structure of graphite is a perfect host for all kinds of substances. Graphite intercalated with calcium for instance yields a superconductor with a $T_c$ of 11.5 K [9]. Earlier research on Bi$_2$Se$_3$ for battery purposes shows that these materials are a suitable host for dopants. Bludská et al. showed that lithium intercalates easily into the layered structure of Bi$_2$Se$_3$ [10]. Previous studies have also shown that the closely related compound Bi$_2$Te$_3$ can easily be intercalated with copper which acts as a dopant [11]. Intercalation can be done in a lot of ways that involve including the dopant in the mixture for the preparation of the original crystal, evaporation followed by diffusion, chemical and others.

The technique used here is an electrochemical technique. In this process the pure crystal acts as an electrode, which is suspended in an electrolyte together with a counter electrode. A potential is applied over the electrodes and the electric field causes the dopant ions to enter the crystal. Inside the crystal, the ion is reduced to prevent charge from building up inside the sample. Meanwhile the counter electrode gets oxidised to resupply ions to the solution. A schematic view of the process is depicted in figure 7.

Figure 6: A large piece of Bi$_2$Se$_3$ single crystals.
In the case of this study the pure crystal acted as the negative electrode, and a coil of circa 10 mm in diameter and a height of around 15 mm wound from copper wire (0.8 mm diameter) was used as a positive counter electrode such that the sample was fully surrounded by the coil (figure 8a). The sample itself was tied to a copper wire of 0.2 mm diameter as can be seen in figure 8b. The small wire was suspended from a copper hook. The hook and the outer coil where connected to the power supply. In the process the outer coil will resupply the ions that are lost from the solution by the intercalation.

The electrolyte used is a solution of Copper-(I)-Iodide (CuI) in acetonitrile (CH$_3$-CN). For the acetonitrile an anhydrous HPLC grade version from Rathburn was used. The CuI was a light grey powder of 99.999% purity from Alfa Aesar. The CuI was stored under continuous dry nitrogen flow since it is believed that air deteriorates the samples, due to reaction with either H$_2$O or O$_2$. One of the reasons this particular combination of substances is used is because they are easy to obtain anhydrous. The reason a monovalent salt is used is because it is believed the copper in the sample should be singly ionised. Another reason for the use of CuI is that possible formed iodine (I$_2$) is easily removed afterwards since iodine evaporates easily when the sample is heated. The CuI solution was always saturated (i.e. a solid layer of CuI crystals was visible on the bottom of the container) so the conditions under which the preparation was done were as constant as possible. Saturation was guaranteed by a deposit of crystals on the side of the container. Solutions prepared from fresh CuI out the bottle have an amber colour, indicating some contamination which is suspected to be molecular iodine. The amber colour could be removed by dipping a piece of copper into the solution. After the piece was taken out it showed a colourful deposit which was probably due to a reaction in the solution forming a thin layer on the copper. The deposit
did not dissolve in ethanol, indicating this was not I\(_2\). Also it did not dissolve in acetonitrile, therefore it was not CuI either. However, electron probe micro-analysis (EPMA, see section 3.6) showed that there were iodine atoms in the substance, but in what form is still unclear at present.

The container used was a custom-built glass container as shown in figure 8a and figure 8c. The container has an inner diameter of 13 mm and a height of about 5 cm. On top is a rubber stopper, preventing air from getting in contact with the solution. The second function of the rubber cap is to keep the electrodes in place which are led through the rubber cap. Two glass tubes are on the side above the fluid level, to allow for a flow of dry nitrogen. This is to prevent contamination with water or oxygen from the air. As a power supply a Keithley model 2400 SourceMeter was used. The supply was set as a constant current source, meanwhile the voltage could be monitored.

