

## Microstructural Factors Influencing Critical-Current Densities of High-Temperature Superconductors

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## ABSTRACT

Microstructural defects are the primary determining factors for the values of critical current densities in superconductors. A review is made to assess, (1) what would be the maximum achievable critical-current density in the oxide superconductors if nearly ideal pinning sites were introduced? and (2) what types of pinning defects are currently introduced in these superconductors and how effective are these in pinning the vortices? Only the case where the applied field is parallel to the c-axis is considered here.

KEY WORDS:  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$ , transport, magnetic

## INTRODUCTION

A period of more than five years has passed since the first report of superconductivity at elevated temperatures for La-Ba-Cu-O [1]. Soon after, this report was followed by discoveries of Y- [2], Bi- [3], and Tl [4] cuprates with critical temperatures well above the boiling point of liquid nitrogen. However, widely expected applications of these superconductors have not been realized yet. As is well known, the primary limiting factor in the use of these superconductors for large-scale applications is the fact that their critical-current densities are rather limited at elevated temperatures, even for intermediate applied magnetic fields (except for some of thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ). There are two primary causes for such a disappointing present situation: (1) poor vortex pinning strengths within the grains of these superconductors when applied fields  $H$  are parallel to the c-axis and (2) weak intergranular coupling for transport currents across the grain boundaries. In the following, we will only address the first of these problems and review what are the current understandings on this important subject.

In order to do this, we first present simplified magnetic vortex pinning mechanisms, and discuss the recent results of the effects of heavy-ion irradiation on critical-current densities of these superconductors [5-10]. Since this heavy-ion irradiation produces dense track of defects owing to a large energy deposition rate, it creates nearly ideal pinning centers. We can ask what would be the maximum possible operating parameters, e.g.  $T$  and  $H$  for each of the primary high- $T_c$  superconductors if these defects are incorporated. Then, the types of the pinning centers, which are purposely incorporated in bulk and thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , are reviewed, and the effectiveness of the defects in increasing the values of  $J_c$  are examined. For the present discussion, only the case where applied fields  $H$  are parallel to the c-axis is considered, since the vortex pinning is generally very strong for  $H$  parallel to the a-b plane.

## VORTEX PINNING

Before discussing the experimental results on the vortex pinning in the high- $T_c$  superconductors, a brief and simplified explanation for the vortex pinning by a cylindrical defect with a radius  $r$  is given [5,11,12]. The vortex energy per unit length of a vortex can be estimated as [8]

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$$U_v = E_c + E_m = (\mu_0 H_c^2 \pi \xi_{ab}^2) + (\Phi_0^2 / 4 \pi \mu_0 \lambda_{ab}^2) \ln(\lambda_{ab} / \xi_{ab}) \quad , \quad (1)$$

where  $E_c$  and  $E_m$  are the core and the kinetic and magnetic energies of a vortex, respectively.  $H_c$  is the thermodynamic magnetic field of the superconductor and  $\xi_{ab}$  and  $\lambda_{ab}$  are the coherence and the penetration length, respectively. Then, the net energy saved (or the pinning energy by placing a vortex in a linear defect of a radius  $r$ ) is

$$U_p = (\mu_0 H_c^2 \pi \xi_{ab}^2) + (\Phi_0^2 / 4 \pi \mu_0 \lambda_{ab}^2) \ln(r / \xi_{ab}) \quad , \quad (2)$$

for  $r \geq \xi_{ab}$ .  $U_p$  for a unit of the volume with a defect radius of  $\sim 5.0$  nm and length of an inter  $\text{CuO}_2$  planer spacing is of the order of 12 MeV while the thermal energy is  $\sim 6.6$  MeV at 77 K.

In the above simplified discussion, other intrinsic contributions to the vortex pinning from the vortex lattice and the line tension were not considered. As pointed out by Brandt [12], the contribution from the lattice shear is negligible because the  $B_{c2}$  for these superconductors is very large. On the other hand, the line tension can be a significant factor for the strongly coupled system (along the c-axis) such as  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The above description, Eq. (2), is valid only for a linear defect along the direction of  $H$  and for a density of the defects which is greater than that of the vortex lines. Particularly at high temperatures, excess unoccupied defects are required as the nearest neighbors for pinning of the lines in the system [11,12].

