In this chapter the effect of the controlled ion irradiation on the superconducting properties of MgB$_2$ thin films is discussed. These effects are studied in terms of magnetoresistance and magnetization measurements done on irradiated MgB$_2$ films. We conclude that bands of MgB$_2$ can be separately tuned by varying the conditions for irradiation.
Chapter 3  Modification of Upper Critical Field...

3.1 Introduction

The most important aspect of MgB2, particularly from the application point of view, is the prospect of achieving optimal upper critical fields by tuning the scattering mechanism of this two band superconductor [1]. In chapter 1, we have seen that the upper critical field in a conventional WHH superconductor can be related to the normal state resistivity of the material. It turns out, that in a multiband superconductor, similar analysis can lead to modification of H-T phase diagram by altering inter and intra band scattering mechanism [1-5]. As a consequence, several studies have indicated that upper critical field (H_{c2}) as high as 60 T is possible in this simple intermetallic compound. However no clear reproducible material processing technique has been suggested to achieve this enhancement. A great deal of understanding on the scattering mechanism is still open to debate. It is well known that irradiation induced point and columnar defects greatly alter the superconducting properties especially in cuprate based high temperature superconductors. While the extended defects contribute to enhanced pinning and consequent increase in critical current density (J_c), the point defects generally shorten the electron mean free path leading to increase in H_{c2}. In the case of MgB2 however, because of the two band gap features, the physics is further compounded depending on the relative effect of disorder on the 2D directional \( \sigma \) band and the 3D isotropic \( \pi \) band [2, 7-10]. Moreover, while there is general agreement that the defects modify the \( \pi \) intraband scattering mechanism, there is no definite implication for the \( \sigma \) band properties. In this chapter we correlate the extrinsic defect structure with the changes in intra-band transport and the consequent effects in connectivity, critical current density and upper critical field.
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3.2  Previous reports on irradiation study in MgB₂

The reported results from irradiation experiments on MgB₂ have provided no clear evidence of formation of columnar defects under heavy ion irradiation [11-15]. The literature on irradiation has been mentioned in chapter 1, and some reports have been tabulated below.

Table 3.1: Summary of the important results of irradiation study in MgB₂

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy&amp;Fluence</th>
<th>Post irradiation effect</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>5.8GeV, (1\times10^{10}, 5 \times 10^{10}, 1 \times 10^{11}, 2 \times 10^{11})</td>
<td>Decrease in magnetization (J_c) at low field, possibly due to degradation of grain boundary connectivity, marginal increase in (J_c) at high field.</td>
<td>Chikumoto [11]</td>
</tr>
<tr>
<td>Ag</td>
<td>200MeV, (3 \times 10^{11}, 1 \times 10^{12})</td>
<td>Marginal enhancement in (J_c) and its dependence is similar to unirradiated; (J_c) increased at high field with higher dose. This was assigned to agglomerated clusters rather than columnar defects.</td>
<td>Shinde [12]</td>
</tr>
<tr>
<td>Electron</td>
<td>2.5MeV, (5 \times 10^{17}, 1 \times 10^{11})</td>
<td>At low field, (J_c) increased slightly and it decreased at high fields.</td>
<td>Okayasu [13]</td>
</tr>
<tr>
<td>Xe</td>
<td>(1 \times 10^{10})</td>
<td>No change in (J_c) at low field, (H^*) improved.</td>
<td></td>
</tr>
<tr>
<td>Doped U, irradiated with neutron</td>
<td>(2 \times 10^{16}, 5 \times 10^{15}, 5 \times 10^{14}, 5 \times 10^{13})</td>
<td>No formation of defect tracks.</td>
<td>Silver [14]</td>
</tr>
</tbody>
</table>
The overall picture that emerges is that irradiation with light ions and heavy ions yield different results on the superconducting properties of MgB$_2$. Our goal is to study the effect of 200 MeV Au$^{15+}$ and 100 MeV Si$^8+$ ion irradiation on high quality superconducting MgB$_2$ thin films. The light ion Si$^8+$ with relatively low energy is used to introduce primarily isotropic point defects where as heavy ion Au$^{15+}$ with high energy is to give rise to relatively extended disorder or clusters along the direction of irradiation.
3.3 Experiment

