Unconventional superconductivity in MgB$_2$: Influence of doping, intraband and interband scattering on properties of a superconductor with a double energy gap

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Niekonwencjonalne nadprzewodnictwo w MgB₂:
wpływ domieszkowania oraz rozpraszania wewnątrzpasmowego i międzypasmowego na właściwości nadprzewodnika z podwójną przerwą energetyczną

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pod kierunkiem Dr. hab. Krzysztofa Rogackiego, Profesora INTiBS

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# Contents

Acknowledgements  
1. Abstract and general goal .......................................................... 1  
2. Introduction  
   2.1. Historical background .......................................................... 2  
   2.2. Properties of MgB$_2$ compound ............................................. 3  
      2.2.1. Crystallographic structure .............................................. 3  
      2.2.2. Electronic structure ..................................................... 5  
3. Substitutional chemistry  
   3.1. Electron doping ................................................................. 9  
   3.2. Hole doping ................................................................. 16  
   3.3. Co-doping ................................................................. 18  
   3.4. Isovalent and magnetic substitutions .................................... 20  
4. Preparation of single crystals  
   4.1. Phase diagrams ............................................................... 23  
   4.2. Process of crystal growth .................................................. 26  
5. Experimental techniques  
   5.1. Thermopower measurements ............................................... 32  
      5.1.1. Experimental set-up ................................................ 32  
      5.1.2. Calibration .......................................................... 34  
      5.1.3. PC program .......................................................... 36  
      5.1.4. Measurement of small crystals ................................... 38  
   5.2. Resistivity measurements  
      5.2.1. Experimental set-up ................................................ 39  
      5.2.2. Preparation of contacts .............................................. 40  
      5.2.3. Measurement sequences ............................................ 43  
6. Results of thermopower studies  
   6.1. Undoped MgB$_2$ crystals ................................................. 44  
   6.2. Crystals doped with electrons ......................................... 45  
   6.3. Crystals doped with holes .............................................. 47  
   6.4. Crystals substituted with Mn ........................................... 48  
   6.5. Examples of co-substituted crystals .................................. 49  
   6.6. Simple model ............................................................. 51  
   6.7. Discussion ............................................................... 54  
7. Results of resistivity studies  
   7.1. Resistivity measurements ................................................. 60  
   7.2. Upper critical field ..................................................... 61  
   7.3. Theoretical description .................................................. 64  
   7.4. Discussion ............................................................... 69  
8. Conclusions ................................................................. 80  
List of publications ................................................................. 83  
Attended Conferences ................................................................. 83  
Appendix A ................................................................. 84
1. Abstract and general goal

This work presents results of the influence of doping and the inter- and intraband scattering on the properties of a two-gap superconductor – the MgB$_2$ compound. As widely known, substitutional chemistry can modify in the controlled way the electronic structure and thus other properties, such as the superconducting transition temperature, the upper critical field, and the superconducting gaps width. Depending on the valence state of the substituted atoms, the crystals can be doped with holes or electrons, or can be substituted isovalently. The introduced atoms may additionally cause some disorder into the crystal structure and, in this way, modify the inter- and intraband scattering and defect structure.

The main goal of this work was to examine the transport normal-state properties and the thermodynamic superconducting properties of MgB$_2$ single crystals substituted with various atoms, to describe the impact of doping and/or impurity scattering on these properties. During the studies, high purity MgB$_2$ single crystals with various substitutions, such as Al, C, Li, Mn, as well as co-substitutions, such as Al-Li and C-Li, have been investigated. We concentrated on thermopower and in-field resistivity properties of the MgB$_2$ single crystals, including the temperature behavior of the upper critical field ($H_{c2}$) and its anisotropy. The experimental thermopower results have been analyzed in the frame of the simplified model using the Mott’s formula within the free electron approach for the diffusive part of the thermopower. The experimental upper critical field results have been studied in the frame of the two-band model in the clean limit, for unsubstituted MgB$_2$ single crystals, and in the dirty limit, for the substituted crystals.

The obtained results allow us to distinguish between the doping and scattering effects, depending on a kind of substitutions. The fundamental properties of the two-gap superconductivity in MgB$_2$, which we have studied here, are important also from the practical point of view, since $H_{c2}$ of the C-substituted compound has surpassed that of Nb$_3$Sn. As we discuss in this work, $H_{c2}$ of MgB$_2$ can be significantly increased at low temperatures by appropriate enhancement of the impurity scattering, particularly in the $\pi$-band. Considering the weakness of the interband scattering in MgB$_2$ it seems to be possible to increase $H_{c2}$ further toward the strong-coupling paramagnetic limit by selective substitutions on Mg or B sites. Thus, understanding the mechanism of the intra- and interband scattering and the competition between scattering and doping effects we find as an important task.
2. Introduction

The discovery of superconductivity in MgB$_2$ initiated a great interest for researchers because of unique properties of this compound. Magnesium diboride has a superconducting critical temperature which is almost twice higher than those observed for other superconducting binary alloys. Also the upper critical field of MgB$_2$ is much higher than that obtained for Nb$_3$Sn, which is widely used in superconducting magnets. Additionally, the so-called weak-link problem, which limits applications of other high temperature superconductors, is strongly reduced in MgB$_2$. Cheap materials combined with high values of critical fields and currents allow to suggest that MgB$_2$ may play a dominant role for applications in the near future.[2.1] For these reasons, the electronic structure and other physical and chemical properties of MgB$_2$ are of large interest to scientists from its discovery until today. Despite the fact that the phenomenon of superconductivity in MgB$_2$ has been intensively studied and can be described in the BCS terms, a lot of questions are still open and require to be examined. One of them is a question about the influence of interband and intraband scattering on the superconducting properties. For the decade of the intensive investigations, there is no clear theoretical description of these interactions that has been published. However, it is well known, that the inter- and intraband scattering plays one of the main roles in the superconducting properties of the MgB$_2$ compound.

2.1. Historical background

When J. Akimitsu (Aoyama Gakuin University, Japan) announced at the symposium on "Transition Metal Oxides" (January 10, 2001, Sendai, Japan) the discovery of superconductivity in MgB$_2$ at 39 K, the community named it as a breakthrough in the superconductivity. The discovery was then published in Nature,[2.2] where the crystallographic structure and the temperature dependences of resistivity and susceptibility of MgB$_2$ were presented. The superconducting transition temperature, $T_c$, is almost twice higher than that for other known binary compounds.

In Fig. 2.1 a brief history of discovering of various superconductors is shown pictorially.[2.3] This Figure shows the so-called BCS-type superconductors (red circles, except of MgB$_2$ and FeAs), high-$T_c$ cuprates (blue diamonds), and several other unconventional low-$T_c$ superconductors. The MgB$_2$ and FeAs-based compounds have the highest $T_c$ amongst the metal-like (non-ceramic) compounds. As mentioned above, now MgB$_2$ is a material with the best relation between its price and the physical properties important for applications. Thus, this compound is still of a great interest for experimental and theoretical studies, both for better
understanding the new interesting physics and for optimization of the costs and high performance of the final products such as tapes and wires. The interesting physics of MgB$_2$ may consist in the two-band two-gap superconductivity, which is considered as a reason of high-$T_c$ for this material and also for recently discovered FeAs-based compounds.

![Figure 2.1. Superconducting transition temperature, $T_c$, versus year of discovery for several superconductors. Few $T_c$'s measured under pressures (marked, e.g., @30GPa) are also plotted.[2.3]](image)

### 2.2. Properties of MgB$_2$ compound

This part presents a general information on the crystallographic and electronic structure of MgB$_2$. It is interesting to note that the crystallographic structure and even electronic one were known more than 30 years ago, but during that time nobody conjectured about the existence of superconductivity in this compound.

#### 2.2.1. Crystallographic structure

The crystallographic structure of MgB$_2$ is shown in Fig. 2.2. The structure is hexagonal with a space group of AlB$_2$-type: $D_{6h}^1$–$P6/mmm$ with $Z = 1$. [2.4] Positions of atoms (in a unit cell) are as follows: Mg: 0, 0, 0; 2B: 1/3, 2/3, 1/2 and 2/3, 1/3, 1/2. Table 2.1 presents the coordination numbers and the coordination polyhedrons of each element. As shown in Fig. 2.2, one of the characteristic feature of MgB$_2$ is its layered structure, as for other high-$T_c$ superconductors. However, contrary to others, the stoichiometric MgB$_2$ is an optimally doped compound, i.e. no doping can increase its $T_c$, which is equal to 39 and 40 K, for single crystals and polycrystalline samples, respectively.
Boron atoms form 2D graphite-like honeycombed layers due to the strong covalent bonds with localized holes. Magnesium atoms are located above centers of boron hexagons. They are separated of boron layers and form quasi 3D bonds of more metallic character with delocalized holes and electrons. Table 2.2 shows the lattice parameters of MgB2. The intralayer B-B bond is much shorter than the interlayer distance and thus the B-B bonding is strongly anisotropic. However, since the intralayer bonds are only twice shorter than the interlayer ones, a finite interlayer hopping of charge carriers seems to be also possible. In graphite, for example, the interlayer to intralayer ratio is equal to 2.4. In diamond the distance between nearest neighbors is equal to 1.55 Å, like for fullerene C60 where it amounts to 1.4 - 1.45 Å.[2.6] Thus, MgB2 shows the strong intralayer bonding with weak interlayer interaction and, as a consequence, relatively large anisotropy.

Figure 2.2. Crystallographic structure of MgB2 compound. The structure consists of Mg and B layers arranged alternately.

Table 2.1. Coordination numbers and polyhedrons of Mg and B atoms in MgB2 compound.[2.4]

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Coordination number</th>
<th>Coordination polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>20</td>
<td>MgB12Mg8</td>
</tr>
<tr>
<td>B</td>
<td>9</td>
<td>BMg6B3</td>
</tr>
</tbody>
</table>

Table 2.2. Lattice parameters of the MgB2 hexagonal structure.[2.4, 2.5]

<table>
<thead>
<tr>
<th>a</th>
<th>c</th>
<th>c/a</th>
<th>B–B intralayer distance, ( a/\sqrt{3} )</th>
<th>B–B interlayer distance</th>
<th>Mg–B distance, ( \sqrt{a^2/3 + c^2}/4 )</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å)</td>
<td>(Å³)</td>
</tr>
<tr>
<td>3.0834</td>
<td>3.5213</td>
<td>1.142</td>
<td>1.780</td>
<td>3.520</td>
<td>2.504</td>
<td>29.01</td>
</tr>
</tbody>
</table>
2.2.2. Electronic structure

In MgB$_2$ the electronic states at the Fermi level are mainly $\sigma$- and $\pi$-bonding orbitals of boron. The $\sigma$- and $\pi$-bonding states are confined in boron planes and out of the planes, respectively. The $\sigma$-bonding states couple strongly to the in-plane vibrations of B atoms and this results in formation of Cooper pairs with the energy gap $\Delta(0) \approx 7$ meV. The $\pi$-bonding states reveal much weaker coupling to the lattice vibrations and thus the characteristic energy gap $\Delta(0)$ is equal to about 2 meV.[2.7] Figure 2.3 shows the $\sigma$- and $\pi$-bonding states at the Fermi level originated from boron $p_{x,y}$ and $p_z$ orbitals, respectively.

![Figure 2.3. Bonding states at the Fermi level of MgB$_2$: (a) $\sigma$-bonding states originated from boron $p_{x,y}$ orbitals, and (b) $\pi$-bonding states originated from boron $p_z$ orbitals.[2.7]](image)

Fermi surface of MgB$_2$ was reported long before the discovery of superconductivity in this compound. The Fermi surface consist of four separated sheets, as shown in Fig. 2.4.[2.8] Two of them (colored in red and orange), which look like cylinders, are originated from the $\sigma$-bonding $p_{x,y}$ orbitals of boron and formed around the four $\Gamma$-A lines. Other two (colored in blue and blue-green), which look like webbed tunnels, are originated from the $\pi$-bonding $p_z$ orbitals of boron and formed around K-M and H-L lines. The smaller cylindrical $\sigma$ sheets (shown in red) have superconducting energy gap of about 7.2 meV with small deviation which is less than 0.1 meV. The wider cylindrical $\sigma$ sheets (shown in orange) have superconducting energy gap which ranges from 6.4 to 6.8 meV. They have a maximum near $\Gamma$ and a minimum near A. On the $\pi$ sheets (shown in blue and green) superconducting energy gap ranges from 1.2 to 3.7 meV. The temperature dependence of the superconducting energy gaps for $\sigma$ and $\pi$ bonding states is shown in Fig. 2.5. Values of the gaps, $\Delta_\sigma$ and $\Delta_\pi$, are greatly different below $T_c$. Both gaps, however, vanish simultaneously at the transition temperature.
The total density of states (DOS) at the Fermi energy is 0.12 states per eV-atom-spin. The $\sigma$ sheets contain 44% of states and the other 56% of states belong to the $\pi$ sheets.[2.7] The holes at two unfilled $\sigma$-bands are localized within the B layers and show 2D properties. The holes and electrons at two $\pi$-bands are delocalized and reveal more 3D properties. As the 2D covalent and 3D metal-like states contribute roughly equally to the total density of states at the Fermi level,
charge carriers from both $\sigma$-bands and $\pi$-bands are expected to contribute significantly to the transport properties of MgB$_2$. For superconductivity, more important are the unfilled (hole-like) $\sigma$-bands, which experience strong interaction with longitudinal vibrations (optical E$_{2g}$ phonons) present in the B layers.[2.6] The $\pi$-bands are only weakly coupled to phonons and thus are much less important. The longitudinal vibrations in the B layers are shown schematically in Fig. 2.6. In this Figure, when B atoms move in the arrow directions, the shortened bonds (marked by $A$) become attractive to electrons, while elongated bonds (marked by $R$) become repulsive.[2.7]

![Figure 2.6. Longitudinal vibrations of boron atoms which couple strongly to $\sigma$-bonding electronic states at the Fermi level.[2.7]](image)

Properties of MgB$_2$ can be changed by doping and/or modification of the intraband (in-plane) and interband (out-of-plane) scatterings. Both these effects can be obtained by appropriate substitutions. This we discuss in the next chapter.

References:

3. Substitutional chemistry

There are two types of substitution effects in MgB$_2$ important for superconducting properties. One of them is the modification of the density of states (DOS) at the Fermi level, and the second one is the introduction of various defects into the structure, which eventually results in increased quasiparticle scattering and may lead to the superconducting pair breaking. For MgB$_2$ multiband superconductor, both of these effects cause a change of the superconducting transition temperature. Therefore, to study the effects of doping and scattering on the superconducting properties of MgB$_2$ we need to study this compound with various substitutions, which may lead to:

- electron doping,
- hole doping,
- electron and hole co-doping,
- isovalent substitution,
- magnetic ion substitution.

Electron, hole and co-doping result usually in both types of effects, changing of the density of states at the Fermi level and introduction of structure defects. Isovalent or magnetic ion substitutions are related mostly to introduction of defect structure or magnetic ion network which both increase the quasiparticle scattering. The effect of various substitutions on the critical temperature $T_c$ of MgB$_2$ single crystals is shown in Fig. 3.1.

![Figure 3.1. Superconducting transition temperature, $T_c$, for MgB$_2$ single crystals with various substitutions. Aluminum and carbon introduce electrons and Li$^{+\text{+}}$ holes. Isovalent Mn$^{+\text{2}}$ is a magnetic ion.[3.1, 3.8]](image-url)
3.1 Electron doping

MgB$_2$ single crystals can be doped with electrons by introduction of aluminum (Mg$_{1-x}$Al$_x$B$_2$) or carbon (MgB$_{2-x}$C$_x$) atoms.

**Aluminum substitution**

For substitution of MgB$_2$ single crystals with aluminum two methods were developed [3.2]. Lower content of aluminum (up to about $x = 0.1$) can be introduced by a method where a part of Mg is substituted with Al in precursor. For higher content of aluminum (up to about $x = 0.3$), a disc made of Al is placed in the crucible together with Mg and B powder. Al-substituted crystals were grown at temperatures between 1860 and 1960 °C and at about 30 kbar pressure in the high temperature and high pressure cubic anvil system, as described in Chapter 4.

The amount of Al was detected by Energy Dispersive X-ray (EDX) spectroscopy. For the substituted crystals, the amount of Al is lower than in precursor and depends on the precursor composition and growth temperature. The Al-substituted single crystals used in our studies have sizes up to 1x1x0.1 mm$^3$. These crystals are listed in Table 3.1 together with their superconducting transition temperature.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{0.97}$Al$</em>{0.03}$B$_2$</td>
<td>35.5</td>
</tr>
<tr>
<td>Mg$<em>{0.92}$Al$</em>{0.08}$B$_2$</td>
<td>32.5</td>
</tr>
<tr>
<td>Mg$<em>{0.915}$Al$</em>{0.085}$B$_2$</td>
<td>33/32.5*</td>
</tr>
<tr>
<td>Mg$<em>{0.84}$Al$</em>{0.16}$B$_2$</td>
<td>28.6</td>
</tr>
<tr>
<td>Mg$<em>{0.8}$Al$</em>{0.2}$B$_2$</td>
<td>27</td>
</tr>
<tr>
<td>Mg$<em>{0.72}$Al$</em>{0.28}$B$_2$</td>
<td>15.5</td>
</tr>
</tbody>
</table>

The Four-Circle Single Crystal X-ray Diffractometer Siemens P4 has been used to determine the lattice parameters of Al-substituted single crystals. For calculation of the lattice parameters, the same set of 40 reflections recorded in the wide range of 2Θ angle (20-40 deg) have been used. The crystals with lower Al content ($x < 0.1$) were identified as single-phase material. However, for crystals with higher Al doping ($x > 0.1$), the precipitation of Al-rich (MgAlB$_4$) phase was detected. The lattice parameters $c$ and $a$ of substituted crystals are shown in Fig. 3.2 versus Al content. As expected, the parameters decrease with rising Al amount, since Al ions are
smaller than the Mg ions. It’s clearly seen that the $c$-axis parameter is more sensitive to the Al content than the $a$-axis parameter. This may reflect the strong in-plane covalent bonding and the 2D nature of the MgB$_2$ structure.

Figure 3.2. Lattice parameters $c$ and $a$ of Al-substituted MgB$_2$ single crystals versus Al content determined with EDX. Full circles indicate the lattice parameters for single-phase crystals or the lattice parameters for the main phase of multiphase crystals, as determined with a Siemens P4 diffractometer. The phase separation occurs at Al contents $x > 0.1$; for these contents the lattice parameters were determined for an averaged lattice. Opened triangles indicate the lattice parameters for crystals studied also by a Mar-300 Image Plate system. For details see Ref. 3.2.

