# Non-resonant microwave absorption studies of superconducting $MgB_2$ and $MgB_2$ + MgO

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**Abstract.** Non-resonant microwave absorption (NRMA) studies of superconducting $MgB_2$ and a sample containing $\sim 10\%$ by weight of MgO in $MgB_2$ are reported. The NRMA results indicate near absence of intergranular weak links in the pure $MgB_2$ sample. A linear temperature dependence of the lower critical field $H_{c1}$ is observed indicating a non-$s$ wave superconductivity. However, the phase reversal of the NRMA signal which could suggest $d$ wave symmetry is also not observed. In the $MgB_2$ + MgO sample, much larger low field dependent absorption is observed indicating the presence of intergranular weak links. The hysteretic behavior of NRMA is compared and contrasted in the two samples. In the pure $MgB_2$ sample, a large hysteresis is observed between the forward and the reverse scans of the magnetic field indicating strong pinning of flux lines. This hysteresis saturates a few degrees below $T_c$ while in the $MgB_2$ + MgO sample, a much slower increase of hysteresis with decreasing temperature is observed, a signature of weaker pinning.

The discovery [1] of superconductivity in the 'off the shelf' intermetallic compound $MgB_2$ has given rise to a flurry of scientific activity which indicates that it is potentially a very useful material for applications. The nature and the origin of superconductivity in $MgB_2$ have been the subject of some controversy. For example, the observation [2] of boron isotope effect implies $MgB_2$ to be a phonon mediated BCS superconductor whereas the temperature dependence of the lower critical field $H_{c1}$ was found to be linear [3] expected for a $d$ wave symmetry of the order parameter. The results of scanning tunneling spectroscopy experiments on thin film and pellet samples of $MgB_2$ [4] indicate the symmetry of the order parameter to be an anisotropic $s$ wave. A model proposing the anisotropic $s$ wave symmetry of the order parameter has been proposed also by Haas $et\ al$ [5]. The specific heat measurements by Yang $et\ al$ [6], indicate either an anisotropic $s$ wave or a multicomponent order parameter. The penetration depth measurements show a quadratic temperature dependence indicating nodes in the superconducting energy gap [7]. Independent of this debate over the symmetry of the order parameter, a pleasant surprise has been the reported transparency of the intergranular contacts to the current in the polycrystalline samples, leading to high critical current density ($J_c$) even in the presence of a magnetic field [8,9]. This result is in quite a contrast to the high $T_c$ superconductors (HTSC), that

abound in intergranular weak links and makes $MgB_2$ attractive for applications requiring high critical current density.

The technique of non-resonant microwave absorption (NRMA) has proven to be a valuable tool in detecting and characterizing superconductivity in the case of HTSC [10–12]. In this technique, the sample is studied using a continuous wave electron paramagnetic resonance (EPR) spectrometer, by recording the magnetic field dependence of the power absorption. In standard EPR spectrometers, the magnetic field is usually modulated at 100 kHz. The magnetic field dependent signal from the sample is then compared with the modulating ac field so as to detect only that component of the signal which appears with the same frequency and phase as the modulating field. Because of this frequency as well as phase sensitive detection, a large signal to noise ratio is obtained. However, the recorded signal is the derivative of the actual power absorbed.

In the case of HTSC, two processes mainly contribute to the field dependent dissipation. One, the decoupling of the Josephson junctions (JJs) due to the magnetic field [13] and the other, the Lorentz force driven motion of the quantized flux lines [14], the so-called fluxons. All but the extremely well-prepared thin film and single crystalline HTSC samples have a large number of weak links acting as JJs and the signal from the JJs is predominant over that from the vortex motion. Usually, the contributions due to JJs and flux motion can be easily distinguished from each other from the characteristic field dependences, reflected in the line shapes [15]. Thus, for moderate modulation amplitudes, the decoupling of the JJs leads to a narrow derivative looking signal centered around zero field while the fluxon motion results in a quasi-linear dependence on field and therefore $dP/dH$ appears to have near field independence.