High quality MgB₂ films used in this study were prepared by depositing boron on Al₂O₃ 0001 substrate by RF magnetron sputtering. The substrate temperature was 500 °C. The film was then placed in a Ta tube with Mg lumps, which was then placed in a quartz tube. The tube was evacuated to ~ 10⁻⁶ Torr and backfilled with 10 Torr of Argon. The sample was then annealed at 900 °C for 5 hours and allowed to cool to room temperature at the rate of 3 degree per minute. The resulting film is ~ 200 nm thick. Details concerning the X-ray and TEM characterization of similar samples are reported elsewhere [19]. Three pieces of size ~ 2×5 mm² and two pieces of ~ 1.1×2.5 mm² were taken out from the single large piece of the film. Leaving out one pristine piece, 4 other pieces were irradiated with a variety of ions, fluence and energy using the 15 UD pelletron accelerator at the Inter-University Accelerator Center, New Delhi.

Sample A, B, C, D, and E stand for unirradiated, Au¹⁵⁺ (1×10¹² ions/cm²) irradiated, Au¹⁵⁺ (5×10¹² ions/cm²) irradiated, Si⁸⁺ (5×10¹² ions/cm²) irradiated, and Si⁸⁺ (5×10¹³ ions/cm²) irradiated respectively. The energy of the Si⁸⁺ and Au¹⁵⁺ ions were set to 100 MeV and 200 MeV respectively. To irradiate the samples the ion beam was focused to a sharp point of size 1mm and the beam was scanned in the area of 10 mm×10mm using magnetic scanner that ensured uniform irradiation of the whole sample. The beam current was kept low (0.5 pnA) to avoid the heating effects.

The irradiation was carried out at room temperature with the beam at an angle ~ 5° from c-axis to avoid channeling effects. Stopping power (Sₑ) and range (Rₑ) of the ions for MgB₂ calculated by SRIM simulation software [20] are found to be Sₑ = 18.08 keV/nm and 2.39 keV/nm and Rₑ = 19.9 μm and 34.3 μm for 200 MeV Au¹⁵⁺ and 100 MeV Si⁸⁺ ions respectively. These depths are well above the thickness of the sample. In turns it indicates that irradiated ions are not impinged in to the sample, in fact they are coming out of the thin film.
sample so variation in the properties are due to modification in the sample rather than these impinged particles. It is important to note that at this energy and fluence, the energy deposited per unit volume of the film is approximately $10^{21}$ keV/cm$^3$ and that is comparable to other studies [17,18].

Standard four-probe technique was used for transport measurements. Contacts were made using 44 gauge copper wires with air drying conducting silver paste. The current used in resistivity measurement was fixed at 500 $\mu$A. Voltage corresponding to this probe current was measured and resistivity calculated by using the dimension of the sample employing the Ohm’s law. The measurements were carried out using Cryogenic 8 T Cryogen-free magnet in conjunction with a variable temperature insert (VTI). Magnetization $J_c$ for the samples was ascertained using a 5 T Quantum Design SQUID magnetometer.

### 3.4 Results and discussion

Fig 3.1 shows the zero field resistivity as a function of temperature for the unirradiated and four irradiated MgB$_2$ thin films. The Inset 1 of this figure zoom the same data up to 40 K. The samples were cooled in zero DC magnetic field down to 30 K and the data were taken in the warming-up cycle. We note that the onset of superconductivity in the pristine sample occurs around 35.7 K and 50% transition is achieved in the temperature interval of 0.4 K.
Fig 3.1: Temperature dependence of resistivity of MgB$_2$ thin films. Data are shown for unirradiated A (■), Au $1 \times 10^{12}$ irradiated B (○), Au $5 \times 10^{12}$ irradiated C (□), Si $5 \times 10^{12}$ irradiated D (□), and Si $5 \times 10^{13}$ irradiated E (△). Inset 1 shows the variation in transition temperature. Inset 2 plots normalized resistivity with respect to temperature.