### 3.3 Determining Cu concentration

Making a good estimation of the copper concentration is vital for characterising different samples. To do this, two techniques were used. Determination by weight and making use of the known current (Coulometry). The weight analysis was carried out using an analytical balance, accurate to circa half a tenth of a milligramme. The sample was weighed before and after intercalation. From the weight difference the copper concentration could be determined. There are however some difficulties with this procedure. Firstly there is the issue of inhomogeneity. If a sample is not homogenous, you can calculate an average concentration but you will never know what parts of the sample actually cause superconductivity and what copper concentrations these parts have. Secondly the weight measurement is easily affected by external factors other than the Cu intercalation. For example when the sample was not left to dry long enough, the small amount of acetonitrile added a substantial error to the weight. Also since the samples sometimes break in between layers, there is actually a lot more surface area than just the outside of the sample. This means an increase in effective porosity of the sample as a whole, leading to increased uptake of solvent through capillary action. Also, due to the brittleness, chips of the samples are easily lost when the electrode is removed. Although great care was taken with collecting these chips again some might be lost in the process. Since the desired weight increase was often very small, these effects can put a substantial error bar on the concentration determined by weight.

The amount of copper deposited in or on the sample is also easily calculated from coulometry. For every coulomb passing through the solution, one Coulomb worth of Cu\(^+\) charges is reduced, and therefore the number of copper ions transported, \(N_{Cu}\), can easily be calculated by the formula:

\[
N_{Cu} = \frac{It}{e}
\]

\(N_{Cu}\) is the number of copper ions transported, \(I\) is the current, \(t\) is the time, and \(e\) stands for the electron charge. The disadvantage of this method is that the copper wire is partially suspended in the solution, therefore copper can also deposit on the wire instead of intercalating the sample. Weighing the wire to correct for this difference would be an option, but then this would have the same drawbacks as the previous method. However, by keeping sample and electrode sizes similar, the technique is useful for a prediction within 20%, which is used to calculate intercalation times before the intercalation begins, to act as a guide for making samples with specific copper concentrations.

### 3.4 Preparation process

Single crystals of Bi\(_2\)Se\(_3\) were cut into pieces of typically 8x2 mm\(^2\) in the a-b plane of the crystal. The thickness was typically 0.5 mm. The crystals were then weighed and mounted into the setup as described in section 3.2. Crystals weighed around 30 mg. Currents between 10 and 200 \(\mu\)A were used, depending on sample weight. The container was flushed with nitrogen and the power supply was then turned on for times ranging from 2 to 20 hours, also depending on the weight of the sample. Usually in the beginning of the process a negative voltage was observed, which slowly rose to positive values after roughly ten minutes. The voltage was typically around 50 mV, but also depending on sample size and current. After intercalation the samples were washed three times in fresh acetonitrile. The wire was then removed and the sample was weighed again.
3.5 Resistance and susceptibility measurements

To test whether the samples were superconducting, resistance and susceptibility measurements were performed. For resistance and susceptibility measurements, a glass Dewar with liquid helium was used. The setup is drawn schematically in figure 9a. The outside Dewar, separated from air by a permanent vacuum, was filled with liquid nitrogen to cool down to 77 K. An inside Dewar separated from the outside Dewar by $10^{-2}$ mbar vacuum was filled with liquid helium, to cool down to 4.2 K. The helium Dewar could be pumped, to lower the pressure and by that lower the boiling point of the helium down to around 1.3 K. Susceptibility measurements were used as a quick check for superconductivity, since multiple samples could be measured at once. For susceptibility measurements a plastic capsule was used, typically filled with 4 or more different samples. This ampoule was placed inside a set of coils that allow to measure the magnetic response of the samples. For a superconductor a sharp drop in susceptibility is expected, due to the Meissner effect explained in the introduction.

To determine resistance-curves, a standard four-point measurement was used. Samples are mounted on an epoxy holder with insulating tape. Copper wires were attached with silver paint as can be seen in fig. 9b. The resistance was measured by a Linear Research AC resistance bridge connected to a computer running LabVIEW.

3.6 SEM and EPMA measurements

Scanning electron microscopy (SEM) is a technique in which a sample is bombarded with electrons in a scanning fashion, i.e. a spot, line after line. Electron probe micro-analysis (EPMA) is a technique for investigating the composition of a material. Similarly high energy electrons are fired at the sample, creating core vacancies. When a valence electron fills up the empty core state it emits characteristic x-rays. Using this technique a quantitative analysis of the sample composition can be made.