In this paper, we examine superconducting $MgB_2$ and $MgB_2 + MgO$ samples with a view to characterizing their JJ properties. There is a large number of studies which report the absence of weak links in $MgB_2$ system. NRMA is a very sensitive technique to JJ response and our preliminary study indicated near absence of intergranular weak-links in $MgB_2$ even in powder form [16]. In this report we compare the NRMA response of pure $MgB_2$ with $MgB_2 + MgO$ sample so as to investigate the effect of MgO as an intergranular medium between the $MgB_2$ grains. This study also sheds some light on the pinning properties of the two types of samples.

The sample of $MgB_2$ (sample 1) used was obtained from M/s Alpha Aesar of John Matthey GmBH, Germany and was used without further processing except for pelletizing under a pressure of 2 tons. Ac susceptibility measurements indicated a $T_c$ of 39 K. The MgO mixed $MgB_2$ sample was prepared as follows: stoichiometric mixture of Mg powder (99.8%) and crystalline boron 325 mesh, were ground and pelletized and placed inside Ta crucible and sealed in Ar atmosphere. This was further sealed in a quartz tube with 350 mbar Ar pressure and heat treated at 950°C in a box furnace for 2 h and air quenched. The samples had about 10% of MgO, which came from crystalline boron containing oxygen impurity. The NRMA signals for both the samples were recorded using a Bruker 200D X band (microwave frequency: 9.43 GHz) EPR spectrometer equipped with Oxford Instruments ESR 900 continuous flow cryostat, in the temperature range of 4.2 K to room temperature. The NRMA measurements are done by the so-called homodyne lock in detection or phase sensitive detection. The modulation field used was 4 Gauss peak to peak. This field is high enough so as to minimize the low modulation field induced hysteresis effects [13]. In the experiment with sample 1, a microwave power of 79 mW was used. The sample was zero field cooled to 4.2 K and the signals were recorded between $-50$ and

4950 Gauss for both forward and reverse scans of the field during both cooling and warming of the sample. Similar experiment was carried out using the MgB$_2$ sample containing MgO (sample 2) also.

Figure 1 shows typical NRMA signals from sample 1 at a few representative temperatures recorded while warming. The signals recorded while cooling (not shown) are essentially similar. In the normal state only a very weak EPR signal due to some impurity in the cavity is observed. Below $T_c$ ($\sim$ 39 K), the NRMA signal appears centered at zero field which on cooling increases both in intensity and extent in the field. By 34 K it is seen to have extended beyond the limits of our magnetic field (5950 Gauss). At zero field, a sudden rise in the signal (note its opposite phase to that of the EPR signal as expected for a normal NRMA signal) is observed and at a temperature dependent higher field there is a change in the slope of the signal. The point at which the slope change is observed (as marked by the arrows on a few signals) can be associated with the lower critical field.
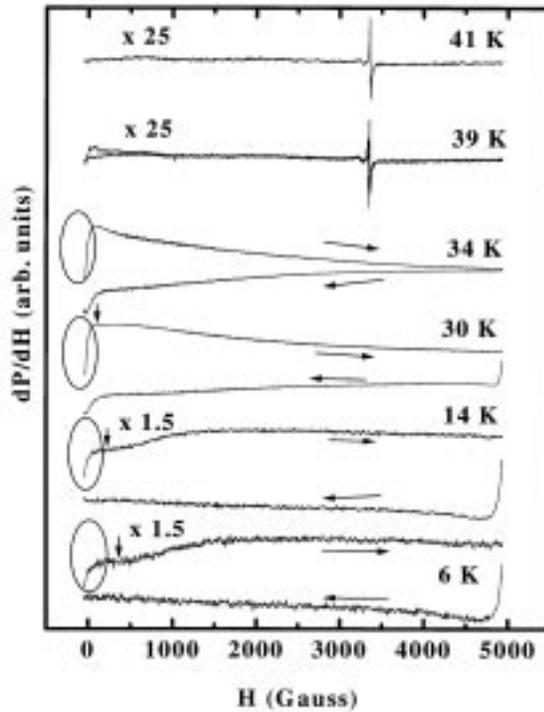


**Figure 1.** Typical NRMA signals recorded from a sample of MgB$_2$ during warming at a few representative temperatures for both forward and reverse scans of the magnetic field. The ellipses indicate part of the signal tentatively attributed to a very small number of weak links forming JJs in the sample. The vertical arrows mark the field at which the slope changes indicating the onset of the entry of the magnetic field in the form of vortices in the sample. The hysteresis between the forward and reverse scans of the magnetic field shows near field independence, thus forming practically rectangular hysteresis loop.

