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MICROSTRUCTURES AND CRITICAL CURRENTS IN HIGH-T_c SUPERCONDUCTORS

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Abstract

Microstructural defects are the primary determining factors for the values of critical-current densities in a high T_c superconductor after the electronic anisotropy along the a-b plane and the c-direction. A review is made to assess firstly what would be the maximum achievable critical-current density in $YBa_2Cu_3O_7$ if nearly ideal pinning sites were introduced and secondly what types of pinning defects are currently introduced or exist in $YBa_2Cu_3O_7$ and how effective are these in pinning vortices.

1. Introduction

A period of more than ten years has passed since the first report of superconductivity at elevated temperatures for La-Ba-Cu-O [1] and subsequent reports of high-T_c superconductivity in Y- [2], Bi- [3], Tl- [4] and Hg- [5] cuprates with critical temperatures well above the boiling point of liquid nitrogen. Widely expected applications of these superconductors for high current applications have not been realized even though some larger model devices for electrical power usages are being constructed and investigated in more recent years. 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, e.g. 77 K, even at intermediate applied magnetic fields [except for some thin films of $YBa_2Cu_3O_7$, (YBCO)]. There are two primary causes for this 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 transporting currents across the grain boundaries. In the Bi-cuprate system, significant improvements in the latter have been made by intensive commercial development of the so-called powder-in-tube processed Bi-2223 and 2212/Ag composite tapes. Now, self-field critical-current densities of ~ 70, 000 A/cm^2 at 77 K in short specimens, and lengths of an order of 1 km with J_c of ~ 35,000 are also reported [6]. Unfortunately, in these superconductors, due to very highly anisotropic electronic properties along their crystallographic axes, vortices do not behave as a solid continuous lines, rather they tend to act as dissociated pancake-like entities making it difficult to pin all of the individual vortex segments. This property makes these superconductors less useful at elevated temperatures in applications requiring production of an intermediate magnetic field such as transformers and motors unless the operating temperatures are significantly reduced.

It is shown that YBCO is less anisotropic and the vortex lines are much more rigid and can be pinned easier than those for the Bi cuprates. The more isotropic electronic property in YBCO also makes it more isotropic in its growth habit along the *a-b* plane and the *c*-direction. This more isotropic growth characteristic also make it more difficult or nearly impossible to make *c*-axis-aligned YBCO tapes by the powder-in-tube method. Thus, one has to rely on more complex fabrication methods to make YBCO texture in bi-axial directions (in the *a*-, and *b*-, and in the *c*-directions) for high current carrying properties. Fortunately, over the last few years, a few methods to prepare bi-axially aligned buffer (diffusion barrier) layers on metallic substrates, for which bi-axially aligned YBCO layers can be deposited, have been developed, and currently tapes with high critical current densities are being manufactured in short lengths [7-9]. This development is at a stage such that the connectivity between the grains is sufficiently improved so that the J_c of the thick films is determined by pinning strength of the YBCO grains. Thus, it is important to understand what types of defects are more effective in pinning vortices, and how one can introduce them in the YBCO. Also, over the last few years, a number of different defects have been shown to be effective in pinning vortices in YBCO. On the other hand, it has, so far, been shown that it is very difficult to modify microstructures sufficiently in Bi-cuprates to change the pinning strength significantly by processes other than bombarding the specimen with high energy heavy ions or very high energy protons. Hence, in the following, we will only examine various defects which were studies for their effectiveness in pinning the vortices in YBCO.

First we present simplified magnetic vortex pinning mechanisms assuming individual vortex pinning. Secondly, a discussion will be given of recent results of the effects of heavy-ion irradiation on critical-current densities in YBCO [10 - 14]. Since this heavy-ion irradiation produces dense linear tracks of defects owing to the large unidirectional energy deposition rate by ions, it creates nearly ideal pinning centers. We can ask what would be the maximum possible critical-current density achievable with such pinning centers in YBCO. This result can be compared with the values of J_c's obtained by pinning sites which are purposely or naturally incorporated in bulk and thin films of YBCO. In these examples, we only consider the effectiveness of the defects in increasing the values of J_c in magnetic fields parallel to the *c*-axis since the vortex pinning is generally very strong for H parallel to the *a-b* plane without defects.

