CHAPTER 6

STUDY OF SUPERCONDUCTING
BEHAVIOR OF MgB$_{2-x}$C$_x$ : TO IMPROVE
THE SUPERCONDUCTING
PERFORMANCE OF MgB$_2$
6.1 INTRODUCTION

Due to high critical transition temperature, \( T_c \) and large coherence length, \( \text{MgB}_2 \) possess a great potential for wide engineering and technological applications in comparison to conventional superconductors like \( \text{Nb}_3\text{Sn} \) and \( \text{Nb-Ti} \) alloy [1] and HTSC compounds [2, 3]. The critical current density is also very high at low fields. But, it falls rapidly in high fields as discussed under section 3.2.2.6 in Chapter 3. It can be due to poor grain connectivity and a lack of pinning centers. Fortunately, through the doping of some specific additives/ substituents of \textit{nano} size in bulk \( \text{MgB}_2 \), the flux pinning forces can be enhanced significantly. This is primarily due to large coherence length (around 5-10 \textit{nm}) of \( \text{MgB}_2 \).

Keeping this key point in mind, enormous efforts have been directed in the last five years, towards the improvement of superconducting performance of \( \text{MgB}_2 \) through substitution/addition of several \textit{nano}-elements [4-6], \textit{nano} oxides [7-9], Silicates [10], Carbohydrates and other Organic compounds [11-13]. The most important role is played by Carbon derivatives. The impact of Carbon doping on the crystal chemistry and miscibility of Carbon in \( \text{MgB}_2 \) lattice was studied in earlier years [14-19]. The solubility of Carbon varies from 2.5% to 30% [15-17].

But from the application point of view, the effect of Carbon doping on flux pinning and critical current density of \( \text{MgB}_2 \) must be appreciated. In the recent years, improvement of \( J_c \) is observed through various Carbon sources like diamond, Carbon \textit{nanohorns}, graphite & Carbon \textit{nanotubes} [20-23].

In this study, we explore the effect of amorphous Carbon \textit{nano}-particle substituted at Mg site in bulk polycrystalline \( \text{MgB}_2 \). Carbon is the only element, which substitutes at Boron site in \( \text{MgB}_2 \) lattice. The partial substitution of Boron by Carbon creates disorder in the superconducting condensate (Sigma band), which is mainly formed by the Boron networks, and may enhance the upper critical field & \( J_c (H) \) via intrinsic pinning. Further, unreacted remaining \textit{nano}-Carbon, which is not substituted, can act as a \textit{nano} additive in
the host matrix, causing extrinsic pinning of flux lines. Thus, *nano* carbon substitution appears most suitable for improving the superconducting parameters because it has double effect, one through intrinsic pinning being a substituent instead of additive and secondly through extrinsic pinning being of *nano* size. Although an additive may substitute at boron site in case of MgB$_2$ but up to a very low extent because of lack of vacancy at the boron site, whereas in case of substitution like MgB$_{2-x}$C$_x$ there are vacant places at boron site stoichiometrically where carbon element can easily place itself.

It is well known that MgB$_2$ is a two band superconductor having double band gap and the unusual Fermi surface topology [24, 25]. Various studies exist on the band structure unfolding the mystery of different nature of Fermi surfaces for different [26-30] bands. MgB$_2$ has two bands namely $\sigma$ and $\pi$. The Fermi surface due to $\sigma$ band has cylindrical sheets while possess tubular networks due to $\pi$ band. This two band nature also affects the critical parameters like upper critical field, $H_{c2}$ of MgB$_2$ as well as of MgB$_{2-x}$C$_x$. The $H_{c2}$ increases linearly near $T_c$ with decreasing temperature but its behavior changes in the low temperature high field region. A sharp jump is predicted by theoretical and experimental reports near $T=0$ K in the $H_{c2}$ vs $T$ line [31-33]. That’s why the exact $H_{c2}(0)$ value is much higher than it seems to be through normal extrapolation of data. The Werthamer-Helfand-Hohenberg (WHH) formula determines $H_{c2}(0)$ value on the basis of slope of $H_{c2}$ vs $T$ line at $T=T_c$ i.e. $dH_{c2}/dT$ at $T=T_c$. But since the slope is varying with the temperature considerably, it results in the erroneous estimation of $H_{c2}$. So, Ginzburg-Landau(GL) theory based upon two band model is used for the calculation of $H_{c2}$ at low temperatures in this study.

The experimental data of $H_{c2}$ vs $T$ plots fits very well with the GL equation. For high field and low temperature, the $H_{c2}$ line is theoretically drawn up to zero Kelvin according to GL theory. $H_{c2}(0)$ calculated by GL equation is found to be much higher than the WHH formula. So, in addition to MgB$_2$, the *nano* Carbon doped samples are also analysed using GL equation.

