Surface barrier and bulk pinning in MgB$_2$ superconductor

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We present a modified method of preparation of the new superconductor MgB$_2$. The polycrystalline samples were characterized using x-ray and magnetic measurements. The surface barriers control the isothermal magnetization loops in powder samples. In bulk as prepared samples we always observed symmetric magnetization loops indicative of the presence of a bulk pinning mechanism. Magnetic relaxation measurements in the bulk sample reveal a crossover of surface barrier to bulk pinning. (PACS numbers 74.60.Ge, 74.60.Jg, 74.60.-w, 74.62.Bf)

I. INTRODUCTION

Recently Akimitsu and colleagues [4,5] discovered superconductivity with remarkably high superconducting transition temperature $T_c \sim 39$ K in the binary intermetallic magnesium boride (MgB$_2$). MgB$_2$ crystallizes in the hexagonal AlB$_2$-type structure, (space group $P6/mmm$) consisting of alternating hexagonal layers of Mg atoms and graphite-like layers of B atoms. Wang et al. [6] using specific and magnetization measurements concluded that MgB$_2$ is a type II superconductor with $H_{c2}(0) \approx 140$ kOe, small condensation energy (in comparison with NbSn and YBa$_2$Cu$_3$O$_7$), $\xi_0 \approx 49\text{Å}$, $\lambda_0 \approx 1850\text{Å}$ and a critical field $H_c \approx 2.6$ kOe. Recent reports [7,8] on bulk MgB$_2$ samples revealed high intergranular critical current densities and large bulk magnetic flux pinning. Further the reduced weak-link nature of the grain boundaries in polycrystalline MgB$_2$ underline the applications potential of this material. However, few works [9,10] presented convincing evidence that the MgB$_2$ is an anisotropic superconductor with an anisotropy parameter $\gamma = (B_{c2}^\parallel / B_{c2}^\perp)$ taking values into interval $2 \leq \gamma \leq 6$, making difficulties in the direct use of unoriented polycrystalline MgB$_2$ in the applications.

The detailed study of the vortex matter properties for this new superconductor is very important from fundamental, as well as from technological point of view. In the present paper, we study the MgB$_2$ superconductor using x-ray powder diffraction and magnetic measurements. In our work we observed that in powder samples, surface barriers control the magnetic irreversibility due to asymmetric magnetic hysteresis loops. In as prepared bulk samples we observed symmetric magnetization loops a fact which implies that the grain (or crystallites) boundaries contribute significantly to the pinning of the flux lines.

II. EXPERIMENTAL DETAILS

MgB$_2$ samples were prepared by liquid-vapor to solid reaction in an alumina crucible placed inside an evacuated, sealed silica tube. First, we mixed thoroughly high purity Mg and B powders, with a slight excess of Mg in order to balance the amount of Mg that is oxidized or freeze in the crucible and the silica walls. Since the melting point of Mg is 610$^\circ$C we heated the sample with a rate of $\sim 10^2$ C/min up to the melting point of Mg. We continued the heating up to 910$^\circ$C with a lower heating rate ($\sim 1$ C/min). At 910$^\circ$C the sample annealed for two hours and then we turned off the furnace.

![Rietveld refinement pattern for the MgB$_2$ sample.](image)

FIG. 1. Rietveld refinement pattern for the MgB$_2$ sample. The observed data points are indicated with filled circles, while the calculated pattern is shown as a continuous line. The positions of the reflections are indicated with vertical lines below the pattern.

X-ray powder diffraction (XRD) data were collected with a D500 SIEMENS diffractometer, using CuK$\alpha$ radiation. DC magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design). Ac-susceptibility measurements were performed at zero dc field by means of a home-made probe at a frequency of 77.7 Hz.

III. RESULTS AND DISCUSSION

The refinement of the XRD patterns was carried out by the Fullprof Rietveld program [23] using the space group $P6/mmm$. Figure 1 shows the corresponding Ri-
etvedl plot of the x-ray powder diffraction pattern. Since Mg and B occupy special positions, the only available parameters for refinement are the unit cell constants, the occupancies and the anisotropic temperature factors. The cell constants were found $a = b = 3.0849(1)$Å and $c = 3.5213(1)$Å. The anisotropic temperature factors ($B_{11}, B_{33}, B_{12}$ in Å$^2$) for Mg and B were estimated to be $(0.0245(1), 0.0189(1), 0.0076(1))$ and $(0.0164(3), 0.0(2), 0.0255(4))$, respectively. In our refinement we also included the MgO as a second phase in order to account for a few additional small peaks.