Figure 3.3 shows the dependence of the superconducting transition temperature on the lattice parameter $c$. The transition temperature decreases systematically with values of $c$, i.e. with increasing amount of substituted Al, and shows a tendency to cluster around few values of $T_c$. This suggests that for crystals with higher Al content, additional than (Mg,Al)B$_2$ phases may occur as impurities. It is indeed the case for the crystals with $x \geq 0.1$, i.e. for Al-substituted crystals with $T_c < 30$ K. Thus special attention has been paid to the material characterization and to the interpretation of obtained results for crystals with $T_c < 30$ K used in our experiments. This we discuss in appropriate chapters devoted to the analysis of experimental results.
Figure 3.3. Superconducting transition temperature as a function of the lattice parameter $c$ of the single-phase crystals or the main $\text{Mg}_{1-x}\text{Al}_x\text{B}_2$ phase of multiphase crystals, determined with the Siemens P4 diffractometer (full circles) and with the Mar-300 Image Plate system (open triangles).[3.2]

Figure 3.4 shows examples of the results obtained from the detailed structure analysis of Al-substituted $\text{MgB}_2$ crystals with $x = 0.022$, $0.044$, $0.085$, and $0.185$. The impurity phases ($\text{MgAlB}_4$ and, most likely, $\text{B}_2\text{O}$) start to appear for the crystal with $x = 0.044$, and are clearly present for the crystal with $x = 0.185$. The Al-rich impurity phase has been studied by a High-Resolution Transmission Electron Microscopy (HRTEM). Figure 3.5(a) shows a part of the Al heavier substituted crystal which includes areas (in the white circles) with a higher Al content. Panels (b) and (c) present the superstructure reflections in the various crystallographic directions. The Al-rich areas, which were identified as $\text{AlMgB}_4$ compound, constitute about $5\%$ of the sample volume. Magnetic susceptibility measurements of all crystals contained Al-rich phases show only a single transition to the superconducting state. It means that the $\text{MgAlB}_4$ phase and other possible minor phases are not superconducting and thus they don’t influence the most important results obtained and discussed in this work, i.e. the $H_{c2}(T)$ dependences.

According to the literature, aluminum occupies magnesium sites and dopes $\text{MgB}_2$ with electrons. This doping decreases both the $\pi$-band and the $\sigma$-band energy gaps (see [3.2] and references therein). As a result, the interband scattering increases and, additionally, DOS in the hole $\sigma$-band decreases. The $\sigma$-band is the most import one for superconductivity, thus superconducting transition temperature gradually decreases with the rising doping level. Aluminum, as being substituted for Mg, is expected to change the intraband scattering mainly in the $\pi$-band, while the intraband scattering in the $\sigma$-band should be only weakly affected, if any.
Figure 3.4. Line profiles along $c^*$ of reconstructed ($h0l$) layers of Mg$_{1-x}$Al$_x$B$_2$ single crystals with various Al content. Data obtained for the crystal with $x = 0.022$ (panel a), $x = 0.085$ (panel b), $x = 0.044$ (panel c), and $x = 0.185$ (panel d) are presented. The indices of the reflections (00l) of Mg$_{1-x}$Al$_x$B$_2$ (phase I; $c \approx 3.46$ Å), MgAlB$_4$ (phase II; $c \approx 6.72$ Å) and an additional impurity (phase III; $c \approx 7.11$ Å) are shown. The peaks of additional phases are absent for the crystals AN229/1 and AN262/2, they are slightly developed for AN217/7 and are well visible for AN210/5.[3.2]

Figure 3.5. Panel (a): Z-contrast image of an area containing rectangular shaped areas with brighter contrast (white circles) for the crushed crystal of AN210/5. These areas are supposed to contain a higher Al-content. Panels (b) and (c): various types of superstructure reflections (gray circles) observed in diffraction patterns taken from regions containing Al-rich areas. Dislocations (marked by arrows) present in the crystal appear to be independent of the local composition.[3.2]
Carbon substitution

Carbon substituted single crystals were grown using the high pressure and high temperature cubic anvil system. In the precursors the following components have been used: magnesium (Fuka, >99% purity), amorphous boron (Alfa Aesar, >99.99% purity), carbon graphite powder (Alfa Aesar, >99.99% purity). For preparation of C-substituted crystals, a precursor with graphite used as a source of carbon has been used. The crystals were grown at the 1900 - 1950 °C temperature and at the 30 kbar pressure, as described in more detail in Chapter 4.

The carbon substituted single crystals were smaller than the Al-substituted crystals and grown with sizes up to 0.8x0.8x0.02 mm³. The list of C-substituted single crystals which we used in our investigations is presented in Table 3.2. The carbon content in the MgB₂ single crystals cannot be determined with satisfactory accuracy by EDX spectroscopy while for this method, C is too light element. Thus, the C content in our crystals was determined from the lattice parameter \(a\), because according to results presented in Ref. 3.3, the C content is linearly related to this parameter. Despite the fact that this method may only be a rough approximation, there is currently no better method for the C content estimation due to similar scattering factors for B and C atoms. Figures 3.6 shows the dependence of superconducting transition temperature \(T_c\) as a function of the lattice parameter \(a\) and the concentration of carbon.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(T_c), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB(<em>{1.97})C(</em>{0.03})</td>
<td>37.05</td>
</tr>
<tr>
<td>MgB(<em>{1.89})C(</em>{0.11})</td>
<td>34.50</td>
</tr>
<tr>
<td>MgB(<em>{1.80})C(</em>{0.20})</td>
<td>29.30</td>
</tr>
</tbody>
</table>

As shown in Fig. 3.6(a), \(T_c\) increases monotonically with increasing \(a\) parameter, thus according to Ref. 3.3, \(T_c\) decreases (monotonically) with the increasing C content. This relation, shown in Fig. 3.6(b), is really very useful to estimate the C content in substituted crystals from the \(T_c\) values, and we used it for our crystals, when crystallographic data were not available. The lattice parameters for few crystals from the same batch and thus with very similar \(T_c\) than our crystals were obtained to confirm the \(T_c\) versus \(a\) relation. All crystals explored in our studies were characterized at least by measuring their superconducting transition temperature by DC susceptibility technique. Figure 3.7 shows the transition to the superconducting state for several
C-substituted single crystals. The transition is relatively sharp, even for highly substituted crystals.

Figure 3.6. Variation of the superconducting transition temperature as a function of: (a) the lattice parameter $a$, and (b) the carbon concentration $x$, as obtained for a series of C-substituted MgB$_2$ single crystals.[3.4]

Figure 3.7. Magnetization versus temperature for several MgB$_{2-x}$C$_x$ single crystals with various carbon content (adopted from Ref. 3.4). The data were obtained for the zero-field-cooled (ZFC) mode and normalized to the signal at 4.2 K.

Detailed structural analysis of C-substituted MgB$_2$ single crystals have been made, as described in Ref. 3.4. Cell parameters were refined from the same set of 23 reflections in a wide range of $\theta$ angles. It was found, that C atoms are statistically distributed in the B sites with the absence of superstructure. The substituted crystals are showed a highly anisotropic broadening in the preliminary study of reflection profiles. Figure 3.8(a) shows two dimensional profiles of reflections along the $c^*$ direction in the reciprocal space for 15% C-substituted crystal. As can be
seen, this crystal shows elongation of reflections along the $c^*$ direction. On the other hand, the $a^*b^*$ plane reflections are similar to those of the unsubstituted compound.

Figure 3.8. (a) $\omega-\theta$ scan of 300 reflections of Mg(B$_{0.85}$C$_{0.15}$)$_2$; $c^*$ is parallel to the plane and to the $\omega$ axis, and $a^*b^*$ is perpendicular to the plane; the contour at 0 (dashed line), 12.5, 25, 50, 100, then contour step 100 sec$^{-1}$. The reflection of the C-substituted MgB$_2$ crystal shows an elongation in the $c^*$ direction. (b) $\omega-\theta$ scan of 300 reflections of Mg(B$_{0.85}$C$_{0.15}$)$_2$; $c^*$ is perpendicular to the plane, $a^*b^*$ is parallel to the plane, and $a^*$ is parallel to the reflection; the contour at 0 (dashed line), 12.5, 25, 50, 100, 200, then contour step 200 sec$^{-1}$. The shape of the reflections is similar to that of the unsubstituted MgB$_2$ crystal.[3.4]

The observed anisotropy of reflections indicates crystal disordering, but simple structural investigations don’t allow to determine the type of disorders. Microscopic phase separations have been suggested by Maurin et al.[3.5], but other reasons for the broadening of reflections have been also considered, such as local inhomogeneities in the distribution of carbon. Detailed refinement of the structural data indicates a small deficiency of Mg ions in the structure, which increases slightly with the C content. Additionally, the Mg ions can be shifted from the ideal positions, leading to the asymmetric coordination in the unit cells with C ions.[3.6] This effect seems to be confirmed by the small positive residual peaks, which have been observed about 0.6-0.8 Å from Mg and 1.8-2.3 Å from B (or C) position. This observation corresponds to the interatomic distances in the structure of MgB$_2$C$_2$ phase considered as impurity. More detailed structure analysis suggests that our C substituted crystals show a local disorder rather than the impurity phase, however the disorder is difficult to be characterized in detail.[3.6]
As mentioned in Chapter 2, C which occupies B sites dopes MgB$_2$ with electrons (see Ref. 3.4 and references therein). As a result, the $\sigma$-band gap decreases, due to the reduction of DOS, while the $\pi$-band gap remains practically unaffected.[3.1] At the same time, the interband scattering seems to increase, because the only reduction of DOS cannot explain the observed decrease of $T_c$ with the given amount of substituted carbon.[3.7] The critical temperature changes in a similar way as for Al substituted crystals, however 2 times smaller percentage-content of substituted C is required to observe similar reduction of $T_c$ (see Fig. 3.1) Concerning the intraband scattering, C which occupies B sites is expected to change the scattering mainly in the $\sigma$-band.

3.2 Hole doping

Lithium substitution

Lithium substituted MgB$_2$ crystals can be grown using the cubic anvil system in the same way as for growing of the unsubstituted crystals. For substitution of Li, the precursor mixture has been enriched with lithium nitride powder of different grain size (Alfa Aesar, >99.5% purity). No distinct influence of the grain size on the distribution of Li atoms in the Mg$_{1-x}$Li$_x$B$_2$ structure has been observed. The amorphous boron was annealed under dynamic vacuum to minimize the contamination by oxygen. For preparation of the precursor mixture, all the components were mixed and pressed into a glove box due to hygroscopic properties of Li$_3$N. The pressed pellets were treated as described in Chapter 4. The best conditions for growing Li-substituted crystals have been found at a pressure of about 30 kbar and a temperature of 1900-1950 °C which were held during 30 minutes. After that, the pressure and temperature were reduced to ambient during 1-2 hours. The single crystals grown in this way have sizes up to 1.5x0.8x0.1 mm$^3$ and similar golden color as unsubstituted ones (see Fig. 4.1 in Chapter 4).

The crystallographic structure of Li-substituted single crystals has been investigated using the x-ray Xcalibur PX Oxford Diffraction and Siemens P4 diffractometers. Content of Li has been determined from structure refinement as described in Ref. 3.8. As was proposed earlier theoretically, only 0.75 atoms of Mg per unit cell are necessary for the chemical bonding in the Mg$_{0.96}$B$_2$ compound.[3.9] The rest 0.21 (0.96-0.75) form the covalent bonding between Mg and B atoms along the [001] direction.[3.10] Thus Li, which provides fewer electrons than Mg, can occupy the Mg site in the MgB$_2$ structure. This has been confirmed by refinement and, additionally, by showing that atomic displacement parameters of both cations are negligible. The deviation of estimated values of the Li content is about 1-1.5%. Figure 3.9 shows the dependence
of lattice parameters on the concentration of Li in Mg\textsubscript{1-x}Li\textsubscript{x}B\textsubscript{2} single crystals. The lattice parameter \(c\) decreases roughly linearly with the Li content confirming the substitution process to be present, while the parameter \(a\) remains almost unchanged.

![Graph showing lattice parameters as a function of Li content](image)

Figure 3.9. Lattice parameters \(a\) and \(c\) as a function of Li content in Mg\textsubscript{1-x}Li\textsubscript{x}B\textsubscript{2} single crystals.[3.8]

The two-dimensional profiles of the (002) reflection for the MgB\textsubscript{2} and Mg\textsubscript{0.89}Li\textsubscript{0.11}B\textsubscript{2} single crystals are shown in Figure 3.10. These profiles were constructed from 30-40 one-dimensional scans using the P4 Siemens diffractometer. Should be noted that for both pure and Li-substituted crystals, the reflection profiles are narrow for the direction perpendicular to the \(c^*\) axis, but elongated along the \(b^*\) axis in the \(a^*b^*\) plane of the reciprocal space. This anisotropic broadening can be a result of lattice disordering. As results from Fig. 3.10, Li-substituted crystals seem to be more ordered than unsubstituted ones. This is consistent with the fact, that unsubstituted crystals show a deficiency in the Mg content of about 4-5 % and thus substitution of Li atoms may lead to better ordering of the crystal structure.

As mentioned, Li occupies Mg sites and dopes the \(\pi\)-band of MgB\textsubscript{2} with holes.[3.8] As a result, DOS in the hole \(\pi\)-band increases but, unexpectedly, \(T_c\) slightly decreases with a growing doping level. This suggests that MgB\textsubscript{2} is optimally doped compound, so any doping can only result in decreasing \(T_c\). The substitution of of Li may also enhance the intraband scattering in the \(\pi\)-band and the interband scattering as well. Table 3.3 contains a list of Li-substituted MgB\textsubscript{2} single crystals which were investigated in this work.
Table 3.3. Superconducting transition temperature of the Li-substituted MgB2 single crystals studied in this work.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mg}<em>{0.91}\text{Li}</em>{0.09}\text{B}_2$</td>
<td>36</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.91}\text{Li}</em>{0.09}\text{B}_2$</td>
<td>36.1</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.92}\text{Li}</em>{0.08}\text{B}_2$</td>
<td>37.05</td>
</tr>
</tbody>
</table>

3.3 Co-doping

In this work we also studied intriguing co-substituted MgB2 single crystals. These crystals can be divided in two groups with different types of doping. One of them constitute the simultaneous doping of the $\pi$-band with both holes and electrons. The second one is a doping of $\pi$-band with holes and of $\sigma$-band with electrons. Lithium (hole doping) is a common substituted element for both cases. Crystals with the first type of doping contains additionally Al atoms.
Crystals which belong to the second type of doping contain additionally C atoms. Table 3.4 presents a list Li-Al and Li-C co-substituted single crystals which were investigated in this work.

Table 3.4. Superconducting transition temperature of Li-Al and Li-C co-substituted $\text{Mg}_{1-x}\text{Li}_x\text{B}_{2-y}\text{C}_y$ single crystals used in our studies.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mg}<em>{0.962}\text{Li}</em>{0.02}\text{Al}_{0.018}\text{B}_2$</td>
<td>35.8</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.854}\text{Li}</em>{0.05}\text{Al}_{0.096}\text{B}_2$</td>
<td>27.5</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.812}\text{Li}</em>{0.05}\text{Al}_{0.138}\text{B}_2$</td>
<td>27.5</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.77}\text{Li}</em>{0.09}\text{Al}_{0.14}\text{B}_2$</td>
<td>26.8</td>
</tr>
<tr>
<td>$\text{Mg}<em>{0.94}\text{Li}</em>{0.06}\text{B}<em>{1.96}\text{C}</em>{0.04}$</td>
<td>35.2</td>
</tr>
</tbody>
</table>

The co-substituted MgB$_2$ single crystals have been grown in the similar way as described above for the Al, C, and Li substituted crystals. For single-substituted crystals, content of Al was determined from the EDX analysis and from the value of $c$ lattice parameter. Concentration of C was estimated from the value of $a$ lattice parameter. Content of Li was evaluated by a structure refinement. For co-substituted crystals, combination of these methods was used to obtain the Li, Al, and C contents. Li-C co-substituted crystals are black but Li-Al co-substituted crystals are more silver.

Two-dimensional profiles of the (002) reflection for the Li-C co-substituted crystal are shown in Fig. 3.11. The shapes of these reflection profiles are similar to those observed for the Li-substituted crystals. This means that single-substituted and co-substituted crystals are ordered (disordered) in a similar degree.
3.4 Isovalent and magnetic substitutions

Despite many tries, the only isovalent substitution, which we were able to carry out for MgB$_2$ single crystals, was the Mn substitution. As Mn is a magnetic element, we could not compare directly the effects of non-magnetic scattering and doping, as we wanted. This makes our data analysis difficult. However, as our excuse, we would like to state that any isovalently substituted MgB$_2$ single crystals with acceptable quality were not reported in the literature.

Similarly to others, the Mn-substituted single crystals were grown using a cubic anvil system, as described in detail in Chapter 4. The best crystals were grown at a pressure of 30 kbar and temperature of 1960 °C, reached in 1 hour, held for 0.5-1 hour, and then decreased to the room temperature during about 1 hour. The crystals have sizes up to 2.0x0.8x0.1 mm$^3$. Their high phase purity was confirmed by x-ray diffraction. The structure refinement was done and the lattice parameters were determined, as described before for other MgB$_2$ single crystals. Amount of Mn was evaluated with an accuracy of ± 0.05% by averaging of several EDX results obtained from different parts of a crystal.

Figure 3.12 shows the lattice parameters $c$ and $a$ versus Mn content, for the Mn-substituted MgB$_2$ single crystals. The $c$-axis parameter decreases much more definitely with the amount of
substituted Mn than the \( a \)-axis parameter. In this Figure (dashed lines) the lattice parameters of the Al-substituted single crystals are also shown in the same range of substitution \( (0 < x < 0.07) \), for comparison. For this range, the lattice parameters \( c \) and \( a \) changes with \( x \) in a similar way. This may suggest that the effective ionic radius for both substituted elements is similar. Moreover, it means that Mn ions enter the crystal structure in a comparable manner to Al ions, \textit{i.e.} Mn substitutes for Mg only. This suggestion has been fully confirmed by x-ray investigations, where Mn atoms were found in the Mg position only. The Mn-substituted MgB\(_2\) single crystals used in this work are listed in Table 3.5.

![Figure 3.12](image_url)

**Figure 3.12.** Lattice parameters \( c \) and \( a \) vs Mn content, \( x \), for \( \text{Mg}_{1-x}\text{Mn}_x\text{B}_2 \) single crystals (closed symbols, solid lines). The crystals are superconducting for \( x < 0.02 \). The solid lines are linear fits to the data. The dashed lines represent the lattice parameters for Al-substituted crystals.[3.11]

**Table 3.5.** Superconducting transition temperature \( T_c \) of Mn-substituted MgB\(_2\) single crystals used in our studies.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_c ), K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}<em>{0.994}\text{Mn}</em>{0.006}\text{B}_2 )</td>
<td>30.9</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.993}\text{Mn}</em>{0.007}\text{B}_2 )</td>
<td>29.3</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.986}\text{Mn}</em>{0.014}\text{B}_2 )</td>
<td>18.6</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.984}\text{Mn}</em>{0.016}\text{B}_2 )</td>
<td>12.2</td>
</tr>
<tr>
<td>( \text{Mg}<em>{0.980}\text{Mn}</em>{0.020}\text{B}_2 )</td>
<td>0</td>
</tr>
</tbody>
</table>
The magnetic and x-ray absorption spectroscopy studies revealed that Mn atoms in MgB₂ are divalent and in the low-spin configuration. Thus, no charge doping is present in that case. However, $T_c$ strongly decreases for even small amount of substituted Mn ($T_c = 0$ for $x = 0.02$; see Fig. 3.1). This effect cannot be explained by the inter- or intra-band scattering, as similar amount of substituted Al decreases $T_c$ only very slightly ($T_c = 34$ K for $x = 0.05$; see Fig. 3.1). The Mn ions are magnetic, therefore the observed drastic suppression of superconductivity has been explained as a result of strong pair breaking due to the spin-flip scattering on magnetic impurities.