The suppression in $T_c$ for the pristine sample is primarily due to impurity in boron target. With an applied external field, the intersection points between the transition slope line with the normal state resistivity line and the zero resistivity line corresponds to the upper critical field $H_{c2}$ and irreversibility field $H^*$ respectively. This is defined schematically in the inset of Fig 3.2.
Fig 3.2: Upper critical field $H_{c2}$ is plotted against reduced temperature $T/T_c$. The magnetic field is applied perpendicular to $ab$ plane. The joining lines are guides to eye. Inset shows in-field transitions from 0 to 7 T for sample D. The curvature in $H_{c2}$-$T$ phase diagram for Au irradiated sample is evident. The inset also shows how we have defined $H_{c2}$ for the measurements.

As expected, with higher irradiation dose, the onset of superconducting transition shifts to lower temperatures. While for low dose Au$^{15+}$ (sample B) the $T_c$ is decreased to 34.5 K, for the five times higher dose sample C, there is significant suppression in $T_c$ (32.5 K). Irradiation with 100 MeV Si$^{8+}$ also shows decrease in $T_c$ ($\sim$ 34.8 K) but curiously there is little difference between the $T_c$ of sample D and E although there is an order of magnitude difference in fluence. These results are in contrast with the results of Gandikota et al. which
reported a systematic decrease in $T_c$ with an increase in normal state resistivity with fluence [18].

We notice that the suppression in $T_c$ in MgB$_2$ is much less compared to high $T_c$ ceramic cuprates where empirically it has been established that decrease in $T_c$ (Δ$T_c$) is related to fluence ($\phi$) through the equation $\Delta T_c/\phi = 2.9 \times 10^{11}$ K per ions per cm$^2$ [21]. In the intermetallic MgB$_2$, expectedly, this equation is not followed and the $T_c$ suppression is not linearly related to the fluence. We also note that the transition broadening in all the irradiated samples is less than 1 K. This confirms that the extrinsic defects are uniformly distributed in the sample.

Table 3.2 summarizes the absolute value of resistivity at 40 K, RRR (residual resistivity ratio) and $\Delta \rho$ ($\rho_{(293 \text{ K})} - \rho_{(40 \text{ K})}$) for the five samples ascertained from Fig 3.1. We find that the magnitude of RRR ($\rho_{(293 \text{ K})}/\rho_{(40 \text{ K})}$) decreases with irradiation. We also note that $\rho_{(40 \text{ K})}$ increases with irradiation dose. This behavior is well supported by other irradiation experiments [17, 18].

Rowell et al. have argued that an increase in $\Delta \rho$ is true measure of post-irradiation decrease in inter grain connectivity [18, 22]. A constant $\Delta \rho$ was interpreted as no change in connectivity up to the fluence of $10^{17}$ ions/cm$^2$ [18]. Our results on the other hand show that while $\Delta \rho$ increases with fluence both for Si and Au irradiation, the effect is much more pronounced for Au$^{15+}$ ions. To further confirm this trend, plotted in Inset 2 of Fig 3.1 is the normalized zero field resistivity as a function of temperature. We see that $\rho$ vs. $T$ behavior is more or less similar for the pristine and Si$^{8+}$ irradiated films but it differs for Au irradiated films.

Mazin et al. have analyzed the multiband superconductivity in MgB$_2$ in the clean and dirty limit [23]. They conclude that between clean and dirty samples, the small change in $T_c$ and similar $\rho$ vs. $T$ behavior are explained by exceptionally low inter-band scattering and the entire transport is well
understood by \( \pi \) intra-band scattering [23]. Our results on Si irradiated and unirradiated samples reflect this analysis.