![FIG. 2. Variation of the normalized real and imaginary part of the fundamental ac-susceptibility of a bulk piece (a) and for a powdered sample (b) of the MgB$_2$ compound. The measurements were taken at a frequency of 77.7 Hz, in zero dc-magnetic field and for several amplitudes of the ac-field. Insets show the imaginary part of the susceptibility as a function of temperature near the $T_c$.](image)

This compound should have originated from the slight excess of Mg used in the starting reaction mixture. The estimation of the amount of this compound was 2.5 wt%. The occupancies for both Mg and B were found equal to one within the statistical errors. An interesting result of the refinement is the anisotropic character of the thermal parameters of Mg and B. We found that boron vibrates almost in the $a-b$ plane. On the other hand the Mg has a significant component along the $c$ axis. Finally, we must note that our structural parameters agree with the neutron diffraction crystal data of Jorgensen et al. [23].

![FIG. 3. Variation of the magnetic moment as a function of the magnetic field at $T = 30$ K for an as prepared bulk sample and for the same sample after grinding of the MgB$_2$ compound.](image)

The peak in the $\chi''$ is located at the middle of the drop in $\chi'(T)$ curve. As the amplitude of the ac-magnetic field increases the corresponding $\chi'(T)$ and $\chi''(T)$ curves broaden and the peak of the $\chi''(T)$ curve (or middle point of the $\chi'(T)$) is shifted to lower temperatures. The same behavior is observed also for the powdered sample but in this case the broadening is larger. In order to investigate the mixed state and the magnetic irreversibility for this material we employed isothermal magnetization measurements. Figure 3 shows the magnetization loops at $T = 30$ K for an as prepared bulk piece of MgB$_2$ and the same measurements after grinding the bulk piece into fine powder, in order to point out the different behavior. Figure 4 shows magnetic hysteresis loops at $T = 5, 10, 20$ and $30$ K for the powder sample.
The very interesting observation is the asymmetric shape of the loops at \( T = 5 \) K when one compares the branches for increasing and decreasing field. In the increasing branch \(-M\) drops as \( \sim 1/H\), while in the decreasing branch the magnetization is flat with values close to zero. This behavior is different from the case where bulk pinning dominates, giving nearly symmetric loops about the \( M = 0 \) axis. We must note that these features extend up to high fields (e.g. 55 kOe at \( T = 5 \) K). The measurements at other temperatures were similar and showed that the loop-width decreases quickly as the temperature increases. Wang et al. \cite{25} report a value for \( \kappa = \lambda/\xi \approx 38 \) for MgB\(_2\). This large value suggests that the surface barriers may play an important role in MgB\(_2\), even when the barriers are suppressed by surface effects. It is instructive to compare our data with the theoretical predictions concerning the influence of the surface barriers on the phase diagram of MgB\(_2\) compound. According to the theoretical suggestions of Clem \cite{24} and Burlachkov et al. \cite{23}, for the case of weak bulk pinning surface barriers may play a crucial role and determine the first field of flux penetration as well as the irreversibility line. Flux penetrates through the surface by the creation of a critical nucleus consisting of one or several vortex loops.

In the case of the powder sample we observed asymmetric loops. The descending branch is nearly horizontal. In addition the location of the peak of the magnetization loops can not be explained by a model where only the reversible and irreversible magnetization are taken into consideration. Consequently, the surface barriers must influence the magnetic properties in the powder sample. We fitted the peak field \( H_p \) with the corresponding formula \( H_p = H_c(T) \) predicted from the surface barrier model ignoring the thermal activation over the surface barrier. The inset (b) of Fig. \ref{fig:loops} shows the variation of \( H_p \) with temperature extracted from magnetization measurements of the powder sample. The variation of the \( H_p \) with temperature is nearly linear. According to the theoretical prediction for \( H_c \), it varies as \( H_c = \Phi_0/4\pi\xi \lambda \). If we suppose a temperature variation for \( \xi \) and \( \lambda \) like \( (1 - (T/T_c))^{-1/2} \) we expect that \( H_p = \Phi_0/4\pi\xi\lambda_0(1 - T/T_c) \). Namely, a linear temperature variation which is exactly what we observe. Despite the nice agreement of our experimental data with the concept of edge barriers for the case of the powder samples, we can not neglect a small contribution coming from the bulk pinning mechanism. As Brandt \cite{20} pointed out, the contribution of bulk pinning inflates the loops nearly symmetrically about the pin-free loop. The width \( \Delta m(H = 0) = m \uparrow (H = 0) - m \downarrow (H = 0) \) of the loop at zero field is related to the degree of pinning, exhibiting higher values for stronger pinning. In our case we observe that the width \( \Delta m(H = 0) \) increases for lower temperatures (see Fig. \ref{fig:loops}). For the bulk samples we observed symmetric magnetization loops which means that the bulk pinning controls mainly the entry and exit of the magnetic flux. Figure \ref{fig:loops} shows the magnetization loops for the bulk sample at \( T = 5, 15, 20, 25 \) K and 30 K. Shown are also the quantities \( m_{\text{irr}} = [m(\downarrow) - m(\uparrow)]/2 \) and \( m_{\text{rev}} = [m(\downarrow) + m(\uparrow)]/2 \) at \( T = 5 \) K, which represent the variation of the critical current density and the irreversible moment, respectively, as a function of the magnetic field. Insets (a) and (b) of Fig. \ref{fig:loops} show the temperature variation of the peak field, \( H_p \) occurring in the virgin magnetization loops and the irreversibility line, \( H_{\text{irr}}(T) \) respectively. \( H_p \)-curves are a measure of the temperature variation of the critical current. \( H_{\text{irr}}(T) \) line deduced from our measurements for the bulk sample, agrees very well with those measured from other groups \cite{27,28,29}, (extrapolates to about \( \sim 80 \) kOe at \( T = 0 \) K). It seems that the \( H_{\text{irr}}(T) \) curve represents a transition of the vortex matter and not a line which depends on the pinning strength. The existence of the peak in the hysteresis loops at small \( H \), is a manifestation of the \( B \) dependence of \( J_c \). \cite{32,33} If the critical current follows the equation \( J_c = J_{c0}/(1 + B/|B_0|) \) (Kim’s model) for any choice of the parameter \( B_0 \), the peak is always located at positive \( H \) on the ascending branch of the loop \cite{32,33} as we observe in our measurements (see inset (c) of Fig. \ref{fig:loops}).