### 6.2 EXPERIMENTAL
6.2.1 **Synthesis of samples**

The details of sample synthesis are mentioned in section 2.2 under Chapter 2. Briefly, the polycrystalline MgB$_{2-x}$C$_x$ samples were prepared by In-situ solid-state reaction route at ambient pressure. The starting materials were Mg powder, Boron powder and *nano*-Carbon (10-20nm) powder. These ingredients were taken in appropriate stoichiometric ratios and were mixed thoroughly by continuous grinding for 2-3 h. The homogenous mixtures so obtained were pressed into pellets using hydraulic press applying a uni-axial pressure of about 7.5 tons/cm$^2$. The samples were enclosed in iron tubes and were subsequently sintered at a temperature of 850 °C for 2.5 hours in a tubular furnace in an inert atmosphere created by continuous Argon flow. After the heat treatment, the samples were allowed to cool naturally in the same atmosphere.

6.2.2 **Characterization of the samples**

The characterizations of the samples were carried out by the following techniques:

6.2.2.1 **X-ray diffraction Studies**

Details of X-ray diffraction technique are described in Chapter 2 under Section 2.3.1.1. Briefly X-ray diffraction patterns of all the synthesized samples were recorded with a Diffractometer using CuK$_\alpha$ radiation.

6.2.2.2 **Resistivity measurements**

Temperature dependent resistivity measurements on MgB$_{2-x}$C$_x$ samples were carried out using four-probe technique on a closed cycle refrigerator in the temperature range from 12-300 K. Details of temperature dependent resistivity measurements are given in Chapter 2 under section 2.3.2.1. Resistivity measurements were also carried out under applied magnetic fields of up to 14 Tesla with field applied perpendicular to current direction, using Quantum Design Physical Property Measurement System (PPMS)(Chapter 2, Section 2.3.2.3).

6.2.2.3 **Magnetization Studies**

Details of magnetic characterization of samples are given in Chapter 2 in section 2.3.2.2
and section 2.3.2.3. Briefly, Magnetization measurements on MgB$_{2-x}$C$_x$ samples were carried out with a Quantum-Design 14 Tesla Physical Property Measurement System (PPMS).

6.3 RESULTS AND DISCUSSION

![X-ray diffraction patterns](image)

Fig. 6.1 depicts the X-ray diffraction patterns of series MgB$_{2-x}$C$_x$ (x = 0.0 to 0.20). Slow scan XRD is done in the angular range $20^\circ \leq 2\theta \leq 70^\circ$ at the interval of 0.02°. It can be seen that the Carbon substitution in MgB$_2$ matrix does not result in the formation of additional phases up to x=0.10. With further increment in carbon content minor peaks of MgB$_2$C$_2$ (marked with #) phase arise as can be seen from diffraction patterns of x=0.15 and 0.20 samples in Fig. 6.1. All samples of MgB$_{2-x}$C$_x$ series crystallize in simple hexagonal structure with space group $P6/mmm$. The characteristic peaks for the pristine sample are recorded at their well-defined positions. Indexing of the peaks is also done in Fig. 6.1. The phase purity of the samples is checked by Rietveld refinement. A minor amount of MgO is found to form, which is determined by the presence of a very low intensity peak at $2\theta = 63.5^\circ$ [34, 35]. MgO peak is marked with symbol * in figure 6.1. The peak (100) shifts slightly towards higher angle side. The enlarged view of shifting of (100) peak with Carbon content is shown in the right hand side inset of Fig. 6.1. It indicates towards the decrease in $a$-parameter with increasing
carbon content. On the other hand, no considerable shift is noticed in the (002) peak indicating that $c$-parameter does not change much with the carbon substitution.

![Rietveld refined diffraction pattern](image)

Fig. 6.2 depicts the Rietveld refined diffraction pattern for the highest Carbon doped sample i.e for $x=0.20$ in MgB$_{2-x}$C$_x$ series. It possesses all the characteristic peaks of MgB$_2$ at correct position and with appropriate intensity. As mentioned above, along with the characteristic peaks of MgB$_2$, some other phases also start appearing with increasing Carbon content. For example, in the present sample, minor peaks of MgB$_2$C$_2$ also appear which are marked by # in Fig. 6.2. The low intensity of this minor phase peaks and shift in the MgB$_2$ peaks indicates that most of the Carbon is substituted at Boron site of MgB$_2$ and after a saturation value of substitution,