#### ARTIFICIALLY PRODUCED VORTEX PINNING CENTERS

In studying the mechanisms of the vortex pinning in Type-II superconductors, various high-energy-particle irradiations were employed in low- $T_c$  superconductors [13]. Similarly, irradiation with neutrons [14] and protons [15-17] were also used to exploit the possibility of increasing the values of  $J_c(H)$  of the newly discovered high  $T_c$  superconductors. However, it was soon shown that the defects which were introduced by these high energy particles were too small to be effective pinning sites except at low temperatures ( $\sim 10$  K) or at low magnetic fields ( $< 1$  T) [14-17]. More recently, realizing this fact and following work by Bourgaud et al.'s work [5], Civale and his coworkers have used heavy-ion irradiations to enhance critical-current densities of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystals drastically [6]. The heavy ions with sufficient stopping power ( $\geq 20$  keV/nm depending on the condition of the oxide [18]) have shown to produce linear latent damaged columns through the oxides [5-10]. The size of the damaged cylinders can be as large as  $\sim 10$  nm or more in diameter depending on the energy of the ions and on the materials and their conditions, e.g. extent of the oxidation [18]. As shown by a number of articles, the observable (by high-resolution electron microscopy) damaged regions are amorphous and expected to be non-superconducting. In addition, at least for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , it was shown, using the electron energy-loss spectroscopy (EELS) in conjunction with a fine electron beam ( $\sim 2$  nm) transmission microscope, that the size of the non- or weak-superconducting region is likely to be significantly greater than the amorphous area. (The EEL spectrum of the oxygen K-edge exhibits a pre edge feature in addition to the main absorption edge. The strength of the pre-edge is related to the hole, the carrier, concentration. Thus, if the pre-edge is weak, it indicates that the oxygen in the Cu-O chain is either missing or disordered.)

The effectiveness of such amorphous columns in pinning the vortex lines is illustrated in Fig. 1 where the critical-current density  $J_c$  of single-crystalline  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , after the introduction of an equivalent density of the amorphous columns to the flux density of 5 T, is plotted as a function of applied magnetic fields  $H$  [6]. Although the values of  $J_c$  for this data were deduced from a measurement of magnetic hysteresis, the values compare very favorably to those of some of the best  $J_c$  for thin films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as shown in Fig. 1. The likely reason for such highly effective vortex pinning by the heavy-ion irradiation damage is the fact that the entire superconducting condensation energy along the length of the column is used for the pinning when the vortices align with the columns. [See Eq. (2).]

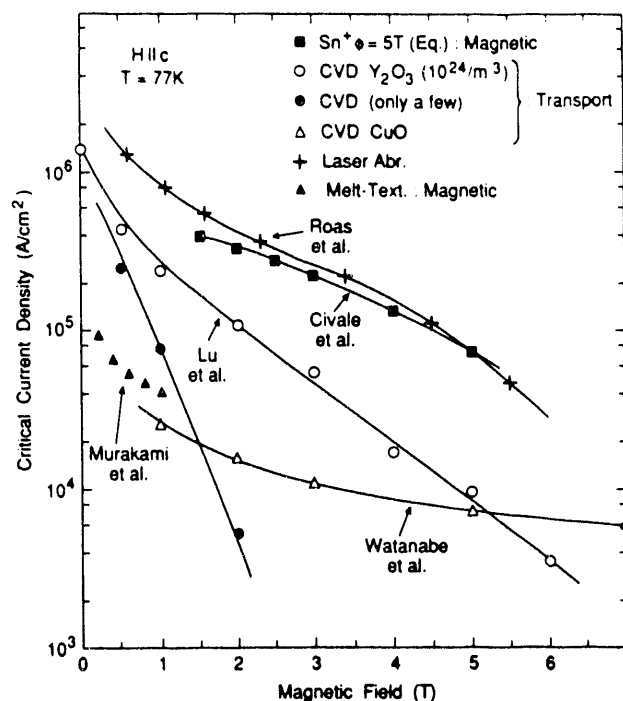


Fig. 1. Comparison of critical current densities of (a)  $\text{YBa}_2\text{Cu}_3\text{O}_7$  films; (b) a heavy ion irradiated single crystalline  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and (c) a melt-textured  $\text{YBa}_2\text{Cu}_3\text{O}_7 + \text{Y}_2\text{BaCuO}_4$ , at 77 K and  $H \parallel c$ .

