

## Effects of the sintering temperature on the flux-pinning mechanism and the activation energy of malic-acid doped MgB<sub>2</sub>

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### Abstract

The flux-pinning mechanism and activation energy of 10 wt % malic acid-doped MgB<sub>2</sub> were investigated by measuring of the critical current density and resistivity as a function of magnetic field and temperature. A crossover field,  $B_{sb}$ , was observed from the single vortex to the small vortex bundle pinning regime. For the sintered sample, the temperature dependence of  $B_{sb}(T)$  at low temperature is in good agreement with the  $\delta\ell$  pinning mechanism, i.e., pinning associated with charge-carrier mean free path fluctuation. The activation energy was decreased by increasing the magnetic field and increased by increasing sintering temperature.

**Keywords:** Malic-acid doped MgB<sub>2</sub>, Critical current density, Flux-pinning mechanism, Activation energy

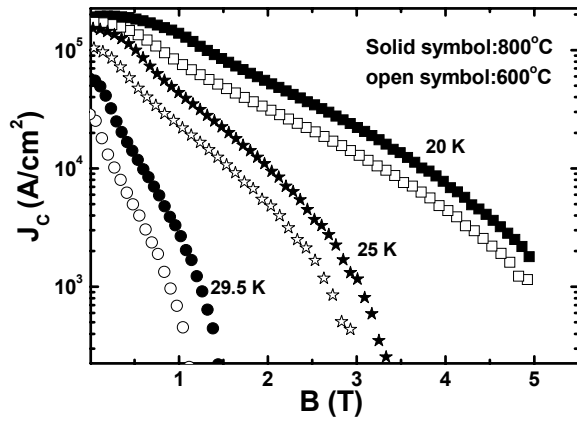
### 1. Introduction

MgB<sub>2</sub> superconductor has been studied extensively by many research groups around the world since its discovery [1]. Because MgB<sub>2</sub> has a simple crystal structures, large coherence length, high critical current density, and a lack of weak-link grain boundaries, it is a good candidate for new applications, such as large-scale engineering applications and electronic devices [2]. However, the critical current density,  $J_c$ , of MgB<sub>2</sub> drops rapidly in high magnetic field. Therefore, research approaches have been directed towards either improving  $J_c$  by improving grain connectivity, or improving in-field performance by different methods.

Flux pinning and the upper critical field determine the magnitude of the current density  $J_c$ . The pinning mechanism has been widely studied for doped MgB<sub>2</sub> samples [3-12]. The critical current density of pure MgB<sub>2</sub> falls rapidly in high fields because of poor grain connectivity and lack of enough effective pinning centers. Introducing flux pinning centers through nanoparticle doping in bulk MgB<sub>2</sub> is an effective way to significantly improve the flux pinning. Many types of chemical doping have been examined for improving the  $J_c$ , the upper critical magnetic field,  $H_{c2}$ , and the irreversibility field,  $H_{irr}$  [13-15]. It has been found that chemical doping with nonmagnetic materials appears to

be the simplest approach for increasing the ability of MgB<sub>2</sub> to carry large currents for practical applications. It has already been shown that  $J_c$  enhancement by more than one order of magnitude in high magnetic fields can be easily achieved with only a slight reduction in the critical temperature,  $T_c$ , through adding nanoparticles of certain elements and compounds, such as SiC, Si, and C, to MgB<sub>2</sub> [16-23].

The most important elementary interactions between vortices and pinning centers are the magnetic interaction and the core interaction [24-30]. The magnetic interaction arises from the interaction at surfaces between superconducting and non-superconducting material parallel to the applied field, but the magnetic interaction is usually very small in type-II superconductors with a high Ginzburg-Landau (GL) parameter  $\kappa$ . The core interaction arises from the locally distorted superconducting properties through the superconducting order parameter fluctuation, which is usually more effective in type-II superconductors. Two mechanisms of core pinning are predominant in type-II superconductors, i.e.,  $\delta T_c$  and  $\delta l$  pinning.  $\delta T_c$  pinning is caused by the spatial variation of the GL coefficient  $\alpha$  associated with disorder and variation in  $T_c$ , while the variations in the charge-carrier mean free path,  $l$ , near lattice defects are the main cause of  $\delta l$  pinning. A high  $\kappa$



**Figure 1.** Magnetic and temperature dependences of the critical current density  $J_c$  for 600 and 800 °C reaction temperatures.