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume ($\text{Å}^3$)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB$_2$</td>
<td>3.0857(8)</td>
<td>3.5230(8)</td>
<td>29.15</td>
<td>1.142</td>
</tr>
<tr>
<td>MgB$<em>{1.96}$C$</em>{0.04}$</td>
<td>3.0793(7)</td>
<td>3.5310(8)</td>
<td>29.0</td>
<td>1.145</td>
</tr>
<tr>
<td>MgB$<em>{1.92}$C$</em>{0.08}$</td>
<td>3.0754(16)</td>
<td>3.5275(16)</td>
<td>28.89</td>
<td>1.147</td>
</tr>
<tr>
<td>MgB$<em>{1.90}$C$</em>{0.10}$</td>
<td>3.0742(24)</td>
<td>3.5287(24)</td>
<td>28.88</td>
<td>1.148</td>
</tr>
<tr>
<td>MgB$<em>{1.85}$C$</em>{0.15}$</td>
<td>3.0692(19)</td>
<td>3.5271(20)</td>
<td>28.77</td>
<td>1.149</td>
</tr>
<tr>
<td>MgB$<em>{1.80}$C$</em>{0.20}$</td>
<td>3.0678(20)</td>
<td>3.5336(21)</td>
<td>28.80</td>
<td>1.151</td>
</tr>
</tbody>
</table>

Table 6.1: Lattice parameters, $c/a$ values and cell volume categorized for MgB$_{2-x}$C$_x$ samples ($x=0.0, 0.04, 0.08, 0.10, 0.15 \& 0.20$)
the other Carbon phases start appearing. Thus, MgB$_2$ with Carbon substitution still exists as a major phase and MgB$_2$C$_2$ exists as a minor phase.

The lattice parameters for all the samples are calculated by Rietveld refinement and are tabulated in Table 6.1. For pristine sample, $a = 3.0857$ Å while it is decreased to 3.0678 Å for $x = 0.20$ carbon doped sample. On the other hand, $c$-parameter changes randomly and overall increases slightly. The change in lattice parameters is identical to the earlier reported values [14-17]. The $c/a$ value is also calculated which increases slightly due to decrease in $a$ parameter. The cell volume decreases due to greater decrease in $a$ parameter as compared to relatively smaller increase in $c$ parameter.

The variation of lattice parameters, $c/a$ value and cell volume with the increasing Carbon content is plotted in Fig. 6.3. Error bars for the lattice parameters ‘$a$’ and ‘$c$’ are also drawn as obtained from Rietveld Refinement. Cell volume and lattice parameter ‘$a$’, both decrease with increase in $x$ (Carbon content in MgB$_{2-x}$C$_x$) while $c/a$ value increases with the increasing Carbon amount because of decreasing $a$ parameter and almost constant $c$ value. The continuous monotonic change in lattice parameters confirm the substitution of Carbon at Boron site in MgB$_2$ matrix but still the exact amount of Carbon substituted at Boron site is not known. The exact Carbon content in MgB$_{2-x}$C$_x$, is evaluated indirectly using the equation

$$\text{Exact carbon content, } x_{\text{cal}} = 2 \times 7.5 \times \Delta c/a$$
where $\Delta c/a$ is the change in $c/a$ value as compared to the pure sample and $x_{\text{cal}}$ is the exact content of Carbon substituted at the Boron site[36-39].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$(x_{\text{exp}})$</th>
<th>Carbon substitution level in terms of Atomic wt% of boron $[x_{\text{exp}/2}*100]$</th>
<th>$c/a$</th>
<th>$\Delta c/a$</th>
<th>$(x_{\text{cal}})$</th>
<th>Actual Carbon substitution level in terms of Atomic wt% of boron $[x_{\text{cal}/2}*100]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgB$_2$</td>
<td>0</td>
<td></td>
<td>1.142</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>MgB$<em>{1.96}$C$</em>{0.04}$</td>
<td>0.04</td>
<td></td>
<td>1.145</td>
<td>0.003</td>
<td>0.045</td>
<td>2.2</td>
</tr>
<tr>
<td>MgB$<em>{1.92}$C$</em>{0.08}$</td>
<td>0.08</td>
<td></td>
<td>1.147</td>
<td>0.005</td>
<td>0.075</td>
<td>3.75</td>
</tr>
<tr>
<td>MgB$<em>{1.90}$C$</em>{0.10}$</td>
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<td></td>
<td>1.148</td>
<td>0.006</td>
<td>0.09</td>
<td>4.50</td>
</tr>
<tr>
<td>MgB$<em>{1.85}$C$</em>{0.15}$</td>
<td>0.15</td>
<td></td>
<td>1.149</td>
<td>0.007</td>
<td>0.105</td>
<td>5.25</td>
</tr>
<tr>
<td>MgB$<em>{1.80}$C$</em>{0.20}$</td>
<td>0.20</td>
<td></td>
<td>1.151</td>
<td>0.009</td>
<td>0.135</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Table 6.2: Experimental and calculated values for carbon content for MgB$_{2-x}$C$_{x}$/Mg(B$_{1-y}$C$_{y}$)$_2$, samples