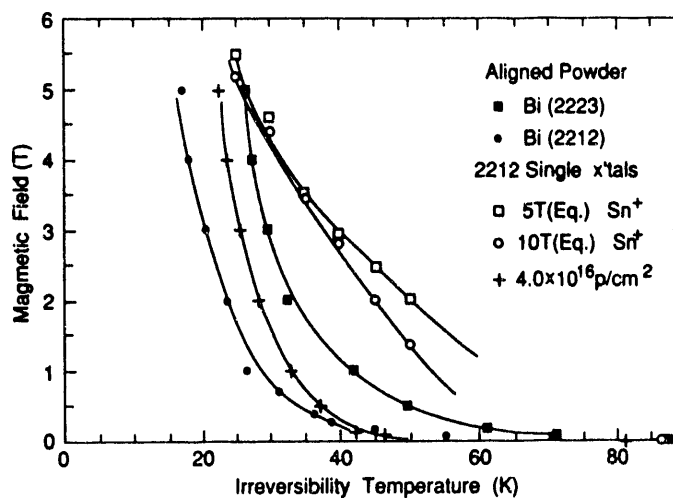


Fig. 2. Comparison of the irreversibility temperatures for a virgin, a proton irradiated, and a heavy ion irradiated  $\text{Bi}(2212)$ .

As shown in the above, the amorphized columns are very effective in pinning vortex lines and thus increasing the critical-current density of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  which is relatively strongly coupled along the c-axis. However, in the case of Bi(2212) and (2223), the coupling along the c-axis is known to be very weak and the magnetic vortices are thought to consist of strings of weakly connected discs along the c-axis [19]. Thus, the individual discs rather than long lines of the vortices through the material can dissociate from the amorphous columns under the Lorentz force and thermal excitation with correspondingly much smaller energies than for the long lines. Thus, it is more difficult to keep the vortices pinned down in the Bi than the Y-system. Hence, improvements in  $J_c(H)$  for Bi(2212 or 2223) will be limited to a relatively low temperature ( $<60$  K) even with the nearly ideally shaped pinning centers as introduced by heavy-ion irradiation [20]. This is illustrated in Fig. 2 by comparing the irreversibility lines for Bi(2223) with and without the irradiation by  $\text{Sn}^+$  (580 MeV) ions. Also shown in Fig. 2 is the irreversibility line for a Bi(2212) crystal after proton irradiation [16]. Again, as for Y(123), the proton irradiation is only effective in increasing  $J_c$  at low temperatures. (The irreversibility lines demark the region for reversible flux lines in the H-T diagram and there will be no useful critical current above this line.)

In the case of Tl(2223), which is believed to have the coupling strength along the c-axis between Y(123) and Bi(2212, 2223), a significant improvement in  $J_c$  as well as the irreversibility temperature toward higher temperatures was achieved by  $\text{Ag}^{+21}$  (237 MeV) irradiation [9]. In addition, what is interesting is the fact that the maximum  $J_c$ , which was achieved for a given applied field, e.g.  $H=5$  T, was obtained after the specimen was irradiated to produce the columnar density well above the fluence equivalent to the magnetic vortex density for 5 T. This observation was consistent with the prediction of the recent articles by Nelson and Vinokur [11] and Brandt [12].

In summary, for the superconductors with the relatively strong coupling along the c-axis such as Y(123), very high critical-current densities can be achieved with an appropriate fluence of heavy-ion irradiation at elevated temperatures (e.g. 77 K) and high magnetic fields. On the other hand, if the coupling is weak, even the introduction of the nearly ideal pinning centers such as those by heavy-ion irradiations can not sufficiently enhance  $J_c$  for high-temperature applications.

#### SYNTHESIZED PINNING CENTERS

In the above, we have discussed the results of artificially incorporated pinning centers on critical-current densities in these cuprates. In this section, we review those pinning centers which have been produced as a part of the synthesis process of the superconductors. Then, the effectiveness of these defects in increasing critical-current densities will be examined and compared with the heavy-ion-irradiation-induced pinning sites. To the present, defects, which are thought to be act as the pinning centers, are primarily found in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and thus the discussion of the process-induced pinning centers will be limited to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

There are a number of commonly observed crystallographic defects in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [21]. These are dislocations, twin boundaries, and stacking faults. However, none of these are in general shown to be particularly effective pinning centers partly due to their low densities in a given specimen as well as low interaction energies with the vortices. However, more recently it was reported that high dislocation densities induced by high-temperature deformation of the melt-textured  $\text{YBa}_2\text{Cu}_3\text{O}_7$  were quite effective in increasing  $J_c$  in the H||C orientation [22]. On the other hand, Goyal et al. have suggested that small stacking faults or dislocation loops near  $\text{Y}_2\text{BaCuO}_4$  precipitates contributes to the increased  $J_c$  in the melt-textured  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [23]. Zhou et al. also have found similar small loops when the  $\text{Y}_2\text{BaCuO}_4$  precipitate density is very high [24]. However, the importance of these small stacking faults or dislocation loops toward enhanced  $J_c$  in the melt-textured  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is not clear at this point.