References


4. Preparation of single crystals

Single crystals of MgB$_2$ used in our investigations have been prepared in the Prof. Karpinski’s High Pressure Synthesis (HPS) group at the Solid State Physics Laboratory of ETH in Zurich, Switzerland. This laboratory has equipment which allows to produce crystals that can be grown at high pressure and temperature. Single crystals of MgB$_2$ are very small; they have sizes up to $1.5 \times 1 \times 0.1$ mm$^3$ and weight up to 230 $\mu$g as maximum. The substituted crystals are even smaller, thus special techniques often have to be developed to study these crystals. Figure 4.1 shows the largest MgB$_2$ single crystals which were grown in the HPS group of the Solid State Physics Laboratory.

![Figure 4.1](image)

Figure 4.1. Examples of MgB$_2$ single crystals: (a) unsubstituted, (b) substituted with Li, and (c) substituted with Al. For (a) and (b), the scale is 1 mm.

In October 2007 I spent a few weeks at the HPS group to grow MgB$_2$ single crystals with various substitutions using a high pressure and high temperature cubic anvil system. The system (in detail) and some of my achievements are described in the next chapters.

4.1 Phase diagrams

The crystals of MgB$_2$ cannot be grown from stoichiometric melt because MgB$_2$ melts non-congruently. Bigger crystals can be grown only at high temperature and high pressure by using the cubic anvil system and by heating the mixture of Mg and B which has to be closed in metallic container. Below the Mg melting point at the ambient pressure (1107 °C) the solubility of MgB$_2$ in Mg is very low. For temperatures above 1600 °C, the solubility is high enough but the partial pressure of Mg rapidly increases up to 50 bars. Another problem is the MgB$_2$ decomposes at temperatures above 1000 °C at ambient pressure. Thus, as it was calculated, the crystals growth is possible in the conditions with the temperatures above the melting point of Mg and at a pressure from 10 to 35 kbar.
In Fig. 4.2 the region named “Liquid + MgB₂” outlines the parameters for which the growth of MgB₂ single crystals from solution in Mg is possible. For pressure $10 < p < 35$ kbar the crystals can be grown at temperatures up to 2190 °C. Figure 4.3 shows the phase diagram “temperature versus boron atomic fraction” at the pressure of 30 kbar. For this pressure, MgB₂ single crystals can be grown from solution at temperatures up to 2400 °C, as well as from the stoichiometric MgB₂ melt.
In the real experiment, the mixture of components (the precursor) is placed in BN crucible which reacts with the melt at the temperature of crystal growth. This means that liquid Mg is very aggressive toward the crucible for temperatures above 1100 °C. As was shown by Lee et al.,[4.3] MgB₂ decomposes at about 1200 and 1600 °C at 20 and 50 kbar, respectively. For these conditions, Mg reacts with BN and the reaction in the ternary Mg-B-N system has to be taken into account. Ternary Mg–B–N system together with compounds involved in the MgB₂ crystal growth is shown in Fig. 4.4. A field marked with $P$ corresponds to the composition of precursor to be used for the crystal growth.

![Figure 4.4. Ternary Mg-B-N system with compounds involved in the growth of MgB₂ single crystals][4.1]

Compositions which have been used for the crystal growth have had a ratio of Mg to B equal to 1:1.2. Excess of Mg is necessary because at high temperatures Mg evaporates very strong. Figure 4.5 shows the $P$–$T$ phase diagram of Mg–B–N system, for a composition with an excess of Mg resulting in the Mg:B ratio equal to 1:1.2. Symbols show phases observed in the samples. Empty squares indicate the MgB₂ single crystals which were grown at the relevant conditions. The MgB₄ compound was present in some samples as a secondary phase. Additionally, BN hexagonal phase and Mg were also present in all samples (not shown on diagram). The MgNB₉ compound above the dashed line appeared only as a metastable secondary phase. The best MgB₂ single crystals have been grown at 1700 °C and at pressure of 30 kbar.
4.2 Process of crystal growth

The process of crystal growth can be performed in two steps. The first step is a preliminary work which consists in preparation of the components and mixing them. The second step is the crystal growth using the high pressure and high temperature cubic anvil system.
For growing single crystals in the cubic anvil system, the following elements (see Fig. 4.6) are required:

- BN crucible with a cover,
- two pyrophyllite pellets,
- graphite cylinder with two covers,
- pyrophyllite container;
- two Ta or Mo discs.

BN crucible has a size of 6 mm internal diameter and 7 mm length. So the volume of the BN crucible is about 0.2 cm³. The graphite cylinder (with covers) is used to conduct the heating current and because this material can stand high temperatures during long time. Pyrophyllite is the Al₂Si₄O₁₀(OH)₂ compound. This material has the required specifications of elasticity and thermal conductivity at high pressure and high temperature conditions. Tantalum and molybdenum have a high melting point, thus they can be used for heating of sample up to 2000 °C and even above. Heating is realized by flowing a large current (about 400 A) through these discs, and the graphite cylinder.

As mentioned above, I have visited the HPS group of the Solid State Physics Laboratory at ETH to study the crystal growth procedure and to grow crystals. We concentrated on the synthesis of MgB₂ single crystals substituted with Li and Zn. As an example, the process of growing 15% Li-substituted single crystals will be here described. For this process, the used chemical components should meet the following relation:

\[ 8.5 \text{ Mg} + 0.5 (\text{Li}_3\text{N}) + 12 \text{ B} + \text{BN}. \]

Thus, the appropriate amounts of the components are:

\[ 0.36565 \text{ g (Mg)} + 0.03082 \text{ g (Li}_3\text{N}) + 0.22959 \text{ g (B)} + 0.04392 \text{ g (BN)}, \]

for a 0.67 gram sample, which fully fills the volume of the BN crucible. The components are carefully mixed and pressed into a pellet with about 20 ton pressure (see Fig. 4.7a). It's necessary to do that in the glove box at argon medium because Li₃N is very hydroscopic. Then the pellet is placed into a BN crucible (Fig. 4.7b), closed with a BN cover, and the whole BN capsule is placed into the graphite cylinder (Fig. 4.7c). After that, the graphite cylinder is put into the pyrophyllite cube and closed with two pyrophyllite pellets (Fig. 4.8a). Then the pyrophyllite cube is closed with two graphite discs (Fig. 4.8b) and two Ta or Mo plates (Fig. 4.8c). Finally, the cube is placed into the high pressure and high temperature cubic anvil system (see Fig. 4.9) and the growing process can be started.
Figure 4.7. Preparation of the crystal growth: a) a pressed pellet, b) the pellet in a BN crucible, c) the crucible in a graphite cylinder.

Figure 4.8. Preparation of the crystal growth: a) a pyrophyllite cube with the pellet in the graphite cylinder covered with a pyrophyllite pellet, b) two graphite covers are added from top and bottom, c) two Ta (or Mo) covers are added from top and bottom and now the pyrophyllite cube with Mg-Li$_3$N-B-BN mixture is ready to be put into the cubic anvil system.

Figure 4.9. The pyrophyllite cube with Mg-Li$_3$N-B-BN mixture in the cubic anvil system at the High Pressure Synthesis group of ETHZ.

For the growing process, the pellet consisting of Mg-Li$_3$N-B-BN mixture is pressed via pyrophyllite material and heated by current flowing through the graphite cylinder, which heats the pellet uniformly. Figure 4.10 shows the cubic anvil system at the HPS group of ETHZ. The
force is supplied by a hydraulic press and the system is configured in a way to provide uniform force acting on the sample, as shown schematically in this Figure.

![Cubic anvil](image)

Figure 4.10. The high pressure and high temperature cubic anvil system: a) general view, b) forces acting on the pellet (schematic view).

In Chapter 3 the conditions of crystal growth have been described in detail, for each type of substitutions. Usually, the single-crystal synthesis has been performed at a pressure of 30-35 kbar and at the temperatures of about 2000 °C. When the pressure of 30 kbar is applied the temperature is ramped up within 1.5 h to the maximum value of about 1700 - 2000 °C, kept for 0.5 - 3 hours (e.g., in the case of Li substituted MgB$_2$ - 1.5 h), and then the pressure and temperature are decreased to ambient conditions in 1-2 h. This process is shown schematically in Fig. 4.11.

![Temperature changes](image)

Figure 4.11. Schematic view of the temperature changes during the typical process of the MgB$_2$ single crystals growth.

When the crystal growth process is finished, the pyrophyllite cube with significantly changed volume (see Fig. 4.12) is taken from the anvil system and the pellet is removed from the cube. Finally, the pellet with potentially grown single crystals is heated to 750 °C and held for about 15 min in a dynamic vacuum to remove an excess of Mg. Figure 4.13(a) shows a graphite
cylinder with a crucible inside. Figure 4.13(b) shows a pellet removed from the crucible and heated at 750 °C in a dynamic vacuum. The BN and Mg(Li)B$_2$ single crystals strongly stick together.

Figure 4.12. Pyrophyllite cube after growing of the Mg(Li)B$_2$ single crystals in the cubic anvil system.

Figure 4.13. A view of the pellet pressed and heated in the cubic anvil system: a) before the annealing in vacuum at 750 °C, b) after the annealing, thus BN and Mg(Li)B$_2$ single crystals may be visible.

Generally, the cubic anvil system allows to grow high purity MgB$_2$ single crystals with various substitutions. Such crystals usually have the superconducting transition width of about 0.4-0.5 K, which confirms their high quality. As mentioned before, we also tried to produce the MgB$_2$ crystals substituted with Zn to obtain the isovalent substitution. The grown crystals have $T_c$ about 35 K with narrow superconducting transition width that allows us to assume that the crystals are free of any additional phases. But, unfortunately, the structural analysis did not provide any proof that Zn was substituted into the structure. No reports have been found in literature about the Zn-substituted MgB$_2$ single crystals of good quality.
References:


5. Experimental techniques

Superconducting and normal-state properties of MgB$_2$ single crystals have been investigated by:

- magnetic measurements, to characterize basic superconducting properties,
- thermopower measurements, to explore normal state properties,
- resistivity measurements, to study both normal state and superconducting properties.

The thermopower was investigated with the help of the hand-made experimental system which allows to measure the Seebeck effect in the temperature range from 10 to 300 K. Resistivity and magnetic measurements were performed in the temperature range from 2 to 300 K by using the Physical Property Measurement System (PPMS) of Quantum Design. Studies in PPMS were done in DC magnetic fields up to 9 T. To measure small single crystals (~ 0.8 x 0.4 x 0.05 mm$^3$), several experimental techniques have to be developed, as we describe in the next chapter.

5.1 Thermopower measurements

5.1.1 Experimental set-up

For the thermopower studies we have used the hand-made experimental set-up, which is shown schematically in Fig. 5.1. The measuring principle is as follows: two heaters ($H_t$ and $H_b$) keep a certain temperature difference ($\Delta T$) along the sample. Two thermometers ($T_t$ and $T_b$) measure the temperature difference and register temperature changes to control the equilibrium conditions. A nanovoltmeter (V) measures the potential difference between the top and bottom ends of a sample. All data are processed and saved with a personal computer.

Figure 5.1. Schematic diagram of the experimental set-up for measurements of the Seebeck effect. $H_t$ and $H_b$ mark top and bottom heaters, respectively, $T_t$ and $T_b$ – top and bottom thermometers, $V$ – a nanovoltmeter, and $PC$ – a personal computer.
Schematic diagram of the sample holder is shown in Fig. 5.2. A sample is placed between two copper blocks. Platinum thermometers are located close to the inner edges of the blocks. The heaters are located close to the outside edges of the blocks. Similar method to study the *thermopower of small (1 mm long) samples has been reported in Ref. 5.1, and the $S(T)$ results* obtained for constantan samples with different cross section and lengths have been discussed in detail. As shown in Fig. 5.2, the temperature difference measured by the thermometers is the sum of three differences: $\Delta T_t$ and $\Delta T_b$, which occur between the thermometers and the sample, and $\Delta T_{S}$, which appears along the sample. We have checked that for the required accuracy and at the experimental conditions we have applied, $\Delta T_t$ and $\Delta T_b$ can be neglected and the measured temperature difference assumed to be $\Delta T \approx \Delta T_{S}$. Due to this assumption and other unknown factors, an experimental error of the thermopower values was lower than 0.2 $\mu$V/K, as we show in the next chapter.

Figure 5.2. Schematic diagram of the sample holder for thermopower measurements. A sample is placed between two copper blocks. Heaters and thermometers are arranged as shown in the Figure and well thermally contacted with the blocks.

Figure 5.3 shows two photos of the sample holder without and with a plastic cover. This holder is put into a helium cryostat, where it stays at helium atmosphere. By moving the holder up and down, a temperature range from 10 to 300 K is available for measurements. A required temperature gradient can be obtained by controlling power released in heaters. For better stabilization of the temperature difference along the sample, the unit is placed into a plastic tube which increases thermal isolation. Using this sample holder, the thermopower of MgB$_2$ single crystals can be measured both in-plane ($S_{ab}$) and out-of-plane ($S_c$).
5.1.2 Calibration

Several testing experiments have been performed to calibrate the measurement system. For clarity, the calibration process has been divided into following main parts:

- correction due to detrimental thermopowers,
- estimation of the accuracy of the measured thermopower,
- determination of an optimal temperature gradient along a sample,
- testing the system by measuring the thermopower of YBa$_2$Cu$_3$O$_7$ single crystal with known $S(T)$ dependence.

Correction of the measurement system has been carried out by using the high purity antimony, which has a large value of thermopower at room temperature and this value smoothly goes to zero at low temperatures. First, the measurement system was tuned to show $S = 0$ for $\Delta T = 0$. This tuning is relatively tiny and corrects the influence of detrimental thermopowers. Then, the $S(T)$ dependence has been measured and the results are shown in Fig. 5.4. The observed behavior of $S(T)$ is characteristic for antimony.

The accuracy of the measured thermopower has been estimated by measurement of a small piece ($\sim 1$ mm$^3$) of pure (5N) lead. Figure 5.5 shows the by-us-measured $S(T)$ dependence of Pb in comparison with the reference data widely accepted as the Pb standards.[5.2] The difference between our results and the standard values is less than 0.2 $\mu$V/K in the temperature range from 20 to 300 K. Thus the relative accuracy of our $S(T)$ data has been estimated to be less than 5% at room temperature, for most of the measured MgB$_2$ single crystals ($S > 4$ $\mu$V/K). The scattering of $S(T)$ values is typically lower than 0.1 $\mu$V/K, thus the statistic relative error can be neglected.
To determine the optimal temperature gradient along the sample, the thermopower has been measured for various temperature differences ($\Delta T$) at a constant temperature. As an example, Fig. 5.6 shows the $S(\Delta T)$ results for $\text{Mg}_{0.98}\text{Mn}_{0.02}\text{B}_2$ and $\text{MgB}_2$ single crystals at $\sim100$ K and $\sim250$ K, respectively. It was possible to determine the characteristic temperature gradient above which the $S(T)$ values not depend on $\Delta T$. For $S_{ab}$ at middle temperatures (see Fig. 5.6a), the thermopower values decrease with increasing temperature gradient and then remain constant at $\Delta T \geq 2$. For $S_c$ at higher temperatures (see Fig. 5.6b), the thermopower values increase with increasing temperature gradient, however also stabilize at $\Delta T \geq 0.7$ K. Thus, both $S_{ab}(T)$ and $S_c(T)$ have been measured with $\Delta T$ from a range of 2-4 K. Exceptionally, at temperatures close to $T_c$ the temperature difference has been reduced to about 1 K, because at the transition to superconducting state $S(T)$ drops to zero rapidly.
Finally, the $S(T)$ dependence has been briefly measured, for a high quality YBa$_2$Cu$_3$O$_7$ single crystal with $T_c = 92$ K ($\Delta T_c \approx 0.8$ K). The $S_c(T)$ results are shown in Fig. 5.7. They stay in good agreement with relevant data reported in literature.[5.3] The YBa$_2$Cu$_3$O$_7$ single we measured has dimensions $\sim 1 \times 0.8 \times 0.1$ mm$^3$. Therefore we believe our experimental method is suitable to measure the thermopower of small samples, namely the MgB$_2$ single crystals.

5.1.3 PC program

Computing program has been developed to control the experiment and collect data. This program has been made by using the “Lab View 8.0” platform, produced by the National
Instruments Company. Figure 5.8 shows the main window of the workspace of this program, where the numbers denote:

1 - textbox with the sample name,
2 - graph of measured values, $S(T)$,
3 - table of stored data,
4 - switcher of the auto-manual mode,
5 - currents flowing through the heaters,
6 - resistance of the thermometers (temperature)

![Figure 5.8](image)

Figure 5.8. The main window of a workspace of the PC program which controls the thermopower measurements and collects the $S(T)$ data.

When a sample is mounted and put into a liquid He-4 transport vessel, the program can be started. Firstly, the user has to enter the name of a sample in the sample name textbox. Then, he should press the START button and input the name of a raw data file. After confirmation the program will start automatically. Next, the user has to initialize the text-boxes, which have to be filled with the values of current flowing through the top and bottom heaters. Then, when the thermodynamic equilibrium is achieved (i.e., changes of the temperature at the top and bottom thermometers are lower than the desired value), the user has to press the button MEASURE and the measured data will be stored in the raw data file. Next, the temperature is changed by moving the sample holder down in a He-4 transport vessel and the procedure is repeated. The temperature dependence of the measured thermopower values will be shown in the graph, point by point.

The PC program allows to perform the $S(T)$ measurements in manual and semi-automatic modes. In the manual mode, the user should notice that the thermodynamic equilibrium has been obtained and decide to write the data down. In the semi-automatic mode, the program determines that the equilibrium conditions are obtained and then the data are collected automatically. Both
methods require the temperature difference ($\Delta T$) to be defined by the user. The saved data (*.txt files) can be opened and worked out in the “Origin 7.5” graphic program.