Table 6.2 shows the calculated values of exact carbon content $(x_{\text{cal}})$ corresponding to all the samples. From the comparision of values of $x_{\text{exp}}$ and $x_{\text{cal}}$ mentioned above in Table 6.2, it is observed that the exact value of carbon content is found to be quite less than the stoichiometrically taken value of carbon content during synthesis. The net maximum carbon substitution level is just 6.75 atomic wt% of boron while the samples were prepared up to 10 atomic wt% of boron. Actually, $x=0.20$ in MgB$_{2-x}$C$_{x}$ corresponds to MgB$_{1.80}$C$_{0.20}$ or to Mg(B$_{0.90}$C$_{0.10}$)$_2$ i.e. 10 atomic wt. % of boron. The remaining unsubstituted nano Carbon remains at the grain boundary or at interstitial site and may act as a pinning centre and can enhance the $H_{c2}$, $H_{irr}$ and $J_c(H)$ values. This is called the extrinsic pinning. The net Carbon, which exactly goes at the Boron site creates disorder in the sigma band and cause intrinsic pinning to enhance the critical parameters. So, Substitution by Carbon at Boron site causes both extrinsic/intrinsic pinning The observed net substitution level of carbon content at boron site in MgB$_2$ is in confirmation with the earlier reports [39].
After studying the structural properties of MgB$_{2-x}$C$_x$ samples, resistivity measurements were carried out on these samples. The variation of resistivity with temperature under zero applied field for pristine and Carbon doped MgB$_2$ samples is shown in Fig. 6.4. The pristine MgB$_2$ sample shows superconducting transition with a $T_c(\rho = 0)$ of 37.75 K. The narrow transition width of about 1.3 K and appropriate $T_c$ onset for pristine MgB$_2$ sample clearly indicate the good quality of samples. All synthesized samples with varying carbon content are found to be superconducting, however, transition temperature decreases with increase in carbon content. The transition temperature is 35.95 K and 34.95 K for $x=0.10$ and 0.20 samples. The relative decrease in transition temperature with Carbon substitution is comparable with other reports [15, 17, 18] and quite lesser than [19].

Residual Resistivity ratio is defined as RRR value ($=\rho_{300}/\rho_{40}$) for MgB$_2$ samples. RRR values are calculated for all synthesized samples with the varying Carbon content and the same are plotted in the inset of Fig. 6.4. Pure sample is found to have highest value of RRR ($=3.6$) among the whole series of MgB$_{2-x}$C$_x$ samples. With increase in Carbon content, the RRR value has a monotonic decrease and the least value of 1.70 is obtained for the highest doped $x=0.20$ sample. It decreases very sharply in the beginning up to $x=0.04$ sample and after that rate of decrease in RRR value with respect to the increasing Carbon content decreases. The Carbon doping enhances the impurity scattering in the doped sample and hence results in the decreased value of RRR. The above trend of
change in RRR values of our samples is in confirmation with the literature [35, 36]. Moreover, it is also observed from $\rho(T)$ plots that the absolute resistivity values for doped samples are higher than the pristine sample, which confirms the increased impurity scattering with increasing Carbon content.

Fig. 6.5 (a), (b) and (c) depict the variation of resistivity with temperature in the transition zone at different field values varying from 0 to 14 Tesla for the undoped, $x=0.20$ and 0.10 sample respectively. Here, we note that the transition is very sharp at zero field for all the samples but the transition width increases with the increase in field value. At low fields, superconducting transition temperature of pure sample is higher than that of doped samples. The transition temperature $T_c (\rho=0)$ is 37.75 K for pure MgB$_2$ while it decreases with the Boron site Carbon substitution to 35.95 K and 34.95 K for $x=0.10$ and 0.20
samples respectively at zero field value. With increment in applied field, resistance curves shift towards lower temperature side both for doped & undoped samples but we can clearly see that relative shift is much lesser in case of doped sample curves than the pure one. As a result, transition temperature for pure MgB$_2$ sample is only 5.80 K under 14 Tesla field, while it is 9.55 K, 11.30 K and 12.80 K for $x = 0.20$, 0.15 and 0.10 samples respectively. It means that although the $T_c$ at zero field for MgB$_2$ is higher than carbon doped samples (Fig. 6.4) but the $T_c$ at applied fields is lesser in comparison to carbon doped samples. Thus, substitution of Carbon improves the superconducting performance of bulk MgB$_2$ sample at elevated fields.