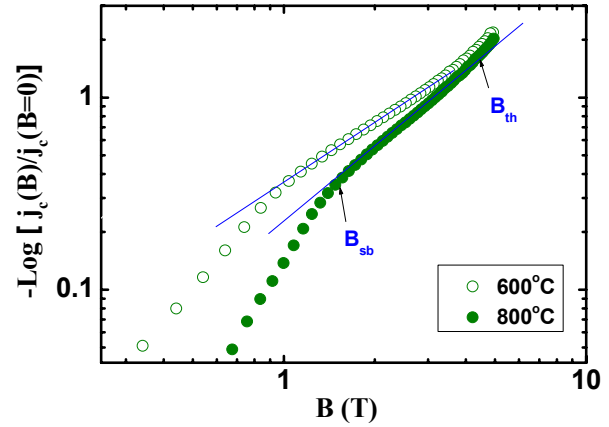
value of 26 has been reported [31] for  $\text{MgB}_2$ , indicating that magnetic interaction is negligible, and the core is more important.

In this paper we report the effects of the sintering temperature on the pinning mechanism and the flux activation energy of the 10 wt% malic-acid doped  $\text{MgB}_2$ . It was found that the  $\delta l$  pinning mechanism was dominant at low temperature, while at temperatures close to the critical temperature,  $\delta T_c$  pinning is effective. Our results suggest that by increasing sintering temperature the  $\delta T_c$  pinning contribution decreases, while the  $\delta l$  pinning effects increases. The results show that the flux-flow activation energy divided by Boltzmann's constant ( $U_o/k_B$ ) increases by in the flux pinning potential.

## 2. Experiment

Boron powder, toluene, and 10 wt % malic acid ( $\text{C}_4\text{H}_6\text{O}_5$ ) were fully mixed and sintered at 210 °C in order to decompose the malic acid. Then, the resultant powder was mixed with Mg, and dried and compressed into a pellet. The pellets were sintered at different temperatures in the range of 600 – 800 °C. The electrical resistivity was measured by a standard dc four-probe method on sintered bars with typical dimensions of  $2.3 \times 3.5 \times 1.1 \text{ mm}^3$ . All magnetic and transport measurements were performed using a physical properties measurement system (PPMS, Quantum Design). From the  $M(H)$  loops, the  $J_c$  was calculated using the Bean approximation,  $J_c = 20\Delta M / (Va(1-a/3b))$ , where  $a$  and  $b$  are the width and the length of the sample perpendicular to the applied field, respectively,  $V$  is the sample volume, and  $\Delta M$  is the height of the  $M-H$  hysteresis loop.

The crystal structure was investigated by x-ray diffraction (XRD) [32]. It was observed that 10 wt%  $\text{C}_4\text{H}_6\text{O}_5$  doped  $\text{MgB}_2$  samples sintered at 600–900 °C seemed to be well-developed  $\text{MgB}_2$  with a small amount of MgO, which is decreased by increasing sintering temperature.



**Figure 2.** Double logarithmic plot of  $-\log [j_c(B)/j_c(0)]$  as a function of  $B$  at  $T = 20$  (circles) and 26.5 K (rectangles) for the samples sintered at 600 (open symbols) and 800 °C (solid symbols). The crossover fields  $B_{sb}$  and  $B_{th}$  are shown by arrows for the sample at 26.5 K.

## 3. Results and discussion

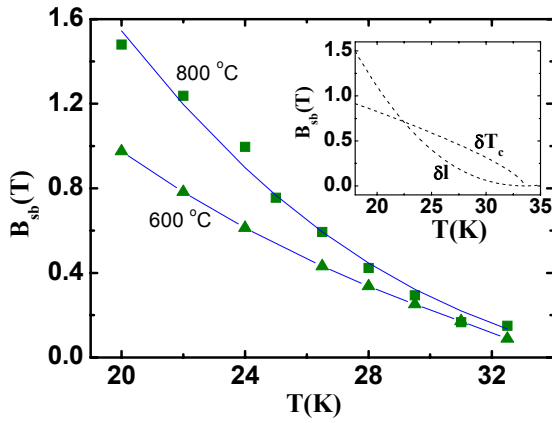
The resultant  $J_c(B, T)$  curves at various temperatures for samples sintered at 600 and 800 °C are shown in a double-logarithmic plot in figure 1. As can be seen from the plateau at low field,  $J_c$  initially has a weak dependence on the magnetic field. When the field is increased beyond a crossover field, it begins to decrease quickly.