### 5.1.4 Measurement of small crystals

Due to very small sizes of MgB$_2$ single crystals, fixing a crystal in the sample holder is a difficult task, especially for measurements performed along the $ab$-plane. Figure 5.9 shows the method to fix a small single crystal for the $S(T)$ measurements in the $ab$-plane. The crystal is placed in a slit cut in a thin plastic ring. To keep the crystal in this ring, an outer plastic ring with a slit has been used as a spring. This is drawn schematically in Fig. 5.9(a) and a picture is shown in Fig. 5.10(a). The whole assembly is placed between the copper blocks as shown in Fig. 5.3(a). In this method, the crystal is thermally isolated from helium gas by piece of plastic and the crystal is cooled/heated through point contacts with the copper blocks only. Such a method results in an enhanced scattering of the measured values at low temperatures.

![Figure 5.9](image)

**Figure 5.9.** Schematic drawing (top view) of the MgB$_2$ single crystal fixed in two plastic rings for measurements of $S(T)$ in the $ab$-plane. Figures (a) and (b) show the described old and new mounting methods, respectively.

![Figure 5.10](image)

**Figure 5.10.** Picture (top view) of the MgB$_2$ single crystal with dimensions of ~0.8 x 0.35 x 0.07 mm$^3$, prepared for measurements of $S(T)$ in the $ab$-plane. The inner (white) plastic ring fixes the single crystal. The outer (yellow) plastic ring works as a spring. Thickness of the plastic rings is about 0.8 mm. The whole assembly is placed between the copper blocks as shown in Fig. 5.3(a). Pictures (a) and (b) show the described old and new mounting methods, respectively.
During the experimental works, a new method to fix small crystals has been developed to assure better thermal equilibrium and to reduce the scattering of the $S_{ab}(T)$ values. For this method, a side part of the single crystal has been opened to the helium atmosphere that provided better cooling/heating of the crystal with the help of helium gas. The new mounting method is drawn schematically in Fig. 5.9(b) and a picture is shown in Fig. 5.10(b).

The proposed modification of the single crystals mounting resulted in lower scattering of the $S_{ab}(T)$ values, as shown in Fig. 5.11. The $S_{ab}(T)$ data has been obtained for the $\text{Mg}_{0.94}\text{Li}_{0.06}\text{B}_{1.96}\text{C}_{0.04}$ single crystal fixed in plastic rings by using the old and new methods. At higher temperatures, the difference between $S_{ab}(T)$ values obtained for both methods is negligible, however, for the new method, the thermodynamic equilibrium has been reached quicker. At low temperatures, the new mounting method gives better accuracy and lower scattering of the $S_{ab}(T)$ values, as can be seen in the Figure.

![Figure 5.11. Thermopower versus temperature measured along the $ab$-plane, for the $\text{Mg}_{0.94}\text{Li}_{0.06}\text{B}_{1.96}\text{C}_{0.04}$ single crystal fixed with the plastic rings according to the old (circles) and new (triangles) methods, as described in text in detail.](image)

5.2 Resistivity measurements

5.2.1 Experimental set-up

Resistivity measurements have been performed using the PPMS (Physical Property Measurement System) by Quantum Design. Figure 5.12 shows the general view and internal structure of the PPMS. To measure resistance, a single crystal is mounted on the sample holder (a puck) and placed into the center of a 9 T superconducting magnet. The crystal can be mounted with the $ab$-plane oriented perpendicular or parallel to direction of the magnetic field. An inaccuracy of the orientation has been estimated to be lower than 1 degree. Resistance has been measured with the classic four-wires method by using the AC transport mode ($f = 19$ Hz) of PPMS in the temperature range of 2-300 K.
5.2.2 Preparation of contacts

A single crystal prepared for resistance measurements is shown schematically in Fig. 5.13. Four wires are attached to the crystal glued to the glass plate. Two external wires are used to supply an AC current, two internal wires are used to measure a voltage signal. Then, the measured resistance is taken to calculate resistivity for the known crystal geometry. As mentioned earlier, MgB$_2$ single crystals are very small, thus the contacts should be prepared carefully and the geometry for calculation of the resistivity should be determined with large accuracy.

First, we prepared the electric contacts by using a two-component silver paste. Figure 5.14 shows a picture of a single crystal with the contacts made by this method. Gold wires with diameter of $\phi = 12.5$ $\mu$m have been attached by small amount of the silver paste. Due to small sizes of the single crystal it was difficult to get the electric contacts with resistance lower than 20
Ohms, which is the upper limit to obtained good quality (error < 1%) results. Also the geometry of single crystal to calculate the resistivity is too arbitrary. Fortunately, we were able to develop a method, which allows to reduce the dimensions and resistance of the contacts considerably. The main idea of this method is to flow a pulsed current through the gold wire, which touches the crystal, and to make the wire soft (close to the melting point) by heating with eddy currents. This results in a good electric contact with the resistance of few Ohms between the wire and the single crystal.

![Figure 5.14. Picture of the MgB₂ single crystal with 12.5 µm gold wires attached with the silver paste. The crystal is glued to a glass substrate with GE-varnish. For illustration reasons, the substrate was located on a piece of millimeter paper.](image)

Further lowering of the contacts resistance has been obtained by using an Ultrasonic Bonding System (UBS), made by the Warsaw University of Technology. The ultrasonic wire-bonding technique has been developed in close collaboration with the Institute of Physics PAS (Warsaw). Figure 5.15 shows a principle of the wire bonding with the UBS. This method uses aluminum wires with a combination of heat, pressure and ultrasonic energy. It is a type of solid state welding where two solids (metallic wire and a crystal) are in close contact that leads to interdiffusion and results in formation of strong bonding. The obtained contact resistance stays much below 1 Ohm and is satisfactory for our measurements. Figure 5.16 shows the pictures of two crystals with electric contacts prepared by using the UBS.

Resistance measurements have been performed in the PPMS equipped with a 9 T magnet. For measurements in a magnetic field oriented perpendicular to the \( ab \)-plane, a single crystal with a substrate was glued directly to the sample holder (a puck). For measurements in the magnetic field oriented along the \( ab \)-plane, a plastic (or metallic) cube was mounted on the sample holder and the crystal with a substrate was placed on its side. Figure 5.17 shows pictures of the sample holders with MgB₂ single crystals prepared for measurements in the magnetic field oriented along the \( c \)-axis (Fig. a) and along the \( ab \)-plane (Fig. b).
Figure 5.15. Schema of wire bonding with the Ultrasonic Bonding System; 1 - single crystal, 2 - Al wire, and 3 - metallic plate (e.g., made with Ag paint).

Figure 5.16. Pictures of MgB$_2$ single crystals (glued on the glass substrates) with electric leads (30 µm Al wires), prepared by using the Ultrasonic Bonding System.

Figure 5.17. Pictures of the PPMS sample holders with MgB$_2$ single crystals for resistivity measurements in a magnetic field oriented (a) along the $c$-axis (top view) and (b) in the $ab$-plane (side view).
5.2.3 Measurement Sequences

For resistance and upper critical field measurements, a PPMS sequence has been written, individually for every single crystal measured, considering the intrinsic physical characteristics such as the temperature of the superconducting transition, orientation of the magnetic field according to the crystal structure, composition, etc. The measurements were performed in the temperature range 2-300 K and the magnetic fields up to 9 T. The sequence is constructed in the way to cool a single crystal to the superconducting state in presence of the magnetic field, \emph{i.e.} the field was applied in the normal state. An example of the PPMS sequence used for the upper critical field measurements is shown in Appendix A.

References:


6. Results of thermopower studies

The aim of the thermopower studies was to investigate the influence of charge doping and/or scattering on this transport property of MgB$_2$. The single crystals we measured were substituted with aluminum, carbon, lithium, manganese, and co-substituted with aluminum-lithium and carbon-lithium. Thus, due to the substitutions, MgB$_2$ single crystals were doped with electrons (Al, C), holes (Li), electrons and holes simultaneously (Al:Li, C:Li), or were substituted isovalently. Substitutional chemistry of various elements and description of obtained (expected) results were described in Chapter 3.

6.1. Undoped MgB$_2$ crystals

A few MgB$_2$ single crystals have been measured as reference samples. Figure 6.1 shows the temperature dependences of the thermopower for two typical crystals. The measurements were performed in the $ab$-plane ($S_{ab}$, Fig. 6.1a) and along the $c$-axis ($S_c$, Fig. 6.1b). As usually for the $S(T)$ experiments, the data were collected with decreasing temperature. Some values of the thermopower were also checked when temperature was increased.

![Figure 6.1](image)

Figure 6.1. Temperature dependence of the thermopower of two similar MgB$_2$ single crystals (open and closed circles) measured: (a) in the $ab$-plane and (b) along the $c$-axis direction.

The obtained results are very similar for both single crystals. $S_{ab}(T)$ data are almost identical and $S_c(T)$ data differ only slightly, roughly within the measurement accuracy. Due to the “old method” (see Chapter 5.1.4) used for mounting of the crystals for the measurements along the $c$-axis, the $S_c(T)$ results scatter more than usually. Above $T_c$, the $S_{ab}(T)$ dependence is close to linear in a wide temperature range, what suggests that the diffusive part of the thermopower is dominating.
6.2. Crystals doped with electrons

The doping of MgB₂ compound with electrons can be done in two ways: by the substitution of magnesium with aluminum and boron with carbon. These substitutions may affect transport properties of MgB₂ in a different way, because as suggested by Kortus et al., substitution at the B site is more effective with reference to superconductivity than substitution at the Mg site.[6.1, 6.2] The authors argued that for substitutions at the B site, the band filling is the main ingredient responsible for changes in $T_c$ and other parameters. On the other hand, Ervin and Mazin suggested that for substitutions at the Mg site, the pair-breaking $\sigma$-$\pi$ interband scattering should be an important factor controlling the superconducting properties of the substituted MgB₂ compound.[6.3] For the normal state properties, the influence of various substitutions seems to be even more complex, since it was shown that holes from two $\sigma$-sheets and one $\pi$-sheet together with electrons from the second $\pi$-sheet are important for conductivity.[6.1-6.4]

*Al*-substituted crystals

Aluminum occupies Mg sites and dopes with electrons mainly the $\sigma$-band of MgB₂, however the $\pi$-band can be also influenced by this doping.[6.2, 6.4] The doping decreases the Fermi energy and leads to the reducing of the density of states (DOS) at the Fermi level. As a result, both the $\pi$-band and the $\sigma$-band energy gaps decrease and $T_c$ drops significantly for larger amount of substituted Al.[3.1, 3.2]

Figure 6.2 shows the temperature dependence of the thermopower of Al-substituted MgB₂ single crystals with various levels of substitution. The measurements were performed in the $ab$-plane and along the $c$-axis. The red curve presents the thermopower for the unsubstituted crystal.

![Figure 6.2](image)
and is shown here for comparison. Thermopower values in the $ab$-plane change only slightly for a weak doping, however these values decrease rapidly for crystals substituted with larger amount of Al, thus for crystals with $T_c$ below 20 K. At low temperatures, $S_{ab}(T)$ changes roughly linearly and deviates from the linear dependence at higher temperatures, $T > T_d$. For the unsubstituted crystal, $T_d \approx 150$ K and this temperature decreases with Al content, similarly as observed for the polycrystalline MgB$_2$ material.[6.5] The linear $S(T)$ dependence has been revealed for all MgB$_2$ single crystals we have studied, unsubstituted and substituted with various elements, however the temperature range where the linear dependence is observed depends on a kind and amount of the substituted atoms. This property of $S(T)$ has been interpreted as caused by the diffusion part of the thermopower of the hole-type charge carriers.

For the $c$-axis direction, the thermopower changes non-monotonically: with increasing Al content, $S_c(T)$ first increases then decreases to very low and even negative values, at least at low temperatures. We suggest that this effect is a result of combined two effects: charge doping and interband scattering. It should be noticed that the single crystals with $T_c < 20$ K have less perfect (or more defected) structure, thus the deformation of the B planes may be larger than expected for the particular Al content. Consequently, the $S_{ab}(T)$ and $S_c(T)$ results for heavily substituted single crystals may not characterize properly the characteristic properties of the Al-substituted homogenous MgB$_2$ compound.

**C-substituted crystals**

Carbon occupies boron sites and dopes the $\sigma$-band of MgB$_2$ with electrons. As a result, the $\sigma$-band superconducting gap decreases due to band filing and the reduction of electronic DOS. Simultaneously, the $\pi$-band gap remains nearly constant due to the compensation of band filling and interband scattering.[3.1, 6.2] Furthermore, anisotropy of the upper critical field also decreases due to increasing of the interband scattering.[3.4]

The temperature dependence of the thermopower of C-substituted MgB$_2$ single crystals is shown in Fig. 6.3. For these crystals, where C is substituted for B, both $S_{ab}$ and $S_c$ decrease with increasing carbon content and, for a larger amount of C, both of them change sign to negative. For $S_{ab}$, the introduction of about 10% ($x = 0.2$) of C is enough to observe negative values. For $S_c$, negative values have been obtained already at 1.5% ($x = 0.03$) of the substituted carbon. Small values of $S_{ab}$ and $S_c$ suggest that the C-substituted MgB$_2$ has more metallic character than the unsubstituted compound. Thus, the substitution of C for B, which donates electrons mostly into the $\sigma$-band, strongly influences the electronic structure and results in substantial changes of the thermoelectric properties in both directions, parallel and perpendicular to the $ab$-plane.
difference between $S_{ab}$ and $S_c$ decreases with C content, so we conclude that the C substitution not only fills the band but most probably also noticeably increases the interband scattering.

Figure 6.3. Temperature dependence of the thermopower of carbon substituted MgB$_2$ single crystals measured (a) in the $ab$-plane and (b) along the $c$-axis direction.

6.3. Crystals doped with holes

As reported in literature, until now there is only one way to dope stoichiometric MgB$_2$ with holes, that is the substitution of twovalent Mg with monovalent Li.[3.1, 3.8] As shown by means of first-principles calculations, Li dopes with holes almost entirely the $\pi$-band.[6.6] Thus this doping results in increasing of DOS mainly in the $\pi$-band and, additionally, in growing of the intraband scattering in this band.[3.7] The enhancement of the intraband scattering has been confirmed by an increase of the in-plane resistivity observed for Li-substituted crystals.[3.8] During the crystal preparation procedure, when Li-substituted crystals are annealed to remove an excess of magnesium, the lithium atoms partially evaporate increasing the hole doping (lack of magnesium corresponds to two additional holes in the conducting band). It should be noted that the superconducting transition temperature for the Li-substituted crystals does not change significantly, even for large amount of introduced lithium.

Figure 6.4 shows the temperature dependence of the thermopower for two Li-substituted single crystals. Both of them have the same estimated concentration of lithium (see Chapter 3.2), but values of the thermopower are different. Perhaps, the single crystal which shows lower values of $S_{ab}$ and $S_c$ is slightly better ordered. In general, the doping of the $\pi$-band with holes has a small influence on both the superconducting transition temperature and the thermopower. The temperature dependence of $S_{ab}$ and $S_c$ for Li-substituted crystals is very similar to that for the unsubstituted compound. This is consistent with the results obtained by band structure calculations,[6.2, 6.6, 6.7] which show that the $\sigma$-band rather than the $\pi$-band is important for
normal-state electronic and even more important for superconducting properties of MgB$_2$. However, as mentioned above, contribution from the $\pi$-band to the normal state properties can not be completely excluded. This we analyze somewhat dipper in Chapters 6.6 and 6.7.

![Temperature dependence of the thermopower of lithium substituted MgB$_2$ single crystals measured (a) in the $ab$-plane and (b) along the $c$-axis direction.](image)

Figure 6.4. Temperature dependence of the thermopower of lithium substituted MgB$_2$ single crystals measured (a) in the $ab$-plane and (b) along the $c$-axis direction.

### 6.4. Crystals substituted with Mn

Manganese occupies magnesium sites isovalently, so there is no charge doping in this case. The Mn$^{2+}$ ions are magnetic, therefore, a drastic suppression of superconductivity is observed as a result of strong pair breaking due to the spin-flip scattering of charge carriers on magnetic impurities.[3.11] Figure 6.5 shows the temperature dependence of $S_{ab}$ and $S_c$ for Mn-substituted crystals. It is interesting that even a small amount of substituted Mn (1.4%) can increase the values of $S_{ab}$ and $S_c$ for about 30% and 60%, respectively. A formula for total thermopower can be written as: $S = S_d + S_{ph} + S_m$, where $S_d$, $S_{ph}$, and $S_m$ are the diffusive, phonon-drag, and magnetic parts, respectively. Thus the observed increase of $S_{ab}$ and $S_c$ is a result of the introduced magnetic scattering centers which scatter charge carriers very effectively.

The Mn-substitution is the only isovalent substitution reported in literature for single phase MgB$_2$ compound. Thus, it is not possible to separate directly the influence of the band filling effects (Al, C, Li substitutions) from the non-magnetic intra- and interband scattering effects. However, we will try to distinguish between the charge doping and scattering effects indirectly analyzing the thermopower, resistivity, and upper critical field results obtained for variously substituted MgB$_2$ single crystals.
Figure 6.5. Temperature dependence of the thermopower of manganese substituted MgB$_2$ single crystals measured: (a) in the $ab$ plane and (b) along the $c$-axis direction.

6.5. Examples of co-substituted crystals

Within the $S(T)$ studies of the co-substitution effects, Al-Li and C-Li substituted crystals were investigated. Such a co-substitution was found to be far from trivial,[3.1, 3.8, 6.6] however we may try to roughly interpret the obtained results. Aluminum dopes MgB$_2$ with electrons and, simultaneously, Li dopes the compound with holes.[3.6] For such co-doping, one may expect the electron-hole compensation and thus the only significant influence of the introduced atoms on the $S(T)$ properties of substituted MgB$_2$ may be the effects of scattering.

Figure 6.6 shows the $S(T)$ results obtained in the $ab$-plane and along the $c$-axis direction for the Al-Li co-substituted crystals. The only small influence of the introduced Al-Li atoms on $S(T)$ has been observed at higher temperatures despite of a large reduction of $T_c$ present in the co-substituted crystals. The observed increase of the thermopower at lower temperatures is most likely due to the increase of the intraband scattering in the $\pi$-band, since Al and Li both substitute for Mg. Slightly different results obtained for crystals with similar $T_c$ may be attributed to somewhat different compositions and thus different doping/scattering effects in these crystals.

As shown in Fig. 6.6, the behavior of $S(T)$ for co-substituted crystals differ substantially from that observed for the Al or Li single-substituted crystals. Considering, that Al-Li co-substitution results only in minor changes of the thermopower, we assume that this substitution can not cause any significant modifications of the Fermi surface. Thus we conclude that electrons coming from Al to the $\pi$-band are compensated by holes coming from Li to the same band.[6.2, 6.4, 6.6, 6.7] The observed reduction of $T_c$ in co-substituted crystals may be explained as a result of uncompensated electrons coming from Al to the $\sigma$-band, which is more important for superconductivity.
Figure 6.6. Temperature dependence of the thermopower of Al-Li co-substituted MgB₂ single crystals (open symbols) measured: (a) in the \(ab\)-plane and (b) along the \(c\)-axis direction. Results for the unsubstituted and the single-substituted crystals are also shown for comparison. The colored symbols correspond: red - to the unsubstituted, blue - to the Li single-substituted, and brown - to the Al single-substituted crystals.