![Graph](image.png)

**Fig. 6.5(c) Resistivity vs temperature plot at different field values varying from 0-14 Tesla for MgB$_{2-x}$C$_x$, x=0.10**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>x</th>
<th>$T_c$(K) $H=0T$</th>
<th>$T_c$(K) $H=1T$</th>
<th>$T_c$(K) $H=3T$</th>
<th>$T_c$(K) $H=5T$</th>
<th>$T_c$(K) $H=7T$</th>
<th>$T_c$(K) $H=9T$</th>
<th>$T_c$(K) $H=11T$</th>
<th>$T_c$(K) $H=13T$</th>
<th>$T_c$(K) $H=14T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>37.75</td>
<td>34.10</td>
<td>29.03</td>
<td>24.55</td>
<td>20.55</td>
<td>16.54</td>
<td>12.30</td>
<td>8.06</td>
<td>5.80</td>
</tr>
<tr>
<td>2</td>
<td>0.04</td>
<td>36.79</td>
<td>33.60</td>
<td>29.04</td>
<td>25.05</td>
<td>22.06</td>
<td>18.55</td>
<td>15.55</td>
<td>12.30</td>
<td>10.55</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>36.19</td>
<td>32.80</td>
<td>27.80</td>
<td>24.04</td>
<td>20.29</td>
<td>17.30</td>
<td>14.04</td>
<td>11.30</td>
<td>10.05</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>35.95</td>
<td>32.80</td>
<td>28.30</td>
<td>24.79</td>
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<td>19.04</td>
<td>15.80</td>
<td>13.80</td>
<td>12.80</td>
</tr>
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<td>5</td>
<td>0.15</td>
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<td>32.55</td>
<td>27.79</td>
<td>23.80</td>
<td>20.30</td>
<td>17.54</td>
<td>15.05</td>
<td>12.54</td>
<td>11.30</td>
</tr>
<tr>
<td>6</td>
<td>0.20</td>
<td>34.69</td>
<td>31.55</td>
<td>26.82</td>
<td>22.81</td>
<td>19.30</td>
<td>16.04</td>
<td>13.30</td>
<td>10.79</td>
<td>9.29</td>
</tr>
</tbody>
</table>

**Table 6.3 Transition temperature ($T_c$ at $\rho=0$) at different field values (0 to 14T) for MgB$_{2-x}$C$_x$ samples ($x=0.0-0.20$)**

The transition temperatures $T_c$ ($\rho=0$) for all the synthesized samples at fields varying from 0-14 Tesla are given in Table 6.3. The increase in transition temperature at elevated
fields simply implies that the critical field, $H_{c2}$ increases with the Carbon doping in MgB$_2$.

The critical field is determined for all the samples using the criterion that $H_{c2} = H$ at which $\rho = 90\% \rho_N$ and $\rho_N$ is the normal resistivity or resistivity at about 40 K. To determine $H_{c2}$, the transition temperature with the criterion of $\rho = 90\% \rho_N$ instead of $\rho = 0$ are estimated from $\rho(T)H$ data for all the samples and are tabulated in Table 6.4.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>x</th>
<th>$T_c$ H=0T</th>
<th>$T_c$ H=1T</th>
<th>$T_c$ H=3T</th>
<th>$T_c$ H=5T</th>
<th>$T_c$ H=7T</th>
<th>$T_c$ H=9T</th>
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<tbody>
<tr>
<td>1</td>
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<td>38.84</td>
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<td>30.73</td>
<td>27.28</td>
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<td>17.60</td>
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<td>12.47</td>
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<td>34.79</td>
<td>30.88</td>
<td>27.81</td>
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<td>22.63</td>
<td>20.28</td>
<td>18.02</td>
<td>16.77</td>
</tr>
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<td>3</td>
<td>0.08</td>
<td>37.19</td>
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<td>30.48</td>
<td>27.63</td>
<td>25.20</td>
<td>23.02</td>
<td>20.91</td>
<td>18.99</td>
<td>17.98</td>
</tr>
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<td>30.52</td>
<td>27.93</td>
<td>25.52</td>
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</tr>
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<td>27.62</td>
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<td>20.76</td>
<td>18.73</td>
<td>17.77</td>
</tr>
<tr>
<td>6</td>
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<td>33.43</td>
<td>29.53</td>
<td>26.87</td>
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<td>22.0</td>
<td>20.05</td>
<td>17.92</td>
<td>17.00</td>
</tr>
</tbody>
</table>