Another type of defect which has received considerable interest in this regard is finely distributed ordered oxygen vacancy regions. These ordered islands of oxygen-deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  with  $\delta \geq 0.2$  can be observed with transmission electron microscopy [21]. Although for a small  $\delta$ , the presence nor the size of the precipitates can not directly be seen in a TEM, Daumling et al. have suggested that the so-called "fish tail" effect in magnetization of a nominally fully oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is due to the precipitates of the vacancy ordered islands [25]. Since the vacancy ordered regions are lower in  $T_c$  than the matrix, these areas become normal and effective pinning sites as the applied field increases. This causes the width of the hysteresis to widen with the field before the matrix becomes normal, and thus the appearance of a "fish tail." More recently, using the EELS technique, Zhu et al. have confirmed the presence of small oxygen-deficient regions ( $<5$  nm) in specimens of nominally fully oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [26]. However, the oxygen concentrations of such regions cannot be determined. This type of pinning center is reasonably effective in pinning the vortices up to  $\sim 60$  K, but at higher temperatures the strength diminishes.

A number of purposely introduced precipitates for enhanced vortex pinning are discussed in literature [24,27-29]. Among these, most studies are on  $\text{YBaCuO}_4$  precipitates in melt textured  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The additions of excess  $\text{YBaCuO}_4$ , which result in refinement of the precipitates have been shown to increase critical-current densities of bulk  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [31,32]. The increase in values of  $J_c$  in this case was correlated with the enhanced pinning potential [33]. However, as shown in Fig. 1, one of the best values of  $J_c(H)$  for  $H||C$  in these materials is still substantially lower than those for the thin films (see Fig. 1) or for heavy-ion-irradiated single crystals (Fig. 1). This is likely to be due to the fact that the  $\text{Y}_2\text{BaCuO}_4$  precipitates are quite large ( $\sim 1$   $\mu\text{m}$ ) and thus the interparticle distance becomes too large for effective pinning. Then, the limitation in  $J_c$  is likely to be related to the line tension of the vortex in this material.

In the area of thin films, fine precipitates of  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  have been incorporated in CVD-processed films of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . When a density of  $10^{24}/\text{m}^3$  of the precipitates of 5-10 nm in size achieved, the values of  $J_c(H)$  at 77 K and  $H||C$  have increased significantly over those for the films without the  $\text{Y}_2\text{O}_3$  as shown in Fig. 1 [34]. Also, shown in Fig. 1 is  $J_c(H)$  for a  $\text{CuO}$  containing  $\text{YBa}_2\text{Cu}_3\text{O}_7$  film also produced by a CVD process [35]. Although both of these films provide very respectable values in  $J_c$ , the critical-current densities in the heavy-ion-irradiated single crystals are higher by an order of magnitude than those for the films with these precipitates.

The above discussion thus has shown that the columnar pinning centers are most effective and it is very difficult to produce similarly effective centers by a process control. In addition, what is very intriguing and interesting is the fact that the best values of  $J_c(H)$  for a film produced by a laser abrasion process are essentially identical to those for the heavy-ion-irradiated  $\text{YBa}_2\text{Cu}_3\text{O}_7$  single crystals (see Fig. 1). (Although the criteria for  $J_c$  in this experiment was  $\sim 30$   $\mu\text{V}/\text{cm}$  and changing it to 3  $\mu\text{V}/\text{cm}$  will reduce the value of  $J_c$  from 2.5 to  $1.7 \times 10^5$   $\text{A}/\text{cm}^2$  at 3 T, the values for this film are still very large for  $J_c$  (77 K and  $H||C$ ).) The films made by laser abrasion processes are generally free of easily detectable defects or precipitates which are identifiable as the pinning sites. Thus, the puzzling question is why these films can carry such high current densities. Understanding this question may lead to other ways to improve critical current densities in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

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