2. Vortex Pinning

Before discussing the experimental results of vortex pinning in high-T_c superconductors, a brief and simplified explanation for the vortex pinning energy, U_p, per unit length of a vortex is given below [12,15]. First, the energy per unit length of a vortex, U_v, is:

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$$U_v = E_c + E_m = (B_c^2\pi\xi_{ab}^2/\mu_o) + (\phi_o^2/4\pi\mu_o\lambda_{ab}^2)\ln(\lambda_{ab}/\xi_{ab}) \quad (1)$$

where E_c and E_m are the core and the kinetic or the magnetic energy of a vortex, respectively. ϕ_o is the flux quanta and B_c is the thermodynamic critical magnetic field of the superconductor. ξ_{ab} and λ_{ab} are the coherence and the magnetic field penetration lengths, respectively. Then the net energy saved (or pinning energy) by placing a vortex in a linear non-superconducting defect of a radius, r, is

$$U_p = (B_c^2\pi\xi_{ab}^2/\mu_o) + (\phi_o^2/4\pi\mu_o\lambda_{ab}^2)\ln(r/\xi_{ab}) \quad (2)$$

for $r \geq \xi_{ab}$. In order to obtain some physical feeling for the effectiveness of a pinning center, we consider a non-superconducting cylinder of radius ~ 5.0 nm placed parallel to the *c*-axis of YBCO, and calculate U_p for a such defect. At 77 K, U_p for the core energy portion is ~ 7.5×10^{-12} J/m while that for the magnetic energy is ~ 1×10^{-12} J/m. Thus, at this temperature for YBCO, the contribution to the pinning energy in such a defect is primarily the core energy saved by placing a vortex in a defect. For example, pinning energy of a circular disk of 5.0 nm in diameter and 1.0 nm in height is ~ 7.5×10^{-21} J. Since the thermal energy at 77 K is ~ 10^{-21} J, any extended defect of this nature would be a very effective pinning center.

In the above simplified discussion, other contributions to the vortex pinning from the vortex lattice and the line tension were not considered. As pointed out by Brandt [16], the contribution from the lattice shear is likely negligible because the B_{c2}'s for these superconductors are very large in comparison with typical magnetic fields which are used in our studies. In addition, we are considering very strong and randomly distributed pinning centers, and thus, the presence of these centers destroys the vortex lattice making the collective effect of the lattice on the pinning minimal. On the other hand, the weak line tension can be a significant limiting factor, particularly for a weakly coupled system (along the *c*-axis) such as Bi-cuprates in their capacities to pin vortices, even in the case where the pinning centers are linear columns as assumed in the above expressions.

2.1 ARTIFICIALLY PRODUCED VORTEX PINNING CENTERS

In studying the mechanisms of the vortex pinning in Type-II superconductors, various high-energy particle irradiation were employed in low-T_c superconductors [16]. Following these examples, irradiation with neutrons [17] and protons [18] were carried out to exploit the possibility of increasing the values of $J_c(H)$ of the cuprate 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 (≤ 20K) or very low magnetic fields (<< 1 T). Realizing this fact and following Bourgault *et al.'s* work [10], Civale and his co-workers have used heavy-ion irradiation to enhance critical-current densities of YBCO single crystals drastically [11]. Heavy ions with sufficient stopping power (≥ 20 kV/nm depending on the condition of the oxide [19]) have been shown to produce linear damaged columns through the oxides [10,11,19]. The size of the damaged cylinders can be as large as ~ 10 nm or more in diameter depending on the energy of the ions and on the materials and their oxidation conditions. As shown by a number of reports, the observable (by high-resolution electron microscopy) damaged regions are amorphous and expected to be non-superconducting. However, the size of the damaged superconducting area is typically much larger than the amorphous area, at least for YBCO [20]. It was shown, using the electron energy-loss spectroscopy (EELS) in combination with a fine-beam (~2 nm) transmission electron microscope, that the size of the non- or weak-superconducting region is approximately twice that of the observable amorphous area. (The EELS spectrum of the oxygen K-edge exhibits a pre-edge feature in addition to the main absorption edge. When the strength of 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 for YBCO in Fig. 1 where the critical-current density J_c of single crystalline YBCO, 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 field H [11]. Values of J_c for these data were deduced from a measurement of magnetic hysteresis, the values compared very favorably to those of some of the best J_c for thin films of YBCO [21] (which will be discussed below) 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 of a vortex along the length of the column is used for pinning when the vortices align with the columns.