We denote this field by $H_{c1}^{*}$ to indicate that it is uncorrected for demagnetization factor and geometric and/or surface barriers.

Figure 2 shows the NRMA signals from sample 2 obtained at corresponding temperatures. These signals at low temperature were recorded at a microwave power of 7.9 mW and from 14 K onwards they were recorded at 20 mW. In spite of much lower microwave powers used and almost the same receiver gains, the signals from sample 2 have almost the same intensity and much better signal to noise ratio than sample 1. The clear slope change in the signals obtained in sample 1 is not observed in sample 2. Just as in sample 1 the signals show hysteresis between forward and reverse scans. However, in this case the hysteresis falls off much more rapidly as a function of field. The low field sharp rise in these samples is much more pronounced in the reverse scan also, in contrast to the near absence of such signals in case of sample 1 in the reverse scan.

Figure 3 shows the temperature dependence of $H_{c1}^{*}$ of pure MgB$_2$. It is seen that the temperature dependence is approximately linear, attributed to a non-*s* wave superconductor [3]. Such linear dependences have also been observed by other workers [17].

The crucial difference between these NRMA signals from sample 1 and those observed in polycrystalline samples of HTSC is the near absence of a narrow derivative looking
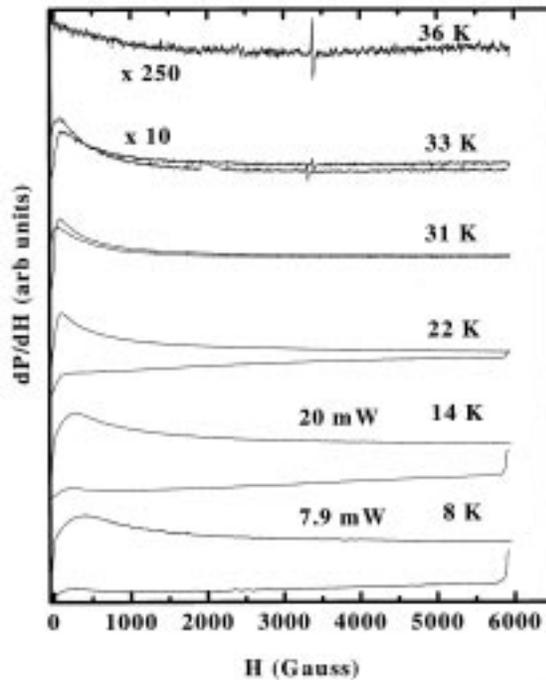


**Figure 2.** Typical NRMA signals from a sample of MgB$_2$ + MgO recorded during warming at a few representative temperatures for both forward and reverse scans of the magnetic field. The signals show strong zero field response indicating the presence of weak links acting as JJs. The hysteresis between forward and reverse scans of the magnetic field shows a strong field as well as temperature dependence.
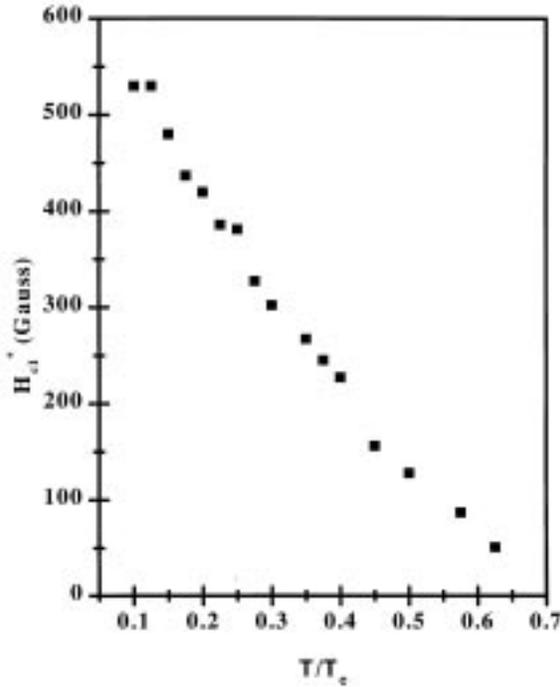
**Figure 3.** $H_{c1}^*$ obtained from the slope change observed in the NRMA signals from MgB$_2$ uncorrected for demagnetization factor and geometrical and/or surface barrier effects, plotted as a function of reduced temperature $(T/T_c)$, showing quasi-linear behavior.