![FIG. 5. Variation of the magnetic moment as a function of magnetic field at \( T = 5, 15, 5, 20, 25 \) and 30 K for the bulk MgB\(_2\) sample. Shown are also the irreversible and reversible magnetization as a function of magnetic field at \( T = 5 \) K. Insets (a-c) show the variations of \( H_{fp} \), \( H_{irr} \) and the detail of the hysteresis loops near \( H = 0 \), respectively.](image-url)
window $t_i = 10^2 \leq t \leq t_f \approx 10^4$ s. From the normalized relaxation rate $S = d \ln(-m(t))/d \ln t$ we calculated the pinning potential as a function of the magnetic field at constant temperature. Figure 3 is a semilogarithmic plot of the $m(t)$ variation (relaxation of magnetization) at $T = 5$ K, for $10 \leq H_i \leq 50$ kOe. In addition, the relaxation curves show a slope change at a certain time. That resembles a crossover from a relaxation controlled by bulk pinning to one controlled by surface barriers. As Burlachkov [30] pointed out the initial stage of relaxation is determined by the weakest one of two sources of the irreversibility: the bulk and the surface. If the bulk pinning dominates over the surface barrier we would expect that the initial stage is actually the surface relaxation, where the magnetization in the surface ($M_s$) decreases at approximately constant $J$. When $M_s = M_{eq}$ ($M_{eq}$ is the equilibrium magnetization) the slope in $dM/d\ln t$ changes (decreases) and the relaxation continues owing to the bulk mechanism. The inverse relaxation rate, which in the framework of the interpolation formula [37] is equal to $S^{-1} = U_c/k_B T + \mu \ln(t/t_0)$ at small time intervals, can give an estimation of $U_c/k_B T$. The $S^{-1}$ vs $\ln t$ curves at $t = 4 \times 10^5$ s (not shown) are nearly constant and decrease slightly as the corresponding magnetic field increases. This means that $U/kT$ decreases monotonically as the field increases. In the inset of Fig. 3 plotted are the estimated values of $U/kT$ (at $t = 4000$ s) for the magnetic field where relaxation was measured.

The key question is why the as prepared bulk sample with an appreciate porosity displays bulk pinning, while the one in the powder form does not? One can explain this behavior with the following arguments. The crystallites (we suppose that after thoroughly grinding we produce single crystal particles) do not have imperfections or disorder capable to pin the flux lines. The Ginzburg Landau coherence length for MgB$_2$ is $\xi \sim 40 \text{Å}$ meaning that only defects of such size can pin effectively the flux lines. Defects of such large size are difficult to be found inside the volume of the crystallites. On the other hand, magnetic measurements of the bulk as prepared sample, show an enhanced critical current, indicating a substantial bulk pinning. It seems that defects in the crystalline boundaries are able to pin the vortices and may be the reason for the strong coupling between the grains. Similar results with ours have been reported by Takano et al. [1] and Kim et al. [2]. In these works symmetric magnetization loops have been observed for high temperature (1000°C) high pressure sintered samples. They observed asymmetric magnetization loops for the powder and the low temperature sintered sample. Although we do not press the sample it seems that the $910$ºC in the final step of the reaction process produce the necessary pinning. Our results are also in agreement with the conclusions of Larbalestier et al. [21] that MgB$_2$ is not compromised by weak-link problems.

In conclusion, we presented a modified preparation method of MgB$_2$ compound. The magnetization loops of the powder samples are controlled by surface barriers. In the bulk samples bulk pinning dominates rather than surface barriers.

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