Temperature dependence of the thermopower \(S_{ab}\) obtained for the C-Li co-substituted crystal is shown in Fig. 6.7. A strong reduction of \(S_{ab}\) is observed for this crystal despite the co-substituted Li. The values and temperature dependence of \(S_{ab}\) are similar to those obtained for the crystal which is single-substituted with similar amount of carbon and shows only slightly higher \(T_c\). Thus, differently than Al-Li, the C-Li co-substitution has a strong influence on \(S_{ab}(T)\) and thus most likely on the Fermi surface. This is possible, since electrons coming from carbon go entirely to the \(\sigma\)-band while holes coming from lithium feed the \(\pi\)-band. As a result no compensation effect is observed and the thermopower is reduced in similar degree as for the C single-substituted crystals.

Figure 6.7. Temperature dependence of the thermopower of C-Li co-substituted MgB₂ single crystals (open circles) measured in the \(ab\)-plane. Colored symbols correspond: red - to unsubstituted, blue - to Li single-substituted, and brown - to C single-substituted crystals.
6.6. Simple model

Basically, the thermopower mostly depends on the scattering and the concentration of charge carriers. The thermopower increases due to additional scattering as well as the reduction of the charge carriers’ number. Thus the temperature dependence of the thermopower is governed by the temperature dependences of the scattering rate and the density of states at the Fermi level. Generally, the temperature dependence of the thermopower of materials without magnetic impurities can be described by equation:

\[
S = S_d + S_{ph} = AT + B/T,
\]

(6.1)

where \(S_d\) is a diffusive part of the thermopower, \(S_{ph}\) is a part related to phonon drag, and \(A\) and \(B\) are constants.

In the case when \(S_{ph}\) is small (negligible), application of a simple model to the temperature dependence of \(S_d\) allows to estimate the Fermi energy of the investigated materials. At low temperatures, where the impurity scattering dominates, Mott’s formula can be used within the free electrons approach for the diffusive part of the thermopower [6.8]:

\[
S_d = \frac{\pi^2 k_B^2 T}{3e} \left[ \frac{\partial \ln \sigma(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon_F},
\]

(6.2)

where \(k_B\) is the Boltzmann constant, \(e\) is the charge of electron and \(\sigma(\varepsilon)\) is a conductivity-like function for electrons of energy \(\varepsilon\). In low temperature region, where the carrier relaxation time is limited by impurity scattering and the resistivity is almost temperature independent, Eq. (6.2) can be simplified to the following one:

\[
\varepsilon_F = \frac{\pi^2 k_B^2 T}{3eS_d(T)},
\]

(6.3)

where \(\varepsilon_F\) is the Fermi energy calculated for holes from the top of the conduction band. However, it should be noted, that this model assumes a spherical Fermi surface and temperature independent relaxation time. The last assumption is valid only at low temperatures, where \(R(T)\) is nearly constant (see Figs. 6.8 and 7.3), and thus Eq. (6.3) is not expected to explain the \(S(T)\) dependence in the whole temperature range. Moreover, the Fermi surface of MgB\(_2\) is far from being spherical and, additionally, apart from the major hole-like sheets the minor electron-like sheet also exists making the analysis of \(S(T)\) even more complicated. Negative charges may result in negative contribution to the Seebeck coefficient and this contribution may increase with increasing temperature. Thus a significant deviation from the linear \(S(T)\) dependence towards lower values is expected at higher temperatures, as it was indeed observed for MgB\(_2\) single crystals studied in this work.
Figure 6.8 shows the temperature dependence of the in-plane resistance reduced with the value at 300 K, for unsubstituted and C-substituted MgB$_2$ single crystals.\cite{3.4} The resistance is almost independent on temperature up to about 100 K. Similar $R(T)$ results have been obtained for unsubstituted and Al-, Li-, and Mn-substituted crystals, as shown in Fig. 7.3 (Chapter 7). Thus, within the simple model which we consider, the linear part of the $S(T)$ dependence allows us to assume that the thermopower of MgB$_2$ mostly depends on the diffusive part and Eq. (6.3) can be valid at low temperatures. Considering that transport properties at low temperatures are defined mainly by hole carriers in the $\sigma$-band, Eq. (6.3) could be used for approximate estimation of the Fermi energy of these carriers, i.e. the energy of holes at the top of the $\sigma$-band.\cite{6.5, 6.9}

![Figure 6.8. Temperature dependence of the reduced residual resistance of the C-substituted MgB$_2$ single crystals with various concentrations of substituted atoms.\cite{3.4}](image)

Equation (6.3) shows that the Fermi energy of the major charge carriers depends on the slope $\Delta S/\Delta T$. Thus, any significant changes of this slope due to substitutions may be interpreted as an influence of the charge doping on the electronic structure. Table 6.1 shows the Fermi energy calculated by using Eq. (6.3) for the MgB$_2$ crystals with various substitutions. Thermopower values measured along the $ab$-plane were taken for these calculations, assuming that electronic transport in the considered temperature range is mainly due to hole carriers in the $\sigma$-band. It should be noted, however, that the reliable estimation of $E_F$ can be done only for relatively large values of $S$, because for small values (e.g., close to $T_c$), it is difficult to properly determine the slope $\Delta S/\Delta T$ due to the increased measurement error. For this reason, $E_F$ for only three Al and one C single-substituted crystals has been included in the Table, despite the fact that $S_{ab}$ for more Al and C substituted crystals has been measured.

Values of $E_F$ listed in Table 6.3 are in reasonable agreement with the difference between the Fermi energy and the top of the $\sigma$-band of about 0.9 eV obtained for MgB$_2$ from the first-
principles calculations.[6.9] Smaller values of $E_F$ which we have obtained may be the result of limited validity of our simple model, however the theoretical value of 0.9 eV can be also overestimated due to the approximation used in the calculations. Results similar to ours have been reported for the thermopower measurements of Al-substituted polycrystalline MgB$_2$.[6.5]

For the polycrystalline samples, $E_F \approx 0.5$ eV has been obtained at low temperatures and this value agrees very well with $E_F \approx 0.4$ eV estimated in our studies. For polycrystalline material, larger $E_F$ derived from the $S(T)$ dependence is expected, since the $S(T)$ values are averaged and thus lower than $S_{ab}(T)$ due to the influence of the smaller $S_e(T)$ component.

Table 6.1. Slopes of the linear part of $S_{ab}(T)$ at the residual resistance temperature region and the Fermi energies calculated by using Eq. (6.3), for unsubstituted, single-substituted and co-substituted MgB$_2$ single crystals.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_c$, K</th>
<th>$\Delta S_{ab}/\Delta T$, $\mu$V/K$^2$</th>
<th>$E_F$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB$_2$</td>
<td>38.4</td>
<td>0.062</td>
<td>0.39</td>
</tr>
<tr>
<td>Mg$<em>{0.97}$Al$</em>{0.03}$B$_2$</td>
<td>35.5</td>
<td>0.077</td>
<td>0.31</td>
</tr>
<tr>
<td>Mg$<em>{0.92}$Al$</em>{0.08}$B$_2$</td>
<td>32.5</td>
<td>0.066</td>
<td>0.36</td>
</tr>
<tr>
<td>Mg$<em>{0.80}$Al$</em>{0.20}$B$_2$</td>
<td>27.0</td>
<td>0.057</td>
<td>0.42</td>
</tr>
<tr>
<td>MgB$<em>{1.97}$C$</em>{0.03}$</td>
<td>37.05</td>
<td>0.022</td>
<td>1.1</td>
</tr>
<tr>
<td>Mg$<em>{0.91}$Li$</em>{0.09}$B$_2$</td>
<td>36.0</td>
<td>0.059</td>
<td>0.41</td>
</tr>
<tr>
<td>Mg$<em>{0.91}$Li$</em>{0.09}$B$_2$</td>
<td>36.1</td>
<td>0.051</td>
<td>0.47</td>
</tr>
<tr>
<td>Mg$<em>{0.90}$Mn$</em>{0.00}$B$_2$</td>
<td>29.3</td>
<td>0.086</td>
<td>0.28</td>
</tr>
<tr>
<td>Mg$<em>{0.98}$Mn$</em>{0.01}$B$_2$</td>
<td>18.6</td>
<td>0.092</td>
<td>0.26</td>
</tr>
<tr>
<td>Mg$<em>{0.94}$Mn$</em>{0.06}$B$_2$</td>
<td>12.2</td>
<td>0.068</td>
<td>0.35</td>
</tr>
<tr>
<td>Mg$<em>{0.96}$Al$</em>{0.04}$Li$_{0.02}$B$_2$</td>
<td>35.8</td>
<td>0.064</td>
<td>0.38</td>
</tr>
<tr>
<td>Mg$<em>{0.81}$Al$</em>{0.14}$Li$_{0.05}$B$_2$</td>
<td>27.5</td>
<td>0.062</td>
<td>0.39</td>
</tr>
<tr>
<td>Mg$<em>{0.77}$Al$</em>{0.14}$Li$_{0.05}$B$_2$</td>
<td>26.8</td>
<td>0.058</td>
<td>0.42</td>
</tr>
<tr>
<td>Mg$<em>{0.94}$Li$</em>{0.06}$B$<em>{1.96}$C$</em>{0.04}$</td>
<td>35.2</td>
<td>0.023</td>
<td>1.1</td>
</tr>
</tbody>
</table>

As discussed, the absolute value of $E_F$ can be estimated with Eq. (6.3) only very approximately. However, the relative changes of $E_F$, e.g., generated by substitutions, may be studied more appropriately. When Al is substituted, both the $\sigma$-band and the $\pi$-band are doped with electrons. Thus, the substitution of Al may influence the Fermi energy in a non-trivial way. As shown in Table 6.1, small amount of Al decreases $E_F$ evidently, most likely due to the reduced number of holes in the $\sigma$-band, however this energy increases for larger amount of Al, probably due to the increased number of electrons in the electron-like sheet of the $\pi$-band. Substitution of Li, which dopes holes mainly into the $\pi$-band, possibly results in a small increase
of $E_F$. This can be interpreted as an effect of the increased amount of holes in the hole-like second sheet of the $\pi$-band. Changes of $E_F$ for Al- and Li-substituted crystals are rather small. However, $E_F$ for the C-substituted crystal increases substantially from $\sim 0.4$ to $\sim 1$ eV. In this case, the hole-like $\sigma$-band is doped with electrons and, moreover, the scattering of charge carriers in this band is expected to increase. Both effects should result in an enhancement of the thermopower values, thus the observed reduction of $S$ for the C-substituted crystals can not be interpreted within the simple model we apply. No electron-hole compensation is observed for the C-Li co-substituted crystal, where $E_F = 1.1$ eV has been derived, which is the same as for the C single-substituted crystal with similar amount of introduced C and only slightly higher $T_c$. This is understood since, as mentioned before, electrons coming from C and holes coming from Li go to different bands.

Formula (6.3) can’t be used to analyze the thermopower results for material with magnetic impurities. When Mn is substituted for Mg, as in our case, it is substituted isovalently. Thus, the observed significant increase of $S_{ab}$ and $S_c$ has to be attributed to the pure scattering effect. Both $S_{ab}$ and $S_c$ increase systematically with increasing amount of the substituted Mn, thus with rising concentration of the magnetic scattering centers. The only exception is the single crystals with very low $T_c = 12.2$ K, where $S_{ab}$ has lower values as expected.

6.7. Discussion

Single crystals of MgB$_2$ doped with electrons show a substantial decrease of thermopower values, if only the doping level is high enough. Moreover, the C and strong Al substitutions even lead to a change of the sign of $S_{ab}$ and $S_c$ which may suggest significant modification of the Fermi surface topology. Although the Fermi surface of MgB$_2$ consists of sheets with hole and sheets with electron states, the hole states dominate.[6.1] This was confirmed by observation of the positive sign and the linear temperature dependence of the thermopower for majority of the single crystals we studied. The linear $S(T)$ region is usually located between $T_c$ and 200 K (e.g., for the unsubstituted crystals). Within the free-electron model, Mott's formula for the diffusive part of $S(T)$ can be applied to estimate the Fermi energy in the low temperature region, where the resistivity is temperature independent, and it is governed by the impurity scattering only. This approach allows to assume that at low temperatures the slope of $S(T)$ reflects properties of the Fermi surface and the density of states at the Fermi level.

For C-substituted MgB$_2$ single crystals, the linear part of the $S(T)$ dependence extends to higher temperatures. Thus, the C-substituted compound shows properties characteristic for the disordered metals, where the phonon heat current is significantly suppressed. It is worth to note
that there is no substantial phonon drag contribution to the thermopower of the MgB$_2$ single crystals, both unsubstituted and substituted with Al, C, Li, and Mn. The phonon drag results in an increase of the thermopower at low temperatures and is typical for pure metals. Deviation from the linear $S(T)$ dependence, which is observed at higher temperatures, can be related to the contribution of charge carriers from the $\pi$-band electronic-like sheets of the Fermi surface.

For Al-substituted MgB$_2$ single crystals, when both $\pi$-band and $\sigma$-band are considered to be doped with electrons, the doping changes the $S(T)$ characteristics moderately or, for heavier doping, more substantially. Comparing the results obtained for C- and A-substituted crystals, we conclude that much larger influence of the electron doping on $S(T)$ and thus, we believe, on the Fermi surface is observed when C is substituted for B and electrons are added to the $\sigma$-band. The hole doping, which appears when Li is substituted for Mg and mainly the $\pi$-band is doped, has only very weak influence on $S(T)$ and thus on the Fermi surface sheets which contribute to conductivity. The discussed results show that the $\sigma$-band rather than the $\pi$-band determines the transport properties of MgB$_2$ in the normal state. In certain conditions, however, an influence of the $\pi$-band charge carriers (holes or electrons) on the transport characteristics may be also taken into account.

**Anisotropy of thermoelectric power**

The relatively strong anisotropy of the thermopower we have observed has to be naturally a result of the anisotropic multiband electronic structure of MgB$_2$. Substitution of different atoms is expected to reduce the anisotropy by introducing disordering into the crystal structure. In turn the disordering usually leads to changes in the Fermi surface. Thus modification of the Fermi surface due to doping or disordering of the crystal structure by various substitutions may be detected through variation of the thermopower anisotropy. As known, it is difficult to find the universal definition of the anisotropy for any values of $S$ (e.g., try to compare the anisotropy for $S_{ab} = 2$ and $S_c = 1$, and for $S_{ab} = 2$ and $S_c = -1$). However, to analyze the $S(T)$ data, we define a practical coefficient of the thermopower anisotropy as:

$$\gamma = \gamma^+ \text{ or } \gamma^-,$$

where

$$\gamma^+ = \frac{S_{ab}}{S_c}, \text{ for } S_{ab} > 0 \text{ and } S_c > 0,$$

and

$$\gamma^- = \frac{S_c}{S_{ab}}, \text{ for } S_{ab} < 0 \text{ and } S_c < 0.$$

Figure 6.10 shows the temperature dependence of the thermopower anisotropy of the MgB$_2$ single crystals which have $|S_{ab}|$ and $|S_c| > 1$. Except of Mn- and Li-substituted crystals, the others show considerable decrease of the thermopower anisotropy in comparison with the unsubstituted compound. Substituted C reduces the thermopower anisotropy $\gamma$ similarly as Al and much more
effectively than Li and Mn. To explain the observed large reduction of $\gamma$ it is reasonable to assume that, apart from the electron doping of the $\sigma$-band, the substituted C increases notably the interband scattering. The reduction of $\gamma$ for Al-substituted crystals is also large and seems to saturate with increasing amount of introduced Al. As Al dopes electrons both into the $\sigma$-band and the $\pi$-band, an increase of the interband scattering could be lower, however it should be also considered in this case. The suggested stronger influence of the substituted C on the interband scattering has been confirmed by point contact spectroscopy measurements where the superconducting energy gaps, $\Delta_\sigma$ and $\Delta_\pi$, near and finally merge with increasing C content.[3.1, 6.10] Such a merging has not been observed for the Al and Mn-substituted MgB$_2$ single crystals.[3.1, 3.2, 6.11, 6.12]

The substitution of Li influences the thermopower anisotropy only slightly. This is because Li, which dopes holes mainly to the $\pi$-band, does not change the carrier content in the more anisotropic $\sigma$-band. For the Al-Li co-substituted crystal (14% Al, 9% Li), the thermopower anisotropy is reduced less than for the Al single-substituted crystal (8% Al), despite of the much larger amount of substituted Al in the co-substituted sample. This feature is considered as a result of the electron-hole compensation effect, which however seems to be limited since $T_c$ for Al-Li co-substituted crystal remains low.

![Figure 6.10](image)

Figure 6.10. Temperature dependence of the thermopower anisotropy $\gamma$ (see text) of MgB$_2$ single crystals with various substitutions.

It is interesting to note, that the Mn, Li, C, and Al-Li substituted crystals reveal a clear temperature dependence of the anisotropy. Such a behavior can be interpreted as an influence of two effects; the crystal structure disordering and the charge doping. For electron doped MgB$_2$, the clear $\gamma(T)$ dependence is observed only for crystals with low $T_c$, thus for crystals with a
substantially modified electronic structure. In the case of C and Al-Li substituted MgB$_2$, the apparent $\gamma(T)$ dependence is observed for crystals which are heavily doped with electrons. In the case of Mn-substituted MgB$_2$, the clear $\gamma(T)$ dependence is present for crystals where magnetic scattering is extremely large.

Evident reduction of the thermopower anisotropy, observed for several compositions at lower temperatures, can be understood since with decreasing temperature the phonon interaction gradually reduces and the thermopower (and resistivity, see Fig. 7.3) depends more on the impurities scattering. Let consider this for the Mn-substituted crystal, which at room temperature shows similar thermopower anisotropy as for the unsubstituted compound. This anisotropy significantly lowers with decreasing temperature and finally drops much below the values obtained for the unsubstituted single crystals. This we try to explain considering that the increase of $S$, observed for Mn-substituted crystals (the isovalent substitution), is caused by the magnetic scattering. This scattering has larger influence on $S$ at lower temperatures where phonons begin to freeze and thus scatter the charge carriers less effectively. Indeed, the ratio $S$(1.4% Mn) to $S$(0% Mn) is equal to about 1.3 at $T = 300$ K and increases to about 2.6 at 50 K. The magnetic scattering in tern seems to be more isotropic than the phonon scattering since the charge carriers strongly coupled to phonons come from the $\sigma$-band which shows a substantial anisotropy.[6.7]

References


7. Results of resistivity studies

Resistance measurements were performed with the four-contact method, as described in Chapter 5.2. Resistivity was calculated by using the formula:

\[ \rho = \frac{R \cdot s}{l}, \]  

(7.1)

where \( R \) is a measured resistance, \( l \) is a distance between the voltage contacts, and \( s \) is a cross-section area. Figure 7.1 shows the schematic diagram of a single crystal with electric contacts. Inner wires register the voltage while the current flows through the outer wires. For MgB\(_2\) single crystals, \( l \gg d \) so formula (7.1) is much more sensitive to the thickness of a crystal than to the distance between the voltage contacts. Thus, to reduce the error of the resistivity calculation, the thickness should be measured very precisely.