signal observed in the latter at low fields commonly attributed to JJs. This might indicate the absence of intergranular weak links. However, the presence of a significant field dependent dissipation below $H_{c1}$ (indicated by ellipses in figure 1) obtained in MgB$_2$ needs to be explained. While quasi-particle excitation is a possible candidate, we believe the temperature and field dependences of the observed signals do not favor this mechanism. NRMA technique being very sensitive to the JJs, can pick up even minute contributions from them. Therefore, we attribute the signal which is observed below $H_{c1}$ to the presence of a few weak JJs in the sample. The temperature dependence of the intensity of the signal below $H_{c1}$ also supports this possibility.

We have done the analysis of hysteresis observed in the forward and reverse scans of magnetic field. The difference in the intensity (d$P$/d$H$) of the signal at two different fields viz 2000 Gauss and 4000 Gauss is measured. The ratio of the hysteresis at 4000 Gauss to the hysteresis at 2000 Gauss is obtained. The choice of 2000 Gauss and 4000 Gauss was made taking into account two things. At very low fields the hysteresis in the signal is contributed mainly by the Josephson junctions response as discussed previously. In the case of sample 1 signal line shape also shows the effects due to the lower critical field. So we measured the hysteresis at 2000 Gauss so as to avoid any such effects. The hysteresis obtained at such a high field can be attributed mainly to the pinning of the vortices. At temperatures

close to $T_c$ the hysteresis in sample 2 starts vanishing very rapidly at higher fields. So we have measured the hysteresis values at 4000 Gauss so as to get maximum number of data points for obtaining the temperature dependence of hysteresis. The procedure of taking the ratio of hystereses at these two different fields helps us to avoid the effects of changes in the microwave power and receiver gain on signal intensities at different temperatures. By this procedure we can take into account the field dependence of hysteresis. A ratio of unity indicates near absence of field dependence. The temperature dependence of this number can give us the information about how the critical current density varies as a function of temperature. A strong temperature dependence would indicate the presence of weak pinning of the flux lines. A ratio of unity nearly independent of temperature would indicate strong pinning.

The temperature dependence of ratio of hysteresis obtained as discussed above in the case of sample 1 is shown in figure 4 (open circles). Up to about 27 K, the hysteresis ratio is ∼1 and remains practically independent of temperature. This near field and temperature independence can be attributed to the strong pinning of flux lines in the sample. As can be seen, the ratio is less than one and is very strongly dependent on temperature just below $T_c$ where the pinning strength becomes ineffective due to thermal activation and weakening of superconductivity in general.
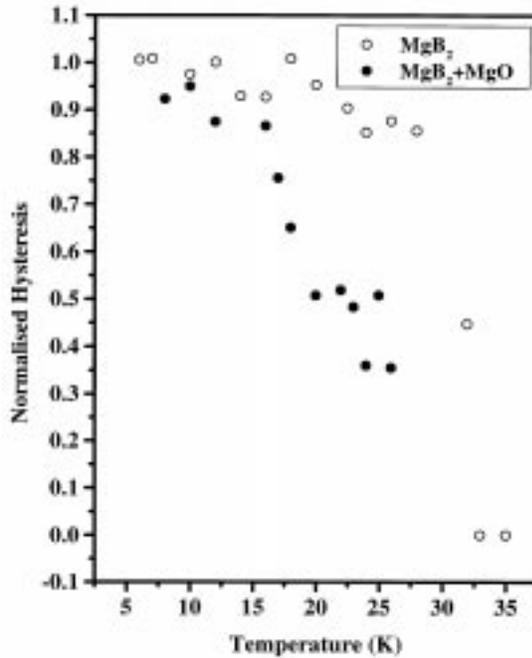


**Figure 4.** The ratio of hystereses at 4000 Gauss to 2000 Gauss plotted as a function of temperature for the samples of $MgB_2$ and $MgB_2 + MgO$. In the case of pure $MgB_2$ (open circles), the ratio of ∼ unity independent of temperature till about 27 K indicates a very strong pinning of flux lines. In the case of $MgB_2 + MgO$ (solid circles) the ratio is strongly temperature dependent and is less than unity in most of the temperature range indicating weaker pinning.