At 4 T and 20 K, the  $J_c$  values for both samples are over  $1 \times 10^4 \text{ A/cm}^2$ , more than one order of magnitude higher than for pure  $\text{MgB}_2$  [25]. This is due to enhancement of flux pinning, which may be ascribed to C substitution into B sites. For all fields and temperatures lower than 29.5 K, the critical current density of samples sintered at 800 °C is higher than for those sintered at 600°C. This is in agreement with the increased grain connectivity, greater C substitution into the B sites, and decreasing MgO phase resulting from the higher temperature sintering.

In order to understand the critical current density results shown in figure 1, the vortex-pinning mechanism was investigated by using dependence of the crossover field in the framework of the collective theory, which has been derived by Blatter *et al.* [25], where  $J_c$  is field independent when the applied magnetic field is lower than the crossover field  $B_{sb}$  (the single vortex pinning regime). For  $B > B_{sb}$  (small-bundle pinning regime),  $J_c(B)$  follows an exponential law,

$$J_c(B) \approx J_c(0) \exp[-(B/B_0)^{3/2}] \quad (1)$$

Where  $B_0$  is a normalization parameter of the order of  $B_{sb}$  and  $J_c(0)$  is the critical current density at zero field. When  $B > B_{lb}$ , the crossover field is between the small and the large vortex bundle regimes, this large-bundle pinning regime is governed by the power law  $J_c(B) \propto B^{-\alpha}$ , with  $\alpha=3$  for RE-123 (RE= rare earth elements) superconductor [25]. Figure 2 presents a double-logarithmic plot of  $-\log [J(B)/J(B=0)]$  as a function of applied magnetic field. At intermediate fields, Eq. (1) fits the experimental data of  $J_c(B)$  very



**Figure 3.** Temperature dependence of the crossover field  $B_{sb}$ . The solid curves are fits to eq. (3). Inset: The  $\delta T_c$  and  $\delta l$  pinning correspond to eq. (2).

well, while deviations from the fitting curves can be observed at both low and high fields.

$B_{sb}$  indicates the crossover field from the single vortex-pinning regime to the small-bundle-pinning regime, while the deviation at high fields has been considered as the crossover field from small-bundle pinning to large-bundle pinning. The high-field deviation, however, is very close to the irreversibility line, which results from giant flux creep, so it is likely that the deviation at high field may instead result from large thermal fluctuations, which lead to the rapid decrease in  $J_c$ . This deviation is therefore denoted as  $B_{th}$ .

It was pointed out [25] that  $B_{sb}$  is proportional to the critical current density  $J_{sv}$  in the single vortex pinning regime. Griessen *et al.* [24] have found that for the  $\delta l$  pinning mechanism  $J_{sv} \propto (1-t^2)^{5/2}(1+t^2)^{-1/2}$ , while for the  $\delta T_c$  pinning mechanism,  $J_{sv} \propto (1-t^2)^{7/6}(1+t^2)^{5/6}$ , where  $t = T/T_c$ . They have obtained the following expression for  $B_{sb}$

$$B_{sb}(T) = B_{sb}(0)(1-t^2/1+t^2)^\beta, \quad (2)$$

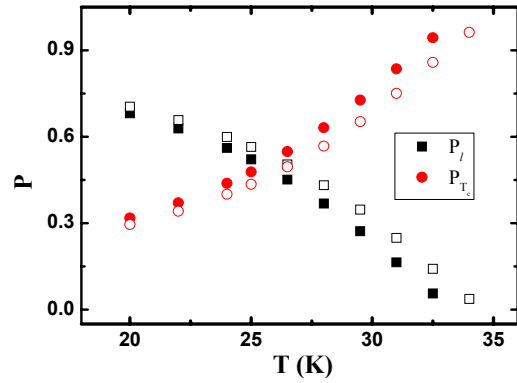
where  $\beta = 2$  and  $2/3$  for the  $\delta l$  and the  $\delta T_c$  pinning mechanisms, respectively. To investigate further the real pinning mechanism of the 10% malic-acid-doped  $MgB_2$  samples, the  $B_{sb}$  data was analyzed using the following expression [33]