![Figure 7.1. Schematic diagram of a single crystal with electric contacts. Inner wires register the voltage while the current flows through the outer wires. In the Figure: \( l \) is a distance between the voltage contacts, \( s \) is a cross-section area, and \( d \) is a thickness of a crystal.](image)

The Scanning Electron Microscope (SEM) has been used for estimation of the thickness of MgB\(_2\) single crystals used for resistance measurements. Figure 7.2 shows the picture of six crystals glued to a substrate for the thickness measurements. With this method the thickness is measured with an accuracy of about few per cent.

![Figure 7.2. Picture of the MgB\(_2\) single crystals glued to a substrate for the thickness measurements.](image)
7.1. Resistivity measurements

Resistivity measurements have been performed in the temperature range from 1.5 to 300 K, for the magnetic field up to 9 T oriented parallel to the $c$-axis or to the $ab$-plane of a single crystal and for current flowing always in the $ab$-plane. The measured crystals and their superconducting transition temperatures are listed in Table 7.1.

Table 7.1. Single crystals studied by resistance measurements and the superconducting transition temperatures obtained from the resistance ($T_{c, R}$) and magnetization ($T_{c, M}$) data.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$T_{c, R}$ (K)</th>
<th>$T_{c, M}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB$_2$</td>
<td>38.4</td>
<td>38.4</td>
</tr>
<tr>
<td>Mg$<em>{0.91}$Li$</em>{0.09}$B$_2$</td>
<td>36.2</td>
<td>-</td>
</tr>
<tr>
<td>Mg$<em>{0.92}$Al$</em>{0.08}$B$_2$</td>
<td>33.0</td>
<td>32.5</td>
</tr>
<tr>
<td>Mg$<em>{0.994}$Mn$</em>{0.006}$B$_2$</td>
<td>30.9</td>
<td>30.0</td>
</tr>
<tr>
<td>Mg$<em>{0.81}$Al$</em>{0.19}$B$_2$</td>
<td></td>
<td>26.8</td>
</tr>
<tr>
<td>Mg$<em>{0.98}$Mn$</em>{0.02}$B$_2$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 7.3 shows the temperature dependences of the resistivity, $\rho(T)$, for all measured single crystals, except of the crystal Mg$_{0.98}$Mn$_{0.02}$B$_2$, which have the values of $\rho(T)$ too large to be shown in the scale of this Figure. For all substituted single crystals, the resistivity increases substantially as a result of doping (for Al substitution) and as an effect of increased amount of scattering centers (for Al, Li, and Mn substitutions). The resistivity of C-substituted MgB$_2$ single crystals has been measured previously for crystals coming from the same source and thus, for our analysis, we will use the published results.[3.4] Independently of substitutions, $\rho(T)$ shows metallic-like behavior, however the resistivity increases and the RRR ratio, defined as $\rho_{300K}/\rho_{50K}$, decreases for all substituted crystals.

Substitution of magnetic Mn increases resistivity much more than substitution of other atoms, however RRR decreases relatively less. For example, introduction of Mn in the amount of 0.6 at.% increases $\rho_{300K}$ from 5.9 $\mu\Omega$cm (unsubstituted MgB$_2$) to about 12 $\mu\Omega$cm. Simultaneously, RRR changes from 6.9 to 3.3. For Al-substituted crystals, 8 at.% of Al increases $\rho_{300K}$ less, only to about 10 $\mu\Omega$cm, however this substitution reduces RRR up to 2.6. It is interesting to note that 2 at.% of substituted Mn increases $\rho_{300K}$ to about 24 $\mu\Omega$cm (see Fig. 7.4) and changes the character of the $\rho(T)$ dependence from metallic to semi-conducting at low temperatures. This shows that the magnetic Mn ions work as very effective scattering centers as
concluded also from the thermopower results. The observed turn-up of the resistivity has been related to the Kondo effect which appears at low temperatures when a small amount of magnetic impurities interact with charge carriers. As shown in Fig. 7.4, the substitution of 2 at.% of Mn completely suppresses the superconducting transition. It was reported that the spin-flip scattering of charge carriers on magnetic moments of Mn ions is responsible for this effect.[3.11]

Figure 7.3. Resistivity as a function of temperature for the MgB$_2$ unsubstituted and Li, Al, and Mn substituted single crystals.

Figure 7.4. Temperature dependence of the resistivity of the Mg$_{0.98}$Mn$_{0.02}$B$_2$ single crystal in comparison with the resistivity of the MgB$_2$ crystal.

7.2. Upper critical field

The temperature dependence of the upper critical field, $H_{c2}$, has been determined from the $R(T)$ measurements performed in a dc magnetic field. Figure 7.5 shows the transition to the superconducting state at various magnetic fields, for the unsubstituted MgB$_2$ single crystal. The
transition is sharp even at high fields confirming good quality of the single crystal. A value of \( H_c(T) \) is determined at the temperature corresponding to 50% drop of \( R \) from the normal-state value, \( R_n \). For this single crystal, a small positive magnetoresistance has been clearly observed at higher fields. For these fields, a deviation from the roughly linear drop of \( \rho(T) \) appears as a result of particular vortex dynamics (melting or distinguishing peak effects) in this compound. Therefore, the superconducting transition temperature was determined as a temperature where the red line crosses with the dashed line which marks a value of \( 0.5R_n \) (see Fig. 7.5). One more example of the in-field resistance results is shown in Fig. 7.6, where the \( R(T) \) data for the Li-substituted MgB\(_2\) single crystal with \( T_c = 36.2 \) K is presented.

![Figure 7.5](image-url)

Figure 7.5. Temperature dependence of the resistance of the unsubstituted MgB\(_2\) single crystal at the dc magnetic field oriented parallel (a) to the \( ab \)-plane and (b) to the \( c \)-axis. The red straight line in (a) corresponds to the resistance (at 6 T) without a shift triggered by vortex dynamics. The middle dashed line corresponds to the criterion \( R = 0.5R_n \), which was used to determine \( H_c(T) \) values. For example, at \( \mu_0H = 6 \) T, the critical temperature is taken as the temperature which is marked by the vertical arrow. The blue short-dashed line shows the evolution of the vortex dynamic effects with magnetic field.
Results similar to those shown in Figs. 7.5 and 7.6 were obtained for all MgB$_2$ single crystals listed in Table 7.1 and these results have been used to determine the $H_{c2}(T)$ dependence for every crystal. The $R(T)$ curves have been obtained with a measuring current density $i = 3.5 - 7$ A/cm$^2$, which secures results practically independent of $i$. As an exception, Fig. 7.6(b) shows $R(T)$ measured with a 4 times larger $i$ to expose the vortex dynamics for $H||c$. Figure 7.7 summarizes the $H_{c2}(T)$ results showing them all together. The $H_{c2}(T)$ curves reveal a systematic change with $T_c$, except of the $H_{c2}(T)||ab$ curve obtained for the Mn-substituted single crystal, which behaves differently. This $H_{c2}(T)||ab$ curve shows a slower increase with lowering temperature than expected from the $T_c$ value. Most likely this reflects increased magnetic scattering of the quasi-particles in high magnetic fields. The $H_{c2}(T)$ results shown in Fig. 7.7 will be discussed in Chapter 7.4.
7.3. Theoretical description

As it was mentioned in Chapter 2, MgB$_2$ has three different impurity scattering channels. Two of them concern the intraband scattering within the $\sigma$ and $\pi$ Fermi surface sheets and one of them involves the interband scattering which occurs between these sheets. Thus the MgB$_2$ compound should be described by the theory of two-band superconductivity, which has to be generalized to include the effects of impurities and, due to high-$T_c$, strong electron-phonon coupling. According to Anderson theorem, the intraband electron diffusion, which is a result of strong impurity scattering in the dirty limit, does not affect $T_c$, but reduces the intrinsic anisotropy of the respected gap. On the other hand, the interband scattering may reduce $T_c$ significantly. It should be noted that in MgB$_2$ the interband scattering is weak since the $\sigma$ and $\pi$ orbitals are perpendicular each other.

Recently A. Gurevich developed a theory of the superconducting magnetic properties of a two-gap superconductor in the dirty limit which could be applied to magnesium diboride [7.1, 7.2]. Based on the Usadel approach he obtained the Ginzburg-Landau (G-L) equations and the equations for $T_c$ and $H_{c2}$, with the account of both intraband and interband scattering by nonmagnetic impurities. Here we shortly summarize his results.

Solutions of the Usadel equations revealed an unexpected feature of the normal state electronic diffusivity tensors $D^{\alpha\beta}_m$, which influence the superconducting properties of a two-gap superconductor, namely the temperature dependence of $H_{c2}$. The index $m$ means a relevant Fermi surface sheet and $\alpha$ and $\beta$ label the Cartesian indices, which correspond to the crystallographic directions. Since $D^{\sigma\sigma}_m$ and $D^{\pi\pi}_m$ describe the underlying symmetry of the Fermi surface, the properties of atomic orbitals, which form the $\sigma$ and $\pi$ bands, are reflected by the properties of $D^{\sigma\sigma}_m$ and $D^{\pi\pi}_m$. Indeed, the value of $D^{\sigma}_m$ is significantly smaller than $D^{\pi}_m$ and $D^{\sigma}_m$ due to the 2D nature of the $\sigma$-band which is formed by in-plane bounding and antibounding $p_{xy}$ orbitals of boron. The values of $D^{\pi}_m$, $D^{\pi}_m$ and $D^{\pi}_m$, however, differ less due to the 3D character of the $\pi$-band formed by the out-of-plane $p_z$ orbitals of boron. Gurevich showed that the property $(D^{\sigma}_m/D^{\pi}_m) \ll (D^{\pi}_m/D^{\pi}_m)$ manifests the anomalous temperature dependence of the anisotropy of $H_{c2}$ in comparison with the predictions of the anisotropic G-L theory for a one-gap superconductor.

Using the Usadel equations for calculation of the London penetration depth, $\Lambda_{\alpha\beta}$, the following formula has been obtained:

$$\Lambda_{\alpha\beta}^2 = \frac{4\pi^2 e^2}{c^2} \left( N_1 D^{\sigma\sigma}_1 \tanh \frac{\Delta_1}{2T} + N_2 D^{\pi\pi}_2 \tanh \frac{\Delta_2}{2T} \right),$$

(7.2)
where \( e \) is electron charge, \( N_1 \) and \( N_2 \) are partial densities of states in the bands \( \sigma \) and \( \pi \), \( \Delta_1 \) and \( \Delta_2 \) are order parameters of the bands \( \sigma \) and \( \pi \), respectively. It’s clearly seen that \( \Lambda_{ab}^2 \) contain the sum of intraband diffusivities of both bands which are notably different with respect to values and anisotropies. Therefore the London penetration depth \( \Lambda_{ab} \) is determined by the cleanest band with maximum diffusivity.

Estimation of the upper critical field is much more complicated, especially in the wide terms, thus it was done first for the case of negligible rates of the interband scattering, \( \gamma_{mm} \). Thus, it could be assumed, that the nonmagnetic impurities do not affect \( T_c \). Taking into account those conditions, the final equation for \( H_{c2} \) close to \( T_c \) has a form:

\[
H_{c2} = \frac{8\phi_0(T_c - T)}{\pi^2 (a_1 D_1 + a_2 D_2)},
\]

where \( \phi_0 \) is the quantum of magnetic flux, and \( a_1 \) and \( a_2 \) are the G-L expansion coefficients of the bands \( \sigma \) and \( \pi \), respectively. Here, for the case \( D_1 = D_2 \), this equation yields the well known result of the one-band theory, \( H_{c2} = 4\phi_0(T_c - T)/\pi^2 D \).[7.3-7.5] Equation (7.3) shows that close to \( T_c \), the upper critical field of a two-gap superconductor is determined by the maximum diffusivity \( D_1 \) or \( D_2 \), similarly as the London penetration depth.

At zero temperature, \( H_{c2}(0) \) is described by the formula:

\[
H_{c2}(0) = \frac{\phi_0 T_c}{2\gamma \sqrt{D_1 D_2}} \exp \left( \frac{g}{2} \right),
\]

where \( \lambda_0, \lambda, \) and \( w \) are complex parameters describing the intra and interband coupling in the BCS matrix, and \( \gamma \) is a constant that \( \ln \gamma = 0.577 \).[7.2] For the case \( D_1 = D_2 \), Eqs. (7.4) and (7.5) yield the result of the one-band dirty limit theory, \( H_{c2}(0) = \phi_0 T_c/2\gamma D \). However, for \( D_1 \neq D_2 \), the theory developed by Gurevich predicts an unexpected increase of the upper critical field close to zero temperature in comparison with well-known universal relation:

\[
H_{c2}(0) = 0.69 H'_{c2} T_c,
\]

where \( H'_{c2} = dH_{c2}/dT \) at \( T_c \). Generally, the slope of \( H_{c2} \) at \( T_c \) can be also defined as:

\[
H'_{c2} = \frac{4eck_B}{\pi} N_F \rho_n,
\]

where \( N_F \) is the density of states at the Fermi level, \( k_B \) – the Boltzmann constant, \( \rho_n \) – the normal
state residual resistivity, and \( e \) is electron charge. Note that Eq. (7.7) describes \( H_{c2} \), for the case of negligible interband scattering, that to some extent is realized in the MgB\(_2\) compound. For very different diffusivities, \( H_{c2}(0) \) is determined by the band with minimum diffusivity [7.1]:

\[
H_{c2}(0) = \frac{\Phi_0 T_c}{2\gamma D_2} e^{-(\lambda_2 + \lambda_0)/2 w}, \quad D_2 \ll D_1 e^{-\lambda_0/w}, \quad (7.8)
\]

\[
H_{c2}(0) = \frac{\Phi_0 T_c}{2\gamma D_1} e^{-(\lambda_2 - \lambda_0)/2 w}, \quad D_1 \ll D_2 e^{-\lambda_0/w}, \quad (7.9)
\]

These equations allow to analyze the main behavior of \( H_{c2} \) at low temperatures when scattering and thus diffusivities are changing due to substitutions.

Figure 7.8 shows the temperature dependence of the \( H_{c2}(T)/H_{c2}(0) \) ratio for different \( D_2/D_1 \) ratios, as obtained in the frame of the presented theory. For \( D_2 \ll D_1 \) (see Fig. 7.8(a)), the unusual upturn of the \( H_{c2}(T) \) dependence is observed at low temperatures. According to Eq. (7.8)

![Figure 7.8](image)

Figure 7.8. Temperature dependence of the reduced upper critical field, \( H_{c2}(T/T_c)/H_{c2}(0) \), obtained in the frame of the two-gap superconductivity theory, for the different \( D_2/D_1 \) ratio, where \( D_2 \) and \( D_1 \) are the \( \pi \)-band and \( \sigma \)-band diffusivities, respectively.[7.1]
this behavior originates from properties of the $\pi$-band, the band with minimum diffusivity. It is also clear that for $D_2 \to 0$, $H_{c2}(T)$ diverges at $T \to 0$. For $D_2 = D_1$ and $D_2 \gg D_1$ (see Figs. 7.8 (b) and (c)), the properties of $H_{c2}$ do not change significantly and the $H_{c2}(T)$ dependence reminds the classical one, except for the temperature region close to $T_c$, where an upward curvature is observed when $D_2 \gg D_1$.

To better understand how diffusivity influences the $H_{c2}(T)$ dependence, it is useful to show total $H_{c2}(T)$ as a sum of contributions from different bands. This is illustrated in Fig. 7.9, for the case $D_2 = 0.1D_1$, i.e. for MgB$_2$ with the dirty $\pi$-band. As shown in the Figure, the unexpected enhancement of $H_{c2}(T)$ at low temperatures is due to the more isotropic $\pi$-band. Taken into account that $H_{c2}(T)$ is determined by cleaner band at higher temperatures (close to $T_c$) and by dirtier band at lower temperatures, it is clear that the upper critical field at low temperatures can be significantly increased by making the $\pi$-band dirtier than the $\sigma$-band. This can be obtained by introducing disorder in the Mg sublattice, which may disturb the $p_z$ boron out-of-plane orbitals.

![Figure 7.9. Temperature dependence of the upper critical field of a two-gap superconductor. The dashed curves show $H_{c2}(T)$ calculated for the $\sigma$ and $\pi$ bands separately, in the one-gap dirty limit theory with $D_{\pi} = 0.1D_{\sigma}$. The solid curve shows $H_{c2}(T)$ calculated within the two-gap dirty limit theory.][7.2]

Another property of a two-gap superconductor which can be described in the frame of the presented theory is the upper critical field anisotropy, $\gamma_H = H_{c2}(T) || ab / H_{c2}(T) || c$. Near $T_c$, this anisotropy can be obtained from the angular dependences of $H_{c2}$:

$$H_{c2}(\theta) = \frac{8\phi_0(T_c - T)}{\pi^2(a_1D_1(\theta) + a_2D_2(\theta))},$$

where the angular-dependent diffusivities $D_1(\theta)$ and $D_2(\theta)$ for both bands are:

$$D_m(\theta) = [D_m^{(a)} \cos^2 \theta + D_m^{(c)} \sin^2 \theta]^{1/2},$$
where $D_m^{(a)}$ and $D_m^{(c)}$ mean the in-plane and out-of-plane diffusivities for the $m$th band, respectively.\[7.1\] For the case $D_1 \neq D_2$, the anisotropy of $H_{c2}$ depends on the in-plane diffusivity ratio, $D_2^{(ab)}/D_1^{(ab)}$, as shown in Fig. 7.10. Since this ratio reflects the mutual relation between the intraband diffusivities (scattering) of the $\pi$ and $\sigma$ bands, we may try to predict the behavior of the $H_{c2}$ anisotropy of MgB$_2$ substituted with different ions. Substitutions which increase scattering (reduce diffusivity) in the $\sigma$-band should result in lowering of $\gamma_H$ near $T_c$ (see Fig. 7.10(c)). Substitutions which increase scattering in the $\pi$-band are expected to reduce $\gamma_H$ at low temperatures (see Fig. 7.10(a)).