Table 6.4 Transition temperature ($T_c$ at $\rho = 90\% \rho_N$) to determine $H_{c2}$ at different field values (0 to 14T) for MgB$_2$-xC$_x$ samples

The value of applied field of a column directly corresponds to the $H_{c2}$ value at the temperature given below in that column for the corresponding samples in Table 6.4. For example, from the last column of $H=14$ T of Table 6.4, it can be inferred that 14 T is the upper critical field at temperature of 12.47 K(First Row, Last Column of Table 6.4) for MgB$_2$ while 14 T is the upper critical field at temperature of 17.0 K(Last Row, Last Column of Table 6.4) for x=0.20 sample. In this way, $H_{c2}$ is determined for all doped and undoped samples.

The variation of upper critical fields with temperature is shown in Fig. 6.6 for undoped as well as for the Carbon doped samples. At lower fields of lesser than 3 Tesla, all samples have competing value of $H_{c2}$ but as the field increases, performance of Carbon doped samples become better than the undoped sample. As the Carbon content increases, $H_{c2}$
also rises and the performance of x=0.08, 0.10 & 0.15 at higher fields is found to be competitive. The other samples with 0.08>x>0.15 have slightly inferior performance but still it is better than the pure sample. This is because for the samples with x<0.08, the optimum level of Carbon substitution is not reached yet and for x>0.15, the extra unsubstituted carbon remains at the grain boundary. This can also induce grain boundary pinning but after a limit, agglomeration of nano Carbon particles take place so that the size of agglomerated clusters no longer remain of the range of coherence length of MgB$_2$ and become unable to pin the vortices.

It is observed that upper critical field is 14 Tesla at 18.5 K, for x=0.10 Carbon doped sample. But since the measurements are done only up to 14 Tesla, it is not possible to estimate the value of $H_{c2}$ at further lower temperatures experimentally i.e. In order to know the upper critical field, $H_{c2}$ below 18.5 K for the x=0.10 sample or the value of $H_{c2}$ at zero Kelvin, some theoretical models are need to be applied.

The simplest model to determine the upper critical field value at zero Kelvin i.e. $H_{c2}(0)$ is the Werthamer-Helfand-Hohenberg (WHH) formulation. According to the WHH formula

$$H_{c2}(0) = 0.69 \times T_c \times (dH_{c2}/dT)_{T=T_c}$$

(1)

For x=0.10 sample, $H_{c2}(0)$ is just equal to 9.5 Tesla by above formula which is not at all acceptable because the critical field of 14 Tesla is already achieved at a temperature of 18.5 K. It is not possible that critical field decreases with decrease in temperature. So, hereby we discard this formula for our system because it underestimates the $H_{c2}(0)$ value. This is also discussed by X. Huang et al [33] that $H_{c2}(0)$ value calculated by WHH formula is lesser than the real value by a factor of 5 or 6.

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**Fig. 6.6.** $H_{c2}$ vs temperature plots for MgB$_{2-x}$C$_x$(x=0.0-0.20) samples.
Another model applied for $H_{c2}$ determination is Ginzburg-Landau theory. The GL equation [40] in two band superconductors like MgB$_2$ for temperature dependence of $H_{c2}$ is given by

$$H_{c2}(T) = \frac{(H_{c2}(0)\theta^{1+\alpha})}{(1-(1+\alpha)\omega+1\omega^2+m\omega^3)}$$

(2)

Where $\theta = 1-T/T_c$ and $\omega = (1-\theta)^{1+\alpha}$ while $\alpha$, $l$ and $m$ are independent constants.

The fitting of $H_{c2}$ vs $T$ data is done according to Equation 2. Both experimental and fitted curves for $H_{c2}$ are shown in Fig. 6.7. The Fitted curves are in solid line while experimental data points are shown by symbol. The theoretical curve fits very well with the experimental data up to the limit we carry out the measurements. The $H_{c2}$ line is drawn theoretically according to Eq. 2 up to zero kelvin.