$$B_{sb} = P_1 B_{sb}^{T_c} + P_2 B_{sb}^l, \quad (3)$$

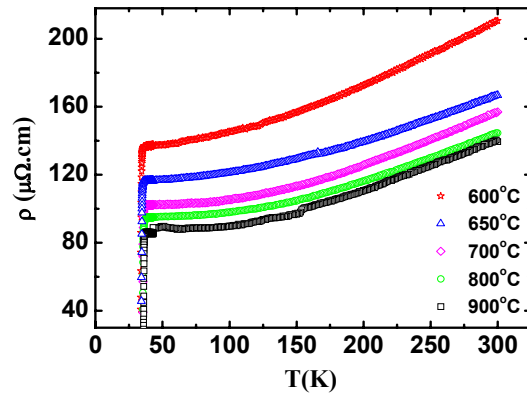
where  $B_{sb}^{T_c}$  and  $B_{sb}^l$  are the expressions for the  $\delta T_c$  and  $\delta l$  pinning, respectively.  $P_1$  and  $P_2$  are fitting parameters with  $P_1 + P_2 = 1$ . The  $B_{sb}$  data obtained from  $J_c(B)$  was well described by eq. (3), as shown by the solid curves in figure 3.

In the inset of figure 3, the dashed curves indicate the  $\delta T_c$  and  $\delta l$  pinning mechanisms, corresponding to Eq. (2). The curve has a positive curvature in the  $\delta T_c$  pinning case, while the curvature associated with the  $\delta l$  pinning is negative. As is clear from figure 3, the  $B_{sb}(T)$  behavior shows a negative curvature.

This results shows that the  $\delta l$  due to spatial fluctuations of the charge-carrier mean free path and  $\delta T_c$  pinning mechanisms due to the variation in  $T_c$  among the grains coexist at both temperatures. In order to compare the effects of the  $\delta T_c$  and  $\delta l$  pinning mechanisms, the P parameter was defined as  $P = P_1 B_{sb}^{T_c} / B_{sb}$  or  $P = P_2 B_{sb}^l / B_{sb}$ ,



**Figure 4.** The  $\delta T_c$  and  $\delta l$  pinning contributions as functions of temperature. Open symbols: 600 °C. Solid symbols: 800 °C.

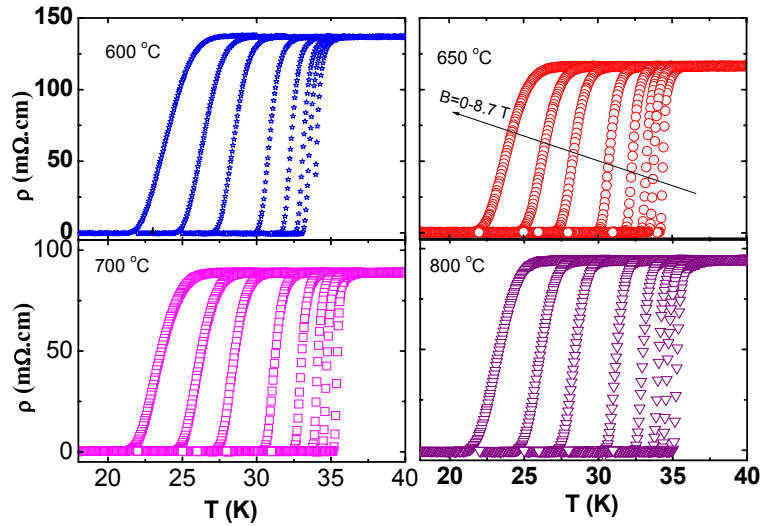


**Figure 5.** Temperature dependence of the resistivity of the 10 wt% malic-acid doped  $MgB_2$  at different sintering temperatures and zero magnetic field.