In conclusion, let us emphasize some points. The properties of the upper critical field of MgB$_2$ strongly dependent on the intraband diffusivity ratio, $D_2/D_1$, which in turn depends on the intraband impurity scattering. Thus, it is possible to increase $H_{c2}$ by smart substitutions at the Mg or B sites. For instance, substitutions for Mg affect mainly the out-of-plane $p_z$ orbitals of B and,
as a result, the $\pi$-band scattering increases decreasing $D_2$. On the other hand, substitutions for B disturb mainly the in-plane $p_{xy}$ orbitals of B and, consequently, the $\sigma$-band scattering increases decreasing $D_1$. Thus, using various substitutions, one has an opportunity to tune the $D_2/D_1$ ratio and, in this way, to change $H_{c2}$ values and the temperature dependence. Considering the $\pi$ and $\sigma$ bands as interplayed films, the total $H_{c2}$ is determined by the film with the highest $H_{c2}$ values (see Fig. 7.9). For this model, $H_{c2}(0)$ can be increased much above the one-gap value by providing the condition: $D_1 >> D_2$. However, we should remember that the substitutions affect the properties of MgB$_2$ in quite complex way, since the introduced atoms change not only the diffusivities but, due to charge doping, also the electronic structure.

Finally, it is important to note that the intraband diffusivities $D_1$ and/or $D_2$ may also determine the slope of $H_{c2}(T)$ at $T_c$, $H_{c2}' = dH_{c2}/dT$. This results from Eq. (7.3), which shows that for $T \approx T_c$, $H_{c2}(T)$ and thus also $H_{c2}'$ depend on both diffusivities. For $D_1$ much different than $D_2$, the slope $H_{c2}'$ is determined by the maximum diffusivity. Thus, for $D_2 \neq D_1$, Eq. (7.3) yields the approximate relation:

$$D_m \propto 1/H_{c2}',$$  \hspace{1cm} (7.12)

where $D_m$ is the diffusivity which is a larger one. Due to the simple inverse relation between $H_{c2}'$ and the maximum diffusivity and $H_{c2}(0)$ and the minimum diffusivity (see Eqs. (7.8) and (7.9)), we may qualitatively determine the influence of various substitutions on the relevant intraband scattering by measuring the $H_{c2}(T)$ dependence in the temperature range from about 0 K to $T_c$. Additional information on the intraband scattering may be obtained from the temperature dependence of the $H_{c2}$ anisotropy, as shown in Fig. 7.10.

### 7.4. Discussion

**Upper critical field**

The model described above can be fully applied only in the dirty-limit case. That is, the coherence length has to be comparable to or larger than the mean free path. The correct evaluation of the mean free path in a multiband compound may be a difficult task, however it was shown in many articles, that superconductivity in MgB$_2$ single crystals may be considered in the clean limit. On the other hand, when MgB$_2$ is substituted or irradiated with neutrons or heavy ions, the mean free path decreases. This requires the superconducting properties to be considered in the dirty limit. For MgB$_2$, the mean free path along the $c$-axis direction is sufficiently smaller than in the $ab$-plane, due to the weak charge tunneling between adjacent boron layers.[7.2] Therefore, the dirty limit can be easier obtained for superconductivity originated from the
electronic properties along the c-axis direction. Consequently, the relation between the mean free path and the coherence length along the c-axis and the spacing between the boron layers seem to be decisive. Table 7.2 shows the coherence lengths of the by-transport measured MgB$_2$ single crystals. Both, $\xi_{ab}(0)$ and $\xi_c(0)$ have been estimated by using the extrapolated to 0 K upper critical fields, $H_{c2}(0)||ab$ and $H_{c2}(0)||c$ (see Figure 7.7), and the formulas given by the anisotropic G-L theory [7.8]:

$$H_{c2}^{||c}(0) = \phi_0 / 2\pi\xi_{ab}^2(0) \quad \text{and} \quad H_{c2}^{||ab}(0) = \phi_0 / 2\pi\xi_{ab}(0)\xi_c(0).$$

(7.15)

The coherence length along the c-axis is shorter than the coherence length in the ab-plane and longer than the distance between boron planes, which is about 3.5 Å (see Table 2.2 in Chapter 2). Therefore, the three dimensional anisotropic model proposed by Gurevich is strictly applicable to the MgB$_2$ compound.

Table 7.2. Superconducting transition temperature, upper critical fields, and coherence lengths, for H oriented parallel to the c-axis (||c) and to the ab-plane (||ab). The coherence lengths have been obtained within the anisotropic Ginsburg-Landau theory.

| Composition          | $T_c$, K | $H_{c2}(0)||c$, T | $H_{c2}(0)||ab$, T | $\xi_{ab}(0)$, Å | $\xi_c(0)$, Å |
|----------------------|----------|-------------------|-------------------|------------------|---------------|
| MgB$_2$              | 38.4     | 6.44              | 22.3              | 72               | 20.1          |
| Mg$_{0.91}$Li$_{0.09}$B$_2$ | 36.2     | 5.26              | 21.4              | 79               | 19.5          |
| Mg$_{0.92}$Al$_{0.08}$B$_2$ | 33.0     | 5.14              | 13.0              | 80               | 31.7          |
| Mg$_{0.994}$Mn$_{0.006}$B$_2$ | 30.9     | 3.15              | 9.4               | 102              | 34.5          |
| Mg$_{0.81}$Al$_{0.19}$B$_2$ | 26.8     | 2.81              | 12.3              | 108              | 24.8          |

The temperature dependences of the upper critical fields of the MgB$_2$ single crystals listed in Table 7.2 are shown in Fig. 7.7. For all crystals, application of the Gurevich model to the $H_{c2}(T)$ results allow to conclude that the experimental dependences are very similar to the theoretical curves with $D_2>>D_1$, for $H_{c2}(0)||ab$, and $D_2\geq D_1$, for $H_{c2}(0)||c$ (see Fig. 7.8). As we mentioned above, the Mg-site substitutions may lead to the break-down of the $p_z$ boron out-of-plane orbitals and result in a substantial increase of the disorder in the $\pi$-band. Consequently, diffusivity in the $\pi$-band decreases and $H_{c2}(T)$ additionally increases at low temperatures, as shown in Fig. 7.8(a). Such the upturn of $H_{c2}(T)$ has not been observed for our Mg-site substituted single crystals suggestive that in this crystals $D_2$ remains larger than $D_1$.

The main influence of the Mg-site substitution on the $H_{c2}(T)$ dependences (shown in Fig. 7.7) is as follows. Close to $T_c$, the upward curvature of both $H_{c2}(T)||ab$ and $H_{c2}(T)||c$ decreases revealing finally the linear $H_{c2}(T)$ dependence, at least for the heavy Al-substituted single
crystals. For all substituted crystals, a reduction of $T_c$ and the $H_c2(T)$ values is observed. Detailed analysis of the obtained results in the frame of the Gurevich model gives rise to the conclusion, that the Mg-site substitutions increase charge carriers scattering mainly in the $\pi$-band and thus decrease the diffusivity $D_2$. However, for all substituted crystals, $D_2$ remains larger than $D_1$, thus any unusual increase (upturn) of $H_c2(T)$ has been observed at low temperatures. On the other hand, an interesting behavior of the $H_c2(T)|_{ab}$ dependence has been revealed for the Al-substituted crystal with $T_c = 26.8$ K. For this crystal, $H_c2(T)|_{ab}$ increases with lowering temperature faster than expected from the $T_c$ value (see Fig. 7.7). This feature can be interpreted as a result of the significant increase of charge carriers scattering in the $\pi$-band and thus as a result of the substantial decrease of $D_2$ toward the relation $D_2 \geq D_1$. Shifting the superconducting properties of the Al heavy-substituted crystal toward the case $D_2 \geq D_1$ can be deduced from Fig. 7.8 (b) and (c), when we compare the results quantitatively.

Modification of the intra-band scattering, and thus diffusivities, due to substitutions may be also determined by the analysis of the $H_c2(T)$ slope at $T_c$, $H_c2'(T) = dH_c2/dT$. The $H_c2'(T)$ values are listed in Table 7.3, for all single crystals we have studied in a magnetic field. The results have been obtained for $H$ parallel to the $ab$-plane or to the $c$-axis. It is clear that the Mg-site substitutions may lead to the significant decrease of the $H_c2'(T)|_{ab}$ and $H_c2'(T)|_{c}$ close to $T_c$, when only the substitution level is high enough. Thus, according to Eq. (7.3), we can assume that in this case $H_c2(T)$ is determined by changed maximum diffusivity, which is $D_\pi$. Thus, for the Mg-site substituted crystals, the $\sigma$-band is still dirtier than the $\pi$-band, even for the Al heavily-substituted crystals.

Table 7.3. Derivative of the upper critical field, $H_c2'(T) = dH_c2/dT$, close to $T_c$, for the single crystals measured in the field parallel to the $ab$-plane or parallel to the $c$-axis direction.

| Composition       | $T_c$, K | $H_c2'(T)|_{ab}$, T/K | $H_c2'(T)|_{c}$, T/K |
|-------------------|---------|-----------------------|----------------------|
| MgB$_2$           | 38.4    | -0.68                 | -0.19                |
| Mg$_{0.91}$Li$_{0.09}$B$_2$ | 36.2    | -0.67                 | -0.18                |
| Mg$_{0.92}$Al$_{0.08}$B$_2$ | 33.0    | -0.47                 | -0.19                |
| Mg$_{0.994}$Mn$_{0.006}$B$_2$ | 30.9    | -0.39                 | -0.13                |
| Mg$_{0.81}$Al$_{0.19}$B$_2$ | 26.8    | -0.32                 | -0.11                |

For the Mg-site substituted crystals, a substantial reduction of $T_c$ has been revealed. Considering that in MgB$_2$ the interband scattering is weak, we conclude that the observed changes of $T_c$ have been caused by charge doping rather than by charge scattering. Thus the systematic lowering of $H_c2(0)$, which remains roughly proportional to $T_c$, seems also to be caused
by the charge doping rather than by the reduction of the diffusivity in the σ-band. Since for Mg-site substituted crystals \( D_\pi \) remains larger than \( D_\sigma \), \( H_{c2}(0) \) is governed by \( D_\sigma \) only and, according to Eq. (7.9), should increase when \( D_\sigma \) decreases. Thus, the observed reduction of \( H_{c2}(0) \) excludes any substantial increase of the intraband scattering in the σ-band due to the Mg-site substitutions at moderate level.

It seems to be clear that the small amount of the Mg-site substituted atoms doesn’t influence significantly also the π-band scattering. As shown for weakly substituted crystals, e.g., with Li (\( T_c = 36.2 \) K), no change of the \( H_{c2}(T) \) slope at \( T_c \), \( H_{c2}' \), has been observed (see Table 7.3). For heavier substituted crystals, e.g., with Al (\( T_c = 26.8 \) K), both \( H_{c2}' |_{ab} \) and \( H_{c2}' |_{c} \) decrease but, according to Eq. (7.12), an increase of \( H_{c2}' \) is expected when the scattering in the π-band, which is the band with maximum diffusivity, increases resulting in lower π-band diffusivity. Thus, for the Mg-site non-magnetic substitutions, the main changes of the \( H_{c2}(T) \) dependences seem to be caused by charge doping and less by weak interband scattering, which control \( T_c \) and thus also the \( H_{c2} \) properties. For the Mg-site substituted crystals, however, the intraband scattering has to increase, since the resistivity systematically increases with the substitution level (see Fig. 7.3). This seeming contradiction can be explain when we assume that the expected increase of \( H_{c2}'(T) \) due to the increased intraband scattering is compensated by the lowering of \( T_c \) and thus \( H_{c2}(0) \) due to the electron doping, which reduces the number of hole charge carriers. Similar explanation of the \( H_{c2}'(T) \) behavior can be derived basing on the simple general formula (7.7).

The substitution of Li, which dopes MgB\(_2\) with holes, has been found to increase the number of Mg vacancies which, in turn, leads to the additional rise of the amount of scattering centers. Thus, studying the influence of the Li substitution on doping and scattering properties, the number of introduced Li atoms and Mg vacancies should be known. Actually, there are only few reports where the Li substitution effects were studied in MgB\(_2\) single crystals.[3.8, 6.6] Generally, the main result of the Li substitution is a weak rise of the intraband scattering in the π-band. Similar conclusion has been derived from our thermopower studies (see Chapter 6). Formerly it was expected that the Li substitution might lead to the substantial increase of the scattering in the π-band and also results in the hole doping. Such an influence should lead to the domination of the σ-band diffusivity and, as a result, to the enhancement of \( H_{c2}(0) \), as was predicted within the two-band model in the dirty limit. Analysis of \( H_{c2}(T) \) and \( H_{c2}'(T) \) showed that Li substitution modifies the electronic structure and superconducting properties of MgB\(_2\) only very weakly, suppressing the critical temperature by 2 K, for the single crystal with 9% of substituted Li. Since in MgB\(_2\) the major charge carriers are holes, the reduction of \( T_c \) due to the Li substitution (hole doping) means that stoichiometric MgB\(_2\) is an optimally doped compound.
Substitution of Mn for Mg suppresses $T_c$ and $H_{c2}$ due to the magnetic scattering of quasi-particles by Mn ions. The Mn-substituted MgB$_2$ single crystals were investigated in details by magnetic measurements in Ref. 3.11. The authors did not found any significant influence of the Mn substitution on the $\pi$- or $\sigma$-band diffusivities. Analysis of the $H_{c2}(T)$ dependences of the Mn-substituted single crystal measured by us shows that the Mn substitution affects the $\pi$-band and, probably, also the $\sigma$-band diffusivities, since the uniform reduction of $H_{c2}'(T)||ab$ and $H_{c2}'(T)||c$ is observed. The increased scattering in the $\pi$-band and, probably, also in the $\sigma$-band has been evidenced as a substantial increase of the resistivity of Mg$_{1-x}$Mn$_x$B$_2$ single crystals with the increasing Mn content (see Figs. 7.3 and 7.4). However, no upturn of the $H_{c2}(T)$ dependence has been revealed at low temperatures, thus we conclude that the $\pi$-band diffusivity still dominates in the Mn-substituted single crystals. According to the formula (7.12), an increase of the scattering, which reduces the diffusivity, should result in an increase of $H_{c2}'(T)$, the slope of $H_{c2}(T)$ at $T_c$. As we observe the reduction of $H_{c2}'(T)$, we claim that this formula doesn’t work for Mn-substituted MgB$_2$, as expected, since the Gurevich model considers the scattering effects due to non-magnetic impurities.

Strong increase of the resistivity of Mn-substituted crystals is shown in Figs. 7.3 and 7.4. Even 2% of substituted Mn destroys superconductivity completely. Moreover, for this single crystal, $\rho(T)$ shows the Kondo effect at low temperatures. The increase of $\rho(T)$ with lowering temperature is distinguishing showing the Kondo temperature equal to about 45 K. This effect is interesting and will be studied separately.

There only substitution which increases $H_{c2}(T)$ in MgB$_2$ is the substitution of C for B. We have not investigated by resistivity the C-substituted single crystals because such a substitution was intensively studied by many groups.[3.4, 7.9-7.12]. An example of the temperature dependence of $H_{c2}$ for the C-substituted single crystals is shown in Fig. 7.11, which has been taken from Ref. 3.4. The data shows that the $H_{c2}(T)$ slope increases and the $H_{c2}$ anisotropy decreases with rising C content. The observed increase of $H_{c2}'$ and thus also $H_{c2}(0)$ saturates at about 4% of substituted C, and then the $H_{c2}'$ and $H_{c2}(0)$ values begin to lower, for the C content higher than about 10%.[7.9] The revealed reduction of the $H_{c2}$ anisotropy with the increasing C content we discuss in the next subchapter.

As described in previous chapters, C which occupies the B site, dopes the $\sigma$-band with electrons and increases the charge carriers (holes) scattering in this band. Thus, the reduction of the mean free path, $l$, appears and the C-substituted MgB$_2$ may be described in the frame of the two-band model in the dirty limit. Indeed, strong reduction of $l$ and the relaxation time, $\tau$, has been observed in all scattering channels, two intraband and one interband, as reported in literature.[3.4, 7.9, 7.12]. However, even for single crystals with large C contents, the $H_{c2}(T)$
dependence doesn’t show the characteristic upward curvature at low temperatures, contrary to the prediction of the Gurevich model, for the case when $D_\pi << D_\sigma$ (see Fig. 7.8a). Figure 7.12 shows the $H_{c2}(T)$ dependences of the C-substituted polycrystalline samples, as reported in Ref. 7.9. More quantitative analysis of the $H_{c2}(T)$ curves reveals properties which are characteristic for the case $D_\pi > D_\sigma$. Thus, taking into account that for unsubstituted MgB$_2$ single crystals $D_\pi >> D_\sigma$, we conclude that the C substitution increases the charge carriers scattering in both bands, however the scattering in the $\pi$-band is more effective, since in the unsubstituted compound this band is much cleaner than the $\sigma$-band.

![Figure 7.11](image1.png)

Figure 7.11. Phase diagram of the Mg(B$_{1-x}$C$_x$)$_2$ single crystals with $x=0.05$ (circles) and 0.095 (triangles). The upper critical fields are derived using the “zero resistance” (solid symbols, solid lines) and the “onset” (open symbols, dashed lines) transition temperatures. The Figure has been taken from Ref. 3.4.

![Figure 7.12](image2.png)

Figure 7.12. Superconducting upper critical field $H_{c2}$ as a function of temperature for polycrystalline Mg(B$_{1-x}$C$_x$)$_2$ samples, $0 \leq x \leq 0.038$. Inset: $H_{c2}(T)$ close to $T_c$, determined from temperature dependent resistivity (solid squares), field dependent resistivity (triangles), and field dependent magnetization (open squares). The Figure has been taken from Ref. 7.9.
Strong charge carriers scattering due to substituted C has been confirmed by systematic resistivity measurements (Ref. 7.11) and our thermopower studies of the Mg(B$_{1-x}$C$_x$)$_2$ single crystals. Figure 7.13 shows the temperature dependence of the in-plane resistivity of the C-substituted crystals, as taken from Ref. 7.11. A drastic increase of the residual resistivity is observed with increasing C content. The values of $\rho_n$ for the single crystal with $x = 0.125$ are 25 times larger than those for unsubstituted MgB$_2$. Such a rise of the resistivity shows definitely the substantial increase of the carrier scattering rate by introduced impurities and thus the decrease of the mean free path and the coherence length.[7.11] The observed increase of $H_{c2}(T)$ is a result of the increased $D_\sigma/D_\pi$ ratio when the $\pi$-band became dirtier than the $\sigma$-band. Thus, we have argued that the carbon substitution decreases the diffusivity in the $\pi$-band more rapidly than in the $\sigma$-band. This conclusion has been confirmed in various experiments, such as point-contact spectra, Hall coefficients, and the thermopower measurements.[7.11, 7.12]

![Figure 7.13. Temperature dependence of the in-plane resistivity of Mg(B$_{1-x}$C$_x$)$_2$ single crystals. The $T_s$ are 38, 35, 33, 30, 25, 10, and 2.0 K, for $x =$ 0, 0.02, 0.035, 0.05, 0.075, 0.10, and 0.125, respectively. The Figure has been taken from Ref. 7.11.](image)

**Anisotropy of $H_{c2}$**

The anisotropy of $H_{c2}(T)$ can be successfully described by the two-band model in the clean limit, for pure MgB$_2$ (e.g., unsubstituted single crystals), and in the dirty limit, for the substituted compound. Within the two-band model in the clean limit the behavior of the anisotropy of $H_{c2}(T)$ mostly depends on the interband coupling. In Ref. 7.13, the anisotropy $\gamma = H_{c2}(T)||ab/H_{c2}(T)||c$ was calculated as a function of temperature for different interband coupling strength. The results show a weak $\gamma(T)$ dependence for separated bands and a strong decrease of $\gamma(T)$ with increasing temperature, for compound with moderate interband coupling. Thus, the increase of the inter-
band coupling leads to changes of the $H_{c2}(T)$ properties from characteristic for an isotropic single-gap superconductor (zero interband coupling) to those which describe a two-gap superconductor (finite interband coupling). Figure 7.14 shows the temperature dependence of the high critical field anisotropy with different values of the interband coupling strength, $\eta$, and dimensionless parameter, $\varepsilon_c$, which describes a small $c$-axis dispersion of the $\sigma$-band Fermi surface cylinder.[7.13] Figure 7.14 reveals that both parameters, $\eta$ and $\varepsilon_c$, are important for determining the anisotropic properties of the upper critical field.