From the fitting, we can clearly see that, initially the behavior of $H_{c2}$ with $T$ is linear near $T_c$ and extends up to a temperature of 10 K and after that it saturates in the range of 3-10 K. Below 3K the $H_{c2}$ line have negative curvature. The $H_{c2}(0)$ for $x=0.15$ sample is found to be about 30 Tesla while the same is just nearly 16 Tesla for the pure MgB$_2$ sample. All the Carbon doped samples have $H_{c2}(0)$ values higher than the undoped sample. So, GL theory also confirms the enhancement of $H_{c2}$ with Carbon doping in MgB$_2$ and determines the $H_{c2}(0)$ value. The exact values of $H_{c2}(0)$ for all samples is written in the inset of Fig. 6.7. The estimated value of $H_{c2}(0)$ for pristine sample is in confirmation with earlier report[41]

There is one more model known as Gurevich theoretical model for two band superconductors [32]. It takes into account the impact of both bands on the critical
parameters. If we would have applied this model, the $H_{c2}(0)$ value had been obtained as high as 40 Tesla$^{33, 42}$ in case of bulk and of 50 Tesla in case of thin films$^{31, 43}$. This actually corresponds to the real situation in case of MgB$_2$ because the negative curvature in $H_{c2}$ line near $T=0$ K according to GL equation is not expected. So, Ginzzburg Landau theory although proves good enough but below 5K, the Gurevich model seems to be the best choice. Such a high value of above 40 Tesla is really appreciable which proves this material to be a merit candidate for practical applications against Nb based superconductors and HTSC materials.

The magnetization hysteresis loop i.e., magnetization vs applied field curves are shown for doped and undoped samples in both increasing and decreasing field directions at 5, 10 and 20 K in Fig. 6.8. The $M$-$H$ loop for pure sample closes much before than the doped sample at each temperature, which clearly demonstrates the enhanced value of irreversibility field ($H_{irr}$).

At 5 K, the loop closes nearly at about 8 Tesla for the pure sample but is still open at 13.7 K for the Carbon doped, $x = 0.08$ sample. All doped samples have better performance than the undoped samples.

To have a clear idea, $H_{irr}$ (irreversibility field) values are estimated for all samples at 5, 10 and 20 K from their respective magnetization loops. $H_{irr}$ is taken as the applied field value at which magnetization loop almost closes with a criterion of giving critical current

Fig. 6.8. Magnetization loop $M$ ($H$) at 5, 10 & 20K for MgB$_{2-x}$C$_x$ samples ($x=0.0$, 0.08, 0.10 & 0.20) up to 14 Tesla field

139
density value of the order of $10^2$ A/cm$^2$. The variation of irreversibility field values with doping content is depicted in Fig. 6.9 at different temperatures. The $x = 0.08$ sample has highest $H_{irr}$ values among all the samples. For pristine sample, the $H_{irr}$ values are 4.5, 7.4 & 8.0 Tesla at 20, 10 & 5 K respectively, whereas it is increased to 6.3, 11.0 & 13.7 Tesla for the $x = 0.08$ sample at the same respective temperatures. These values are slightly higher than those reported earlier [44]. The increased values of $H_{irr}$ confirm the flux pinning by added nano Carbon particles.

The critical current density is calculated from the magnetization hysteresis loops using Bean’s Critical Model. The variation of $J_c$ with applied fields is shown in figure 6.10(a) & (b) at 10 & 20K respectively for pristine and doped samples. All samples have $J_c$ of the order of $10^5$ A/cm$^2$ at low field values both at 10 & 20 K. As field increases, $J_c$
values decrease very rapidly for the pure sample and becomes of the order of $10^2$ A/cm$^2$ at a field of 6 Tesla at 10 K while it is still of the order of $10^4$ for the $x = 0.08$ sample.

Quantiatively, $J_c$ is about $1.04 \times 10^4$ A/cm$^2$ at 6 Tesla and 10 K for $x=0.08$ nano-Carbon doped sample, where as it is $5.4 \times 10^2$ A/cm$^2$ for pure sample at same field and temperature values. More specifically, $J_c$ of this sample is 21 times higher than the pure sample at 6 Tesla & 10 K. The similar is the situation at 20 K as well for the $J_c(H)$ of $x = 0.08$ sample, which is 13 times higher than that of the pure sample at a field value of 4 Tesla. The critical current density value is enhanced much profoundly in the case of carbon doped, $x = 0.08$ sample at both the temperatures. The observed values of $H_{c2}$, $H_{irr}$ and $J_c$ are competitive or slightly better than those being reported yet [45-48].

In order to have a confirmative claim about the flux pinning behavior, flux pinning force $F_p$ is calculated. The dependence of reduced flux pinning force with applied field is demonstrated in Fig. 6.11(a) & (b) at 10 & 20 K respectively. The relationship between flux pinning force and critical current density could be described by [49,50]

$$F_p = \mu_0 J_c(H) H$$  \hspace{1cm} (1)

where $\mu_0$ is the magnetic permeability in vacuum. The curves become broader with Carbon doping as compared to the undoped sample. It directly confirms that added nano-
Carbon had successfully pinned the vortices which results in increased critical field values and subsequently enhanced values of critical current density. The shape of flux pinning curve is explainable by grain boundary pinning [51].