4 Results

A list of prepared samples (excluding the contaminated pieces) is presented table 1. The first samples, prepared without cleaning the solution first (i.e. removing the amber colour with a piece of copper), were contaminated by a substance similar to the material found on the electrode. The samples became really colourful and typically looked like the one shown in figure 10. The colourful pattern is most likely

1Susceptibility and resistance measurements were performed by H. Luigjes
2SEM and EPMA measurements were performed by Dr Y. Huang.
### Table 1: List of prepared samples. The concentration that is shown in the column labelled “sample” is determined by the weight difference method. In the last five columns a bar indicates not annealed or not superconducting above 1.3K and an asterisk means no measurement was taken. EPMA values were normalised to Selenium at 3, so the given concentrations are for the nominal formula Cu$_x$Bi$_y$Se$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Start weight (mg)</th>
<th>Final weight (mg)</th>
<th>Current (µA)</th>
<th>Time (min)</th>
<th>Time per weight (min/mg)</th>
<th>Annealing temp (°C)</th>
<th>Annealing time (hrs)</th>
<th>$T_c$ (K)</th>
<th>Cu$_x$ (EPMA)</th>
<th>Bi$_y$ (EPMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_{0.13}$Bi$_2$Se$_3$</td>
<td>30.86</td>
<td>31.22</td>
<td>65</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.18}$Bi$_2$Se$_3$</td>
<td>32.90</td>
<td>33.40</td>
<td>200</td>
<td>145</td>
<td>4.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.040</td>
</tr>
<tr>
<td>Cu$_{0.25}$Bi$_2$Se$_3$</td>
<td>32.19</td>
<td>32.99</td>
<td>200</td>
<td>180</td>
<td>5.6</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.32}$Bi$_2$Se$_3$</td>
<td>14.66</td>
<td>15.16</td>
<td>200</td>
<td>150</td>
<td>10.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.40}$Bi$_2$Se$_3$</td>
<td>17.92</td>
<td>18.57</td>
<td>200</td>
<td>150</td>
<td>8.4</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.73}$Bi$_2$Se$_3$</td>
<td>5.46</td>
<td>5.85</td>
<td>10</td>
<td>1200</td>
<td>218.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{1.03}$Bi$_2$Se$_3$</td>
<td>128.2</td>
<td>141.2</td>
<td>300</td>
<td>1200</td>
<td>9.4</td>
<td>-</td>
<td>-</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.13}$Bi$_2$Se$_3$-A</td>
<td>30.86</td>
<td>31.22</td>
<td>200</td>
<td>65</td>
<td>2.1</td>
<td>550</td>
<td>4</td>
<td>2.1</td>
<td>0.041</td>
<td>1.92</td>
</tr>
<tr>
<td>Cu$_{0.18}$Bi$_2$Se$_3$-A</td>
<td>32.90</td>
<td>33.40</td>
<td>200</td>
<td>145</td>
<td>4.4</td>
<td>550</td>
<td>4</td>
<td>2.3</td>
<td>0.054</td>
<td>1.79/1.91</td>
</tr>
<tr>
<td>Cu$_{0.25}$Bi$_2$Se$_3$-A</td>
<td>32.19</td>
<td>32.99</td>
<td>200</td>
<td>180</td>
<td>5.6</td>
<td>550</td>
<td>4</td>
<td>1.5</td>
<td>0.041</td>
<td>1.93</td>
</tr>
<tr>
<td>Cu$_{0.35}$Bi$_2$Se$_3$-A</td>
<td>14.66</td>
<td>15.16</td>
<td>200</td>
<td>150</td>
<td>10.2</td>
<td>200</td>
<td>50</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{0.45}$Bi$_2$Se$_3$-A</td>
<td>17.92</td>
<td>18.57</td>
<td>200</td>
<td>150</td>
<td>8.4</td>
<td>550</td>
<td>4</td>
<td>2.4</td>
<td>0.040</td>
<td>1.92</td>
</tr>
<tr>
<td>Cu$_{0.73}$Bi$_2$Se$_3$-A</td>
<td>5.46</td>
<td>5.85</td>
<td>10</td>
<td>1200</td>
<td>218.2</td>
<td>200</td>
<td>50</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Cu$_{1.03}$Bi$_2$Se$_3$-A</td>
<td>128.2</td>
<td>141.2</td>
<td>300</td>
<td>1200</td>
<td>9.4</td>
<td>200</td>
<td>50</td>
<td>-</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