**Table 3.2:** Summary of our irradiation study on MgB\(_2\) thin films.

<table>
<thead>
<tr>
<th>Ion (Sample) Energy (MeV)</th>
<th>Fluence (ions/cm(^2))</th>
<th>( T_c ) (K) ( H = 0T )</th>
<th>RRR ( \rho_{293}/\rho_{40} )</th>
<th>( \rho_{(40K)} ) (( \mu \Omega ) cm)</th>
<th>( \Delta \rho_{(293-40)} ) (( \mu \Omega ) cm)</th>
<th>( (d\rho/dT)_{293} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated (A) 0</td>
<td>0</td>
<td>35.7</td>
<td>1.50</td>
<td>19.5</td>
<td>9.8</td>
<td>0.07</td>
</tr>
<tr>
<td>Au(^{15+}) (B) 200</td>
<td>( 1 \times 10^{12} )</td>
<td>34.5</td>
<td>1.41</td>
<td>32.4</td>
<td>13.8</td>
<td>0.08</td>
</tr>
<tr>
<td>Au(^{15+}) (C) 200</td>
<td>( 5 \times 10^{12} )</td>
<td>32.5</td>
<td>1.31</td>
<td>79.4</td>
<td>25.1</td>
<td>0.15</td>
</tr>
<tr>
<td>Si(^{8+}) (D) 100</td>
<td>( 5 \times 10^{12} )</td>
<td>34.9</td>
<td>1.41</td>
<td>22.6</td>
<td>10.1</td>
<td>0.07</td>
</tr>
<tr>
<td>Si(^{8+}) (E) 100</td>
<td>( 5 \times 10^{13} )</td>
<td>34.8</td>
<td>1.42</td>
<td>40.3</td>
<td>16.8</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Clearly, the ion irradiation effectively alters the \( \pi \) intra-band defect scattering. But the question still remains what happens to the \( \sigma \) band scattering post irradiation. Between sample D and E we observe that for an order of magnitude difference in dose, the \( T_c \) for Si\(^{8+}\) irradiation changes negligibly. However between sample B and C, with heavy ion irradiation, there is drastic change in \( T_c \) when the dose is increased 5 times. As seen in Inset 2 of Fig 3.1, the \( \rho \) vs. \( T \) curves for Au irradiation do not superimpose on each other unlike the case with Si irradiation. It clearly mentions towards the variation in the mechanism for \( T_c \) suppression with extended defects than that for the point defects in MgB\(_2\).
We further discuss the transport properties of irradiated samples in the presence of external magnetic field. Any modification in the upper critical field $H_{c2}$ can only be explained by change in transport mean free path [24]. Plotted in the inset of Fig 3.2 is the in-field transition for the sample D. Similar measurements were carried out for sample A, B, C, and E. Fig 3.2 shows $H_{c2}$ versus reduced temperature ($T/T_c$) for all the five samples.

It is evident that an increase in $H_{c2}$ is obtained for the Au irradiated samples B and C. For Si irradiated samples at high fields, $H_{c2}$ decreased compared to unirradiated sample. We further note that for the same dose of irradiation while Au$^{15+}$ ions lead to curvature in the H-T phase diagram, a linear behavior is observed for Si$^{8+}$ irradiation. The slope of H-T line near $T_c$ has been analyzed by Gurevich et al. [2, 5]. They have treated the multiband transport in MgB$_2$ through the exact solutions of Uzadel equations with anisotropic diffusivities associated with the two bands. In this model the zero temperature upper critical field $H_{c2}(0)$ is estimated from the minimum in diffusivity where as the slope $dH_{c2}/dT$ near $T_c$ is determined by maximum in diffusivity. The model concludes that a relatively dirty $\sigma$ band leads to curvature in H-T phase diagram where as a dirtier $\pi$ band leads to linear H-T phase diagram.

In this light our data indicate that while irradiation invariably alters the $\pi$ intra-band scattering, extended defects effectively alter the $\sigma$ band too. More support for this is arrived from $d\rho/dT$ values at room temperature. For $\pi$ band scattering the room temperature $d\rho/dT$ is predicted to be approximately 0.065 $\mu\Omega$ cm/K [25]. From Table 3.2 for the pristine and Si irradiated samples similar values are obtained. For high dose Au on the other hand $d\rho/dT$ is doubled. This again points to the fact that for extended defects $\sigma$ band properties are vastly altered along with accompanied changes in $\pi$ band.