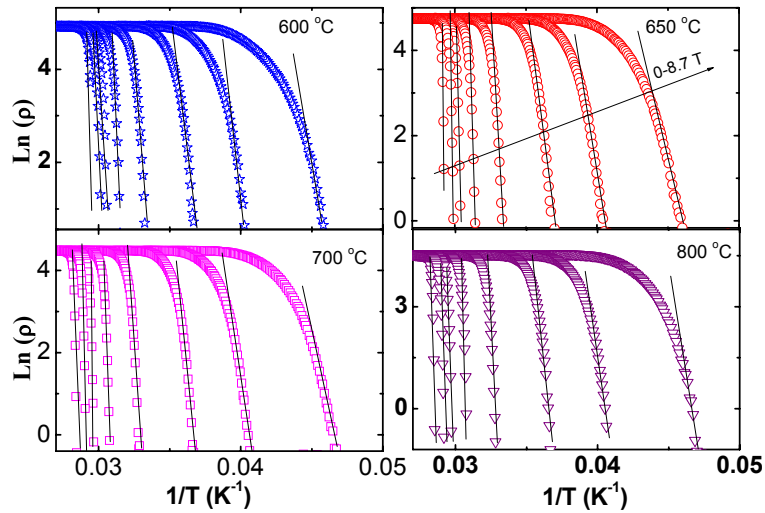
which represent the  $\delta T_c$  and  $\delta l$  pinning effects, respectively.

The results of both pinning effect contributions are shown in figure 4. For both 600 and 800°C reaction temperatures, the actual values of the pinning contribution are slightly different, while the trends in both the  $\delta T_c$  pinning and the  $\delta l$  pinning are the same. As can be seen in figure 4, results show that the  $\delta l$  pinning is the dominant mechanism at low temperature, but by increasing temperature, the  $\delta l$  pinning decreases, and the  $\delta T_c$  pinning increases. At the equivalence temperature,  $T_{eq} = 25.2$  and  $26.6$  K for 800 and 600 °C reaction temperatures, respectively, both pinning mechanisms have equal effects, and above these temperatures, the  $\delta T_c$  pinning is dominant. This result suggests that for temperatures close to  $T_c$ , the  $T_c$  fluctuation increases, and therefore, the  $\delta l$  pinning is suppressed completely. When the temperature is far below  $T_c$ , the  $T_c$  fluctuation disappears, and the  $\delta l$  pinning is dominant. Both malic acid-doped  $MgB_2$  samples at sintered at 600°C and 800°C have the same trend in both the  $\delta l$  and  $\delta T_c$  pinning mechanisms. It was found that by increasing sintering temperature the  $\delta T_c$  pinning contribution decreases, while the  $\delta l$  pinning effects increase.

Figure 5 shows the temperature dependence of the resistivity of the 10 wt% malic-acid doped  $MgB_2$  at different sintering temperatures and zero magnetic field.



**Figure 6.** The electrical resistivity as a function of temperature in fields of 0-8.7 T for 10wt% malic acid doped  $\text{MgB}_2$  sintered at 600, 650, 700, and 800 °C.



**Figure 7.** Arrhenius plot of the electrical resistivity for samples sintered at 600, 650, 700, and 800 °C. The activation energy  $U_0$  is given by the slopes from linear fitting, as shown.

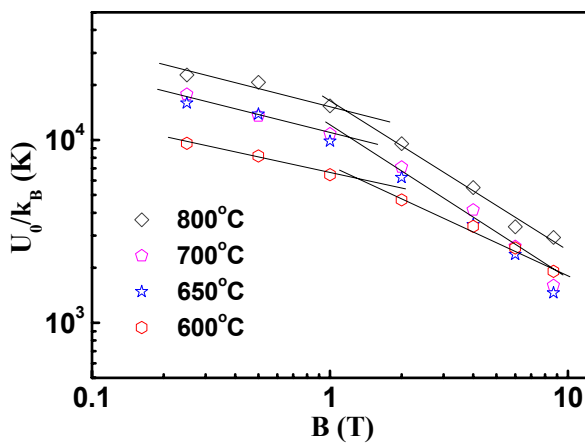
As can be seen, the room temperature resistivity decreases by increasing sintering temperature. Thus, the impurity scattering is reduced as the sintering temperature increases, demonstrating the feasibility of improving the upper critical field [32]. Therefore, the highest upper critical fields were obtained for samples with lower sintering temperature, in this case, 600 °C, as was found by Hossein et al. [32].