to be due to a very thin transparent layer on the sample which has a thickness close to the size of the wavelength of visible light.

### 4.1 Susceptibility

Results for two sets of samples are shown in fig 11. A dip can be seen around 7 K, this is a known artifact from this setup. In these samples no significant diamagnetism is detected, hence no superconductivity is observed.

### 4.2 Resistance

A typical resistance curve is shown in figure 12, a more detailed view of the low temperature range is shown in the inset. Both cool down and warm up are shown for the same sample. For a good comparison between samples a resistivity curve is preferred over a resistance curve. Unfortunately samples showed colourful deposits on cleaving. From this we know the sample already might have some fractures, hence the real thickness of the samples can not be determined accurately. Therefore the resistance curves are normalised to room temperature resistance to allow for a better comparison between samples. For superconductivity zero resistance is expected. However none of the samples show zero resistance. In some of the samples we observed a significant drop, indicating a partial transition to superconductivity but not a bulk superconducting state. Normalised resistance measurements of superconducting samples are shown in figure 13. Samples have critical temperatures ranging from 1.9 K to 2.4 K indicated for each sample in table 1, where the $T_c$ is defined by the intersection of the lines shown.
Figure 11: A typical susceptibility measurement. The sharp dip (∼ 7 K) is a known artifact in the setup. No effects of superconductivity are visible in this graph.

Figure 12: A typical resistance measurement, with both cool down and warmup curves. The results are very similar, indicating the measurement method is fairly precise.
Figure 13: Normalised resistivity measurements for all the samples that were found to be superconducting. The inset shows the low temperature region of the same data set. The $T_c$ is determined for all the samples by taking the intersection of the black lines shown on the blue curve in the inset.

Figure 14: Normalised resistivity measurements for samples that were found to be non-superconducting.
for one of the curves in the inset of figure 13. The critical temperature
does not seem to be depending on the nominal copper concentration in the samples. All samples that
showed a partial superconducting transition had been annealed at either 500°C or 550°C. Samples that
were not annealed were never found to be superconducting and exemplary resistance curves are shown
in figure 14.

4.3 SEM and EPMA

A typical SEM result is shown in figure 15. The figure shows a large image of the cleaved a-b plane of an
annealed superconducting sample. In figure 16 various superconducting samples are shown, all of which
are annealed. All of the samples show a kind of pattern with lines of different contrast. The existence
of a pattern becomes all the clearer if one compares with a sample that was not annealed. Two SEM
images are shown in figure 17b and 17a. These are two samples from the same batch, both with the same
nominal formula Cu$_{0.18}$Bi$_2$Se$_3$, but one of them is annealed. The original sample is not superconducting
while the annealed one is. The annealed sample definitely shows more pattern. This might point to a
different structure, copper concentration or type of intercalation which may very well be related to the
superconducting properties of the sample.

Figure 15: A SEM image of the superconducting Cu$_{0.18}$Bi$_2$Se$_3$. EPMA measurements outside the red
domain give an unusual high copper concentration of $x = 0.5$ in Cu$_x$Bi$_2$Se$_3$, where the value expected
from other measurements is $x = 0.05$. The black dots, of which two are highlighted with a yellow circle,
are the spots where EPMA was performed.