Figure 7.14. The anisotropy parameter $\gamma = H_{c2}(T)_{\parallel ab}/H_{c2}(T)_{\parallel c}$ as a function of reduced temperature, for the various interband coupling strength, $\eta$, and the dimensionless parameter, $\varepsilon_c$, as taken from Ref. 7.13. The parameter $\varepsilon_c$ describes a small $c$-axis dispersion of the $\sigma$-band Fermi surface. The closed circles correspond to results taken from Ref. 7.14.

The anisotropy of $H_{c2}(T)$ for our MgB$_2$ single crystals is shown in Fig. 7.15. To get the $\gamma(T)$ results for unsubstituted, and Li and Al substituted crystals, the $H_{c2}(T)$ data (shown in Fig. 7.7) was extrapolated to lower temperatures. Results for the C-substituted crystals were taken from Ref. 7.11. For all single crystals, the anisotropy increases with decreasing temperature. Except of the C-substituted crystals, the increase of $\gamma(T)$ is rather small confirming a weak interband coupling in the MgB$_2$ compound ($\eta = 0$ in Fig. 7.14). According to Fig. 7.14, the stronger $\gamma(T)$ dependence observed for the C-substituted single crystals signifies a stronger interband coupling in these crystals than in others. This is consistent with a general belief that the substitution of C for B increases both the intraband and the interband scattering and may also result in larger interband coupling.

The anisotropy for our unsubstituted MgB$_2$ single crystal is lower than published in literature (see, e.g., Refs. 3.2, 3.11). This could be ascribed to differences in the methods of the $H_{c2}(T)$ estimation. Indeed, the $H_{c2}(T)$ values in Refs. 3.2 and 3.11 were obtained from magnetization measurements, thus the different criterion to get the $H_{c2}(T)$ results was applied. As the $H_{c2}$
anisotropy is very sensitive to $H_{c2}$ values, this could be the reason for the observed discrepancy.

The superconducting $H_{c2}$-$T$ phase diagram of MgB$_2$ single crystals with $H_{c2}$ obtained by different methods has been studied in Ref. 7.15. The paper shows that depending on the definition the results for $H_{c2}(T)$ and thus for $\gamma(T)$ may differ. However, generally, our $H_{c2}(T)$ and $\gamma(T)$ dependences agree well with those in Ref. 7.15 obtained with the “onset resistance” definition of $T_c$ in a magnetic field. Note, that our resistance measurements were performed on single crystals with low-resistance electric contacts (below 0.5 Ohm) and thus the obtained results are expected to be very reliable.

Figure 7.15. Temperature dependence of the anisotropy coefficient $\gamma = H_{c2}(T)||_{ab}/H_{c2}(T)||_{c}$ of the MgB$_2$ single crystals with various substitutions. The anisotropy of the carbon substituted crystals has been taken from Ref. 7.11.

Now let us discuss the upper critical field anisotropy in further details in the frame of the two-gap theory in the dirty limit, which we have discussed in the previous chapter. As shown in Fig. 7.15, $\gamma(T)$ decreases with increasing temperature for all single crystals, both unsubstituted and substituted with various elements. According to the Gurevich model, the observed negative slope $d\gamma/dT$ means that the diffusivity in the $\pi$-band dominates. However, the temperature dependences of $\gamma$ obtained for the unsubstituted and Li, Al and Mn substituted crystals differ significantly from those for the C-substituted crystals, which reveal much sharper decrease of $\gamma(T)$ with increasing temperature. Considering the theoretical results shown in Fig. 7.10 we summarize our $\gamma(T)$ experimental results as follows. For unsubstituted pure MgB$_2$ compound, diffusivities in the $\pi$-band and the $\sigma$-band fulfill the condition: $D_{\pi} \gg D_{\sigma}$. When C is substituted for B, the intraband scattering in both the $\pi$-band and the $\sigma$-band increases, the diffusivity in these bands decreases,
however the relation between them becomes $D_\pi > D_\sigma$ (see Fig. 10c), since the scattering in much cleaner $\pi$-band is more effective.

When Al is substituted for Mg, the intraband scattering in the $\pi$-band increases, the diffusivity in this band decreases, and the electronic transport properties of MgB$_2$ change toward the case where $D_\pi \geq D_\sigma$ (see Fig. 10b). For the Al-substituted crystals, saturation of the $\gamma(T)$ dependence is observed at low temperatures. This tendency (lowering of $d\gamma/dT$), when keeping for increasing amount of substituted Al, could lead to a positive slope of $\gamma(T)$, which corresponds to the case when diffusivity in the $\sigma$-band begins to dominate (see Fig. 7.10a). The $\gamma(T)$ dependence cannot be obtained at very low temperatures, because at these temperatures the $H_{c2}$ values are larger than the magnetic field available in our experiment.

One striking feature of the $H_{c2}$ anisotropy is its reduction revealed for substituted single crystals. This, we believe, is a result of increased interband scattering in crystals with introduced scattering and doping centers. Due to the increased interband scattering and/or doping, the $\pi$ and $\sigma$ bands can merge, as shown in Refs. 3.1 and 6.10, and explained in Ref. 6.2. The reduction of the $H_{c2}$ anisotropy is much stronger in the C-substituted single crystals, since C introduced for B provides the scattering centers into both the $\pi$-band and the $\sigma$-band and dopes with electrons the $\sigma$-band, which is a crucial band for superconductivity. The non-monotonic change of $\gamma$ with the substitution level is observed for the Al-substituted crystals. This effect could be a result of the combination of two mechanisms - scattering and doping. The main difference between the Al- and C-substituted compound is that Al substitutes for Mg and thus introduces the scattering centers mainly into the $\pi$-band. Moreover, substituted Al dopes with electron both the $\pi$-band and the $\sigma$-band, as discussed many times in this work.

References:


8. Conclusions

Availability of sizeable MgB$_2$ single crystals doped with electrons and holes enabled us to perform advanced studies of the anisotropic thermoelectric and superconducting properties of a two-band superconductor. The thermopower of MgB$_2$ single crystals substituted with C, Al, Li, Mn, C-Li, and Al-Li has been investigated in the temperature range 10–300 K. Due to these substitutions, MgB$_2$ was doped with electrons (C, Al), holes (Li), electrons and holes simultaneously, or it was substituted isovalently with magnetic element (Mn). Both the in-plane ($S_{ab}$) and the out-of-plane ($S_c$) thermopowers are positive for the non-substituted crystals and both $S_{ab}$ and $S_c$ change a sign for crystals doped with electrons, when C is substituted for B in the amount larger than ~5 at% or when Al is substituted for Mg in the amount larger than 20 at%. The observed substantial difference in the reaction of the thermopower on the substituted C and Al has been associated with the fact that C introduces electrons mainly into the $\sigma$-band while Al into both bands, mainly into the $\pi$-band, but also into the $\sigma$-band. When Li is substituted for Mg, the $\pi$-band rather than the $\sigma$-band is doped with holes and the doping effect on the thermopower is much more subtle. For the Li-substituted crystals, the intraband scattering seems to be enhanced, while no evidence for the increased interband scattering has been found. When magnetic Mn is substituted for Mg, it is substituted isovalently and thus the observed significant increase of both $S_{ab}$ and $S_c$ has been interpreted as a result of strong magnetic intraband scattering.

The anisotropy of unsubstituted crystals, defined as a ration $S_{ab}/S_c$, is slightly lower than 4, and this anisotropy is reduced to about 2 by the substitution of C or Al. The reduction of $S_{ab}/S_c$ due to substitution was interpreted as a result of both charge doping and interband scattering. A lowering of the thermopower anisotropy with decreasing temperature has been observed for the Li, Mn and C substituted single crystals, i.e., for crystals with enhanced intraband scattering. The reduction has been explained as an effect of the gradual decrease of the more anisotropic phonon interaction and thus an effective increase of the more isotropic scattering on impurities. The phonon scattering seems to be anisotropic since the charge carriers strongly coupled to phonons come from the quasi 2D $\sigma$-band which shows a substantial anisotropy.

The thermoelectric power and the resistance are both strongly influenced by doping when C is substituted for B. This substitution results in a substantial decrease in both $S_{ab}$ and $S_c$, leading to the change of their sign to negative for the C content equal to about 7% and 2%, respectively. The observed decrease of the thermopower indicates more metallic and electron-conducting character of the C-substituted crystals. The substitution of C reduces also the thermopower anisotropy, most likely by increasing the interband scattering. The substitution of C, which
donates electrons mostly into the $\sigma$-band, strongly increases the Fermi energy of MgB$_2$ and thus results in the observed substantial changes of the thermoelectric properties.

For the Al-substituted MgB$_2$ single crystals, when both $\pi$-band and $\sigma$-band are considered to be doped with electrons, the doping changes the $S(T)$ characteristics moderately and only for heavily doped crystals more substantially. Comparing the results obtained for the C- and Al-substituted crystals, we conclude that much larger influence of the electron doping on $S(T)$ and thus, we believe, on the electronic structure of MgB$_2$ is observed when C is substituted for B. This is the case when electrons are donated entirely to the $\sigma$-band. The hole doping, which appears when Li is substituted for Mg and the $\pi$-band is mainly doped, has only very weak influence on $S(T)$ and thus on the Fermi surface sheets which contribute to conductivity. The discussed results show that the $\sigma$-band rather than the $\pi$-band determines the transport properties of MgB$_2$ in the normal state. As widely known the $\sigma$-band is also more important for superconductivity. In certain conditions, however, an influence of the $\pi$-band charge carriers (holes or electrons) on the transport characteristics should also be taken into account.

When Li is additionally introduced into the crystal with substituted C, $S_{ab}$ practically does not change, however $S_c$ increases substantially. This effect suggests that holes, which go most likely to the $\pi$-band, change the conducting features only in this band including an increase of the intraband scattering and thus also the $S_c$ values. Therefore, no (or very weak) electron-hole compensation effect is observed for the C-Li co-substituted MgB$_2$. The Al-Li co-substitution results only in minor changes of the thermopower and thus this substitution can not cause any significant modifications of the Fermi surface. We conclude that electrons coming from Al to the $\pi$-band are compensated by holes coming from Li to the same band. The observed reduction of $T_c$ in co-substituted crystals may be explained as a result of uncompensated electrons coming from Al to the $\sigma$-band, which is important for superconductivity. Generally, the electron and hole doping effects seem to be asymmetric for the thermoelectric normal-state properties, similarly as for the superconducting properties.

Superconducting properties of MgB$_2$ has been studied by measuring the upper critical field of the single crystals substituted with Li, Al, and Mn. The obtained results have been compared with those for C-substituted crystals reported in literature. The most conclusive results have been derived from the behavior of the upper critical field anisotropy, $\gamma = H_{c2}(T)||_{ab}/H_{c2}(T)||_{c}$. For the Al-substituted single crystals, a non-monotonic change of the $\gamma$ values with the substitution level is observed. Small amount of Al leads to the decrease of $\gamma$ but higher amount results in the increase of $\gamma$ in the whole temperature range from $T_c$ to zero. Such a behavior of the $H_{c2}$ anisotropy has not been reported in literature. We believe it could be a results of the complex
effect of the electron doping of the both bands, \( \pi \) and \( \sigma \), and of the increased scattering in the \( \pi \)-band. Analyzing the behavior of \( \gamma(T) \) for the single crystals we have studied, we claim that the results correspond to the case where the \( \sigma \)-band is dirtier than the \( \pi \)-band. The mutual relation between the diffusivities in the \( \pi \) and \( \sigma \) bands, \( D_\pi \) and \( D_\sigma \), depends mainly on the intraband scattering, which can be modified in different way by different kind of substitutions. For the Al-substituted crystals, the effect of the by-doping changed density of states at the Fermi level has to be taken into account to explain the observed results.

Reduction of the \( H_{c2} \) anisotropy is smaller for the Li-substituted single crystal. This could be understood if we consider that Li increases the intraband scattering (an increase of resistivity is observed) in the \( \pi \)-band and dopes this band with holes. Thus, due to different doping, the Li substitution works in different way than the Al substitution. The reduction of \( \gamma \) observed for Li-substituted crystal can be small, because for this crystal, the interband scattering does not change substantially. Similar conclusion has been derived from the thermopower results.

The anisotropy of \( H_{c2} \) for the C-substituted crystals exhibits different behavior than observed for other crystals. The values of \( \gamma(T) \) decrease with increasing temperature much faster. This has been attributed to the increased intraband scattering in the \( \sigma \)-band and, consequently, different diffusivities in both bands, \( i.e. \ D_\pi > D_\sigma \). The strong reduction of the \( H_{c2} \) anisotropy with the C content has been observed and related to the increased interband scattering, as also concluded from the thermopower results.

Concerning the by-substitution-induced scattering, the following general conclusions can be derived. For the MgB\(_2\) single crystals, the substitution with Li increases the intraband scattering in the \( \pi \)-band moderately, without changing noticeably of the interband scattering. The substitution with Al increases the intraband scattering also in the \( \pi \)-band, and in the similar scale, however, most likely this substitution results also in the weak interband scattering. The most interesting and important seems to the substitution of MgB\(_2\) with C. This substitution increases the intraband scattering both in the \( \sigma \)-band and the \( \pi \)-band, and influences substantially the interband scattering as well. As a result, the upper critical field significantly increases and its anisotropy decreases. Substituted C reduces also the anisotropy of the normal state properties, as showed our thermopower results. These knowledge, we believe, could help to modify the normal-state and superconducting properties of the MgB\(_2\) compound to obtain material even more interesting for small or large scale applications.
List of publications:


Attended Conferences:

1) The Second International Conference on Rare Earth Materials (REMAT), 13-15 June 2011, Wroclaw, Poland; *Magnetic studies of GaN nanoceramics doped with 1% of Ce*.

2) Applied Superconductivity Conference, 1-6 August 2010, Washington, USA; *Anisotropy of Li, Al, C and Mn substituted MgB$_2$ single crystals studied by thermopower and upper critical field*.

3) XIV Krajowa Szkoła Nadprzewodnictwa, Nadprzewodnictwo i niejednorodne układy skondensowane, 13-17 października 2009, Ostrów Wielkopolski, Poland; *Anisotropy of Li, Al, and C substituted MgB$_2$ single crystals studied by thermopower*.

4) 9th European Conference on Applied Superconductivity (EUCAS'09), 13-17 September, 2009, Dresden, Germany; *Anisotropy of Li, Al, and C substituted MgB$_2$ single crystals studied by thermopower*.

5) 13 Krajowa Szkoła Nadprzewodnictwa, Nadprzewodnictwo, uporządkowanie spinowe i ładunkowe, 6-10 listopada 2007, Łądek Zdrój, Poland; *Thermoelectric power of MgB$_2$ single crystals doped with holes and electrons*.

6) 8 Seminar and Workshop, Applications of Superconductors, 17-20 June 2007, Nałęczów, Poland; uczestnictwo bez prezentacji.
Appendix A

As was mentioned in Chapter 5.2.3, for resistance and upper critical field measurements, a PPMS sequence has been written, individually for every single crystal measured, considering the intrinsic physical characteristics. In instance, following sequence has been used in $H_{c2}\parallel ab$ measurement of Mg$_{0.92}$Al$_{0.08}$B$_2$ single crystal.

ACT Append Datafile "C:\Documents and Settings\PPMS\Desktop\Users Data\MgB2\Karen\MgB2-Al_AN415-K2\2010-02-03_MgB2-Al_AN415-K2_RvT_HIIab.dat"
Set Temperature 300K at 12K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Scan Temp from 300K to 40K at 10K/min, in 53 steps, Uniform, Fast
   ACT Resistivity Ch.1 0.500mA 19.00Hz 2.00sec
End Scan
Scan Temp from 38K to 34K at 0.5K/min, in 9 steps, Uniform, Sweep
   ACT Resistivity Ch.1 0.500mA 19.00Hz 2.00sec
End Scan
Scan Temp from 33.5K to 30K at 0.05K/min, in 71 steps, Uniform, Sweep
   ACT Resistivity Ch.1 0.500mA 19.00Hz 2.00sec
End Scan
Set Temperature 35K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Set Magnetic Field 10000.0Oe at 200.0Oe/sec, Linear, Persistent
Wait For Field, Delay 10 secs, No Action
Set Temperature 33K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Scan Temp from 33K to 28K at 0.1K/min, in 34 steps, Uniform, Sweep
   ACT Resistivity Ch.1 0.500mA 19.00Hz 2.00sec
End Scan
Set Temperature 35K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Set Magnetic Field 30000.0Oe at 200.0Oe/sec, Linear, Persistent
Wait For Field, Delay 10 secs, No Action
Set Temperature 35K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Set Magnetic Field 30000.0Oe at 200.0Oe/sec, Linear, Persistent
Wait For Field, Delay 10 secs, No Action
Set Temperature 28K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Scan Temp from 28K to 20K at 0.1K/min, in 41 steps, Uniform, Sweep
   ACT Resistivity Ch.1 2.000mA 19.00Hz 2.00sec
End Scan
Set Temperature 35K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Set Magnetic Field 60000.0Oe at 200.0Oe/sec, Linear, Persistent
Wait For Field, Delay 10 secs, No Action
Set Temperature 23K at 10K/min. Fast Settle
Wait For Temperature, Delay 10 secs, No Action
Scan Temp from 23K to 10K at 0.1K/min, in 66 steps, Uniform, Sweep
   ACT Resistivity Ch.1 0.500mA 19.00Hz 2.00sec
End Scan
Set Temperature 40K at 10K/min. Fast Settle
Set Magnetic Field 0.0Oe at 200.0Oe/sec, Oscillate, Persistent
Wait For Temperature, Field, Delay 10 secs, No Action
Shutdown Temperature Controller