In case of sample 2, the signals resemble the HTSC signals much more closely. Due to the presence of insulating MgO phase, a large number of weak links may be formed. These weak links can act as superconductor–insulator–superconductor (SIS) junctions and give rise to the strong near zero field NRMA signal. This strong signal can easily mask any signs of $H_{c1}$ which might be present in the signals from the grains of sample 2.

The analysis of hysteresis for this sample was also done using the same technique as for sample 1. The ratio of hystereses is plotted as a function of temperature in figure 4 ($\bullet$). As can be seen from the figure, the ratio is a strong function of temperature and for most of the temperature range it is less than unity indicating a strong field dependence also. This strong temperature and field dependence of hysteresis indicates weaker pinning effects.

It has been reported in some of the previous works that the presence of MgO causes the $J_c$ of the $MgB_2$ films to increase [18]. This has been explained in terms of increased pinning due to MgO insulating regions in the sample. In our case however 10% MgO dispersed in pure MgO phase seems to be giving rise to JJs rather than pinning centres. This difference in the pinning properties may be attributed to the different experimental techniques. In the resistivity measurement, which is a dc measurement, the effects of depinning frequency of the sample does not come into the picture. In the high frequency measurement such as ours, the depinning frequency plays a significant role in determining the pinning properties. It has been found by Dulcic *et al* [19], that the depinning frequency for pure $MgB_2$ sample is of the order of 9.43 GHz. Because of this reason the pinning due to the insulating MgO regions seems to become ineffective at the operating frequency of 9.43 GHz. This also reflects in the hysteresis behaviour discussed earlier.

Another interesting feature of the NRMA signals is the absence of 'phase reversal' of the signal as a function of temperature in both the samples. 'Phase reversal' refers to the anomalous field dependence of the NRMA in which instead of having a minimum at zero field followed by an increase with increasing field, as is to be normally expected, the absorption shows a local maximum at zero field. This is reflected as the derivative of opposite phase to that of the NRMA signals. Such a phase reversal has been observed in almost all HTSC materials [20] especially in their granular form. As discussed in detail in ref. [20], the phase reversal can have a number of different origins such as flux compression [21], *d* wave symmetry of the superconducting order parameter [22] and the so-called $\pi$ type Josephson junctions [23–25]. In $MgB_2$, since the linear temperature dependence of $H_{c1}$ might point toward non-*s* wave superconductivity, if the NRMA exhibited phase reversal it could support the possibility of *d* wave symmetry. However, in spite of varying microwave power and modulation amplitude we were unable to observe any such phase reversal in the NRMA signals either from $MgB_2$ or from $MgB_2 + MgO$ sample. It appears therefore, that the linear temperature dependence of $H_{c1}$ and the absence of the phase reversal in NRMA signals in these systems need to be examined and understood further with regard to their implications for the symmetry of the order parameter. It is also possible that though the phase reversal is absent in the microwave frequency range, it might show up at radio frequencies (rf) similar to the observation in the HTSC Bi–Sr–Ca–Cu–O sample [26]. Such experiments in the rf range are underway at present.

In conclusion, we have studied the novel superconductor $MgB_2$ and $MgB_2$ alloyed with 10% by weight of MgO using the technique of NRMA. The NRMA signals from $MgB_2$ are very different from that of HTSC. Low field derivative like narrow signals characteristic of the Josephson junctions are absent while the rectangular hysteresis loops indicative of large critical current densities due to strong pinning are observed. The lower critical field

is observed to decrease linearly with temperature. $MgB_2$ when alloyed with MgO however shows the presence of intergranular contacts acting as weak links and a weaker pinning as compared to pure $MgB_2$. The absence of phase reversal of the NRMA signal at microwave frequency is noted as another unique feature of this system.

## Acknowledgements

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