All superconducting samples were measured with EPMA, and also a sample that was not superconduct-
inging. The averages of the results are shown in table 1. What is very puzzling about these results is that,
despite the differing nominal Cu concentrations determined by the weight difference, the copper
concentration in all of the samples is extremely similar and except for one case, always a lot lower. In
this one differing sample, the concentration was $x = 0.5$ instead of $x = 0.05$, except for one small domain
appearing to be visible using SEM. The border of this domain is highlighted in red in figure 15. The
small round black dots are the spots where an EPMA measurement was taken, two of which are circled
in yellow. All of the points inside the red-bordered domain show a $x = 0.05$ concentration, whereas all
points outside this domain only show $x = 0.5$. This indicates domains with high and low copper con-
centration where either the high or low concentration of copper might cause the superconductivity. This
could be investigated in future experiments by preparing samples out of such domains and performing
Figure 16: SEM images of four annealed samples, all of which are superconducting. The samples all show a patterned cleaved surface. Copper concentrations are from top to bottom, left to right: $x = 0.13$, $x = 0.18$, $x = 0.25$ and $x = 0.40$ in the general formula $Cu_xBi_2Se_3$.

Figure 17: SEM images taken from two samples with nominal formula $Cu_{0.18}Bi_2Se_3$. The annealed sample is superconducting, the other is not.

The low copper concentration EPMA results could be explained by taking the bismuth vacancies into account. Earlier EPMA measurements on $Bi_2Se_3$ have shown that if the results are normalised to take selenium to be 3, the bismuth concentration is always 1.9 instead of the expected 2. However, in the copper intercalated samples, the homogeneous copper background in EPMA added to the bismuth is always more or less two. It’s a possibility that copper takes the empty bismuth sites, then on top of that
you would have a part of the copper that actually sits in between the layers.

5 Discussion

Figure 18: Schematic view of an inhomogeneous sample. The grey area would be the non superconducting bulk, where the coloured dots denote small (schematic is exaggerated) superconducting domains with different copper concentrations and therefore possibly different \( T_c \)'s. The blue arrow indicates a possible path of lowest resistance.

5.1 Comparison with original paper

In this study we were not able to reproduce the results of the group from Osaka. The \( T_c \) reported in the literature, is always around 3.5 K whereas the critical temperatures found in this study are always significantly lower. Also our samples do not reach zero resistance. Finally, Kriener et al. report on a shielding fraction of 43%, indicating bulk superconductivity whereas the samples prepared by us do not yet show a diamagnetic signal measurable by our setup. Together this means that in the limited time we had, the technique depicted in the original paper was found to work. In the meantime our group has succeeded in growing \( \text{Cu}_x \text{Bi}_2\text{Se}_3 \) crystals that do show zero resistance by introducing the copper in the crystal growth step. Thus, the research carried out in this project project shows that although the intercalation method as set-up here does work, it is open to improvements in terms of sample quality and superconducting properties comparing to the Osaka group or our own group's one-step doping route.

5.2 Inhomogeneity of the sample

There are various explanations for the resistance not going all the way to zero. A possibility is that the transition is just very broad and that cooling down below 1.3 K would eventually bring the samples to actual zero resistance. However, the slopes of the resistance curves in figure 13 do not indicate this. A more plausible explanation is that the copper is not homogeneously distributed throughout the sample as depicted schematically in figure 18. There could be an island structure in the samples. If this is the case it would be possible to have a path from contact to contact where there are some islands in the path. If these islands were superconducting, the resistance in the path would drop substantially, but not go to zero, since there are still some non-superconducting parts. The idea for small superconducting domains in the sample is supported by the susceptibility measurements since the signal for susceptibility is proportional to the volume fraction that is superconducting. Since we did not measure a significant transition in susceptibility and did find a total resistance drop, the volume that is superconducting should be very small. This feature could possibly be investigated with transmission electron microscopy, to gain an idea of where the copper goes inside the sample. The results from EPMA also indicate an inhomogeneous sample, since the copper concentration observed in all of the samples (with the exception of one) was always substantially less than the concentration determined by the weight difference. This supports the idea of small domains and some more or less homogeneous background. To get an idea about how big these possible domains are, we measured a second sample from a superconducting batch. The results are shown in figure 19. The residual resistance ratio differs slightly and the percentage of resistance drop below \( T_c \) is lower, but the critical temperature stays the same. From this we can conclude that if there is such an inhomogeneity it is on a much smaller scale than the sizes of the samples, since the measurements were not very different.