To confirm whether the increase in $\Delta\rho$ actually translates into decrease in connectivity and therefore decrease in critical current density, we carried out
isothermal magnetization measurements for sample A, C and D. We chose these samples because sample C showed maximum increase in $\Delta \rho$, where as sample D exhibited minimum increase. Fig 3.3 shows the magnetization $J_c$ calculated from the magnetization loops using Bean’s model [26]. It is interesting to see that critical current density for sample C falls below that of the unirradiated sample A. Sample D on the other hand exhibits an increase in $J_c$ because of combination of two facts, a) increase in intra-grain pinning and b) negligible decrease in intergrain connectivity. Transport $J_c$ obtained from I-V scans at external field $\mu_0H = 1$ T also confirmed that inter grain connectivity is severely suppressed in sample C.

**Fig 3.3**: Variation of magnetization critical current density $J_c$ as a function of field for unirradiated $A$ ($\bullet$), Au $5 \times 10^{12}$ irradiated $C$ ($\Box$), and Si $5 \times 10^{12}$ irradiated $D$ ($\psi$) at 5 K and 20 K. The inset shows magnetization loops at $T = 5$ K. Improvement in $J_c$ is observed only for light ion irradiation.
As pointed out earlier, the modification of $H_{c2}$ vs. $T$ behavior in a multiband superconductor critically depends on the size and directional properties of the created defects. In Fig 3.4 we compare the upper critical field as a function of reduced temperature when the field is applied parallel and perpendicular to the ab-plane of the sample. For clarity only the data for sample A, B, and E are shown. In the inset the temperature scans at a constant field of 7 T for sample B and E are plotted. When the field is applied parallel to ab-plane, not much difference in $H_{c2}$ for the three samples is observed. This means that the anisotropy which is defined as $\gamma = H_{c2}^\parallel / H_{c2}^\perp$ could be higher or

![Figure 3.4: Upper critical field $H_{c2}$ is plotted against normalized $T_c$ in perpendicular (closed symbol) and parallel (open symbol) to ab-plane direction for sample A, B, and E. Inset shows superconducting transition with an external field $\mu_0 H = 7$ T for sample B and E. An increase in anisotropy for Si irradiated sample is observed.](image)
lower compared to the pristine sample depending on $H_{c2}^\perp$ values. Here $H_{c2}^\parallel$ and $H_{c2}^\perp$ stand for upper critical field parallel and perpendicular to ab-plane of the sample respectively.

From Fig 3.4 it is interesting to infer that while the anisotropy decreased with irradiation for extended defects [27], with point defects there is a possibility to increase it. Thus by choosing ions of different energy and atomic number one can in principle tune the scattering mechanism selectively in MgB$_2$.

### 3.5 Conclusion

We have carried out a systematic study of ion-induced defects on superconducting properties of thin film MgB$_2$. We find that while all defects alter the $\pi$ band scattering mechanism, extended defects along the c-axis preferentially affect the $\sigma$ band too. Three different aspects of our data e.g. change in $\frac{dp}{dT}$ at room temperature, curvature in H-T phase diagram and drastic reduction in $T_c$ support this observation. This has significant implication for $H_{c2}$-$T$ phase diagram and can lead to controlled tuning of two-band scattering in MgB$_2$. The intergrain connectivity is suppressed with extended defects leading to decrease in critical current density. The upper critical field anisotropy can be tailored by selectively creating different types of extrinsic defects.

Our results indicate that the $H_{c2}$-$T$ phase diagram show distinctly different characteristics for point defects and extended defects. It has been argued that $\sigma$ intraband and $\pi$-$\sigma$ interband scattering is negligible even in dirty MgB$_2$ and the entire transport property can be explained primarily on the basis of $\pi$ intraband scattering [23]. The key feature for this argument is the lack of correlation between residual resistivity ratio in a variety of MgB$_2$ samples with the suppression of $T_c$. In our experiments, on the other hand, the drastic suppression of $T_c$ and corresponding curvature in $H_{c2}$-$T$ phase diagram in heavy
ion irradiated samples can only be explained by dominant alteration in $\sigma$ band scattering mechanism. We find the suppression of intergrain connectivity to be fairly independent of defect density but significantly dependent on size of the defects. The critical current density and intragrain flux pinning, however, are best improved with light ion irradiation.
Chapter 3 Modification of Upper Critical Field...

References