Figure 6 shows the resistivity as a function of magnetic field for samples sintered at 600, 650, 700, and 800 °C in magnetic fields of 0-8.7 T. It can be seen from these curves that the critical temperature,  $T_c$ , decreases and the transition temperature width increases by increasing magnetic field. In large magnetic fields, due to flux penetration inside the grains, the onset part of the transition will be broadened. The amount of the broadening and the shift of  $T_c$  to lower temperature as a function of the magnetic field are proportional to the magnitude or strength of the pinning force.

Usually, the broadening of the lower parts of the resistive transition,  $\rho(T) < 1\% \rho_n$  (where  $\rho_n$  is the resistivity in the normal state just above the transition), in a magnetic field is interpreted in terms of the dissipation of energy caused by the motion of vortices [34]. This interpretation is based on the fact that the resistance is caused by vortex creep, so that the  $\rho(T)$  dependence is due to the thermally activated flux. In this region, the experimental results have been found to follow the Arrhenius relation

$$\rho(T, B) = \rho_0 \exp[-U_0/k_B T] \quad (4)$$

Here,  $U_0$  is the flux-flow activation energy, which can be obtained from the slope of the linear part of an Arrhenius plot, and  $\rho_0$  is a field-independent pre-exponential factor. Activation energy for the broadened transition usually is independent of the temperature, and it can be obtained from the slope of the linear part of the  $\ln \rho$  vs.  $1/T$  curves, which are shown in figure 7 for different sintering temperatures.



**Figure 8.** Magnetic field dependence of the activation energy  $U_0$  for  $\text{MgB}_2$  superconductor doped with 10wt% malic acid for sintering temperatures of 600- 800 °C.

Figure 8 presents the obtained flux pinning energy,  $U_0$ , from the above fitting for different magnitudes of field for samples sintered at temperatures of 600, 650, 700, and 800 °C. It is clear from figure 8 that the activation energy increases by increasing sintering temperature. As can be seen for each sample, the flux pinning energy decreases by increasing applied magnetic field. The value of  $U_0$  in high field for the malic acid doped  $\text{MgB}_2$  is roughly 2000 K that is 10 and 5 times larger than that of  $\text{Bi2223}$  [35] and  $\text{Bi2212}$  [34], respectively. This indicates that the malic acid doped

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$\text{MgB}_2$  has a very much stronger pinning than that of  $\text{Bi2223}$  and  $\text{Bi2212}$  superconductors.

It has been reported that the pinning potential of bismuth strontium calcium copper oxide (BSCCO) crystals exhibits a power-law dependence on magnetic field,  $U_0(H) \approx H^n$ , with  $n = 1/2$  for  $H < 5$  T and  $n = 1/6$  for  $H > 5$  T for  $H//c$  [34,35]. We have fitted this power law relation for  $U_0$  versus  $H$  for each sample. The values of  $n$  have been obtained to be roughly  $0.76 \pm 0.02$  in  $H > 1$  T for sintering temperatures larger than 600 °C and  $n = 0.52$  for the sintering temperature of 600 °C. However, for  $H \leq 1$  T,  $n$  does not depend on the sintering temperature and has the value  $0.28 \pm 0.04$ .

In conclusion, we have found that the  $\delta l$  due to spatial fluctuations of the charge-carrier mean free path and  $\delta T_c$  pinning mechanisms due to the variation in  $T_c$  coexist at both temperatures and both pinning mechanism contributions are strongly temperature dependent. The  $\delta l$  pinning mechanism is dominant at low temperature in 10 wt% malic-acid doped  $\text{MgB}_2$  which is sintered at different temperatures, while at temperatures close to the critical temperature,  $\delta T_c$  pinning is effective. Our results suggest that the  $\delta T_c$  pinning contribution decreases while the  $\delta l$  pinning effects increases by increasing sintering temperature. The results show that  $U_0/k_B$  increases by increasing sintering temperature, which suggests an increase in the flux pinning potential

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