5.3 Annealing

To obtain samples that are superconducting, our results show it is necessary to anneal although until now it is not clear what effect the annealing has. Figure 20 shows the resistance curves of two samples,
Figure 19: Normalised resistance measurement of two different samples from the same batch. The two samples show similar behaviour indicating the possible inhomogeneity is on a much smaller scale than the size of the sample (5mm).

Figure 20: Normalised resistance measurement of two samples from the same batch, of which one is annealed (suffix -A). The annealed sample is superconducting while the sample directly taken after intercalation is not. Also visible is a different shape in the curves, meaning the electrical properties above $T_c$ are also altered by annealing.
both from the same batch, however one is annealed and one is not. The sample that is annealed is clearly superconducting, where the sample measured directly after preparation is not. Also interesting to note is that the annealed sample has a more or less linear resistance curve, whereas the sample taken directly after intercalation has a broad “bump” in the curve. Looking back at other samples, all superconducting samples show similar curves, and all non-superconducting samples show this bump. Something changes during the annealing of the samples, which also alters the electrical conductivity when the sample is not superconducting. SEM shows a change in morphology, with the appearance of lines in the image, but as mentioned before it is uncertain if this feature is directly related to the superconducting properties of the sample. The annealing should affect the copper in some way though, since superconductivity is only observed in samples that are annealed at temperatures around 500-550 °C. What actually happens remains to be uncovered in future research. The copper might settle in the bismuth vacancies, or may get redistributed in some way. A curious thing to note is that samples, grown here in Amsterdam before, in which the copper is included in the original growth had to be annealed as well to become superconducting. This is strange, because at the end of the growth process the samples are already kept at a similar temperature as the one used for annealing for some time. The suspicion arises whether contact with air and annealing afterwards might be important in the process. This could be easily investigated in the future by leaving the crystals in the quartz tube after growth, and anneal straight away after the tube has cooled down.

6 Conclusion

In this research project it is shown that copper can be successfully introduced in Bi$_2$Se$_3$ by electrochemical intercalation. The process of electrochemical intercalation is neatly in accordance with our expectations regarding the theory since the copper concentration is reproducibly predictable by means of coulometry. It is also confirmed that some superconducting activity can in fact be achieved in samples of Bi$_2$Se$_3$ by introducing copper post growth by means of electrochemical intercalation. To attain these results however, the samples did have to be annealed at a temperature around 500 °C. The odd nature of the superconducting activity in the samples made in this project are probably caused by inhomogeneity or some structure with domains. This is something that should be investigated in future research by for instance doing more structural EPMA and SEM measurements on superconducting samples. Future research should also include a more detailed view on the function of annealing which should lead to a better understanding of suited temperatures and times. Furthermore it is advised that Hall measurements are performed on samples with different copper concentrations to see how the doping influences the carrier concentration. With this one can gain understanding about in what form the copper is introduced and from this one can deduce where the copper actually settles in the crystal. This may also give an insight in the slightly odd EPMA measurements discussed in this report.

7 Acknowledgements

First and foremost I would like to thank my supervisor Dr Yingkai Huang for guiding me through the whole project. Without his help I would never have been able to get this far. Also I am very grateful for the fact that I was introduced to the world of crystal growth by an expert on this terrain. His experience and knowledge kept amazing me throughout the whole project. I would also like to thank Huib Luigjes for his patience and hard work in performing susceptibility and resistance measurements. Furthermore I would like to say a very big thank you to the rest of the Quantum Electron Matter group for their hospitality and help. This thesis not have been written in this way without their feedback. Furthermore the daily lunch with everyone was always able to brighten up my day and often it helped me by getting a fresh perspective on the problem. Lastly I would like to thank all my fellow students for having a great time in the past three years. Together we battled against physics, and in every war there are casualties but in the end we won.
References