The point to be noticed is that although $x = 0.08$ sample seems to show best results for this batch of samples, but depending on the factors like precursor material and processing conditions, the optimum Carbon content for best performance may change slightly. That's why different groups reported different compositions ($x = 0.04$ to $0.15$) showing best performance [44-46, 52,53]. Even in our different batch of samples [54], the $x = 0.10$ sample showed best results up to a field of 8 Tesla. Thus, the
only fact to be hiked is that \textit{nano}-Carbon substitution results in enhancement of $H_{c2}$, $H_{irr}$ and $J_c$ values. All doped samples show better performance than undoped sample.

Further the $J_c$ values are supposed to increase further with improvement in grains connectivity [55]. The grains connectivity can be estimated directly by knowing the extent of disorder i.e., $\rho^{300K} - \rho^{40K}$ values [55]. In present case of MgB$_{2-x}$C$_x$ this value is somewhere between 80-120$\mu\Omega$.cm, which is $\sim$ 7-8 $\mu\Omega$.cm for pure good thin films [55, 56]. Interestingly, poor grains connectivity results in effective lowering of the cross-sectional area of the sample and hence the lower $J_c$. Thus, Improvement of the grains connectivity of the studied bulk polycrystalline MgB$_{2-x}$C$_x$ samples is yet warranted to further increase the critical current density of the samples.

Another important point to mention is that all the superconducting parameters increases with carbon content only up to a fixed composition for example $x=0.08$ or 0.10 and decrease with further increase in carbon content. One of the possible reasons is that the \textit{nano} particles which are not substituted get agglomerated when their concentration increases and the particles no longer remain of nano size. At that time, only one effect i.e. intrinsic pinning enhances the parameters. That’s why for higher carbon content i.e. $x=0.20$, the critical paramereres are higher than the pristine sample (due to presence of intrinsic pinning) but are lower than the optimized sample like $x=0.08$ (due to absence of extrinsic pinning).

\textbf{6.4 SUMMARY AND CONCLUSIONS}

- The MgB$_{2-x}$C$_x$ samples with $x=0.0-0.20$ are studied for the significant enhancement in critical parameters like $H_{irr}$, $J_c(H)$ and $H_{c2}$.
- The structural studies i.e. X-ray diffraction patterns reveal that no impurity phase arise up to $x=0.10$ and carbon is substituted completely in MgB$_2$ lattice. With further increase in carbon content, a minor phase of MgB$_2$C$_2$ starts appearing indicating that the saturation level of carbon substitution has been reached. The net maximum substitution level of carbon in MgB$_2$ is calculated and found to be
just 6.75 atomic wt. % of boron while the samples were prepared up to 10 atomic wt.% of boron. Lattice parameters are calculated and it is observed that value of $a$ parameter decreases continuously but $c$ changes randomly with the increasing carbon content.

- Resistivity measurements reveal a continuous decrease in $T_c$ with an increase in $nano$-C content for MgB$_{2-x}$C$_x$ system under zero applied field. On the other hand, $T_c$ of the $nano$-C doped samples improves remarkably at higher fields in comparison of pure MgB$_2$.

- The upper critical field values, $H_{c2}$ are obtained from $\rho$-$T(H)$ data based upon the criterion of 90% of normal resistivity i.e. $H_{c2} = H$ at which $\rho = 90\% \rho_N$ where $\rho_N$ is the normal resistivity or resistivity at about 40 K in MgB$_{2-x}$C$_x$ samples. Theoretical models are applied on temperature dependence of upper critical field in order to estimate the critical field at low temperatures. $H_{c2}(0)$ for all the Carbon doped samples is found to be higher than the pure MgB$_2$ sample. The $H_{c2}(0)$ value for pure sample is just 15.7 Tesla which got profoundly enhanced and the highest value of $H_{c2}(0)$ of about 30 Tesla is achieved for $x=0.15$ sample.

- Besides, the upper critical field, other critical parameters like $H_{irr}$ and $J_c(H)$ also improve significantly for the Carbon doped samples. More specifically, critical current density ($J_c$) for the Carbon doped, $x=0.08$ sample is increased 21 times as compared to the pristine sample at 10 K and 6 Tesla field. The flux pinning force is also enhanced with the Carbon doping.

- The present investigations show that $nano$ carbon substitution is a promising way to synthesize high performance MgB$_2$ bulk material with improved values of $H_{c2}$, $H_{irr}$ and $J_c(H)$.
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147