The example highlighted above demonstrates that amorphous columnar defects are very effective in pinning vortex lines and thus increasing the critical-current density of YBCO which is relatively strongly coupled along the *c*-axis. In the case of Bi-cuprates, however, particularly Bi-2212, coupling along the *c*-axis is known to be very weak and vortices are thought to consist of strings of weakly connected disks, or 'pancakes', along the *c*-axis [22]. Thus, the individual pancakes, rather than an entire line of a vortex in a superconducting material, can easily escape from the amorphous columns under the Lorentz force assisted by thermal excitation, i.e., it is more difficult to keep the vortices pinned in the Bi than the YBCO. Hence, pinning energy for an identical defect is much smaller in the Bi-cuprates than in YBCO due to the difference in the electronic anisotropy, which determines the line rigidity in these materials. Improvements in $J_c(H)$ for Bi-cuprates will be limited to a relatively low temperature (< 50 K) even with the nearly ideally shaped pinning centers such as the heavy-ion irradiation-induced columnar defects [23]. This is illustrated in Fig. 2 by comparing the irreversibility lines for Bi(2212) with and without the irradiation by Sn (580 MeV) ions. Also, shown in Fig. 2 is the irreversibility line for a Bi2212 crystal after proton irradiation [18]. Comparing this irreversibility line with those for unirradiated and heavy-ion irradiated ones, it is clear that damage caused by elastic collisions of protons with nucleus in the solid, are too small to be effective pinning centers for temperatures above 30 K, even though they become very strong, as good as the heavy-ion damage, at lower temperatures. Similarly, irradiation of YBCO crystals by protons also showed ineffectiveness in increasing J_c at high temperatures. More recently, however, it was shown that similar, but randomly oriented, columnar defects could be formed by nuclear fission of Bi atoms in Bi-cuprates if protons of very high energies (~ 800 MeV) were used to bombard the specimens, and correspondingly J_c increased to the levels seen by the heavy-ion irradiation in Bi(2223)/Ag tapes [24].

In summary, for the superconductors with relatively strong coupling along the *c*-axis such as YBCO, very high critical-current densities at elevated temperatures and high magnetic fields (e.g., 77 K and ~ 4 T) can be achieved with an appropriate fluence of heavy-ion irradiation. 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 cannot sufficiently enhance J_c for high-temperature applications because of the weak rigidity of the flux line.

2.2 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 relative 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 act as pinning centers, are primarily found in YBCO, although very recently, an indication of possible pinning by the controlled oxygen vacancies in Bi 2212 was reported [25]. Thus, this discussion of the process-induced pinning centers will be limited to YBCO.

There are a number of commonly observed crystallographic defects in YBCO [26] which have been proposed to act as significant pinning centers. These include dislocations, twin boundaries, stacking faults, and Y_2BaCuO_4, (often called 211), precipitates. However, most of these are shown not to be particularly effective pinning centers. This is partly due to their low densities in a given specimen and to their unfavorable orientations with respect to the magnetic applied field along the *c*-axis. Both dislocations and the stacking faults lie in the *a-b* plane which is perpendicular to the applied field direction under consideration here. More recently, it was shown that very finely spaced twin boundaries in thick YBCO films appear to contribute significantly to their values of J_c [27,28]. Also, the parallel set of dislocations in a low-angle grain boundary [29] as well as a set of periodic linear strain fields, which are associated with facets in high-angle grain boundaries and lie along the *c*-axis [30], were also shown to pin the vortices in thin films and bulk bi-crystals, respectively, of YBCO.

In the following, we will first discuss pinning by small precipitates. These are small regions of the ordered oxygen-deficient YBCO, CuO, Y_2O_3, and 211 precipitates. Then, we will discuss linear defects at grain boundaries, (dislocations and localized strain fields), and twin boundaries in order. Comparing critical-current densities of YBCO containing these defects will illustrate the importance of the extended shape, the size, and the density of the defects for pinning vortices to effectively achieve high J_c values. Finally, $J_c(H)$ for a thin film of YBCO is compared with the values of J_c achieved by all of the defects discussed above. It will be shown that J_c for a thin film is generally as large as those due to the heavy-ion irradiated YBCO, and the possible sources for high pinning strength in the films are discussed.

2.2.1 *Precipitates*

A type of defect interaction, which has received considerable interest, is pinning by finely distributed oxygen-vacancy-ordered regions [31,32] in slightly reduced bulk YBCO due to the observation of the so-called "fish tail" effect in the magnetic M vs. H hysteresis [33]. Originally, Däumling *et al.* suggested that this increased critical current-density with increasing field was due to these precipitates, i.e., the ordered islands or clusters of the oxygen deficient regions since the oxygen-vacancy-ordered regions are lower in T_c than the matrix and these areas become normal and effective pinning sites as the applied field increases [33]. This causes the width of the hysteresis to widen with increasing field before the matrix becomes normal, and thus the appearance of a "fish tail". Unfortunately, these presumed oxygen-vacancy-ordered regions are very small and cannot be easily seen by a transmission electron microscopy. Thus, following this suggested interpretation of the fish tail, an abundance of articles appeared in the journals arguing about the correctness of such an interpretation. The clear resolution of this problem had to wait until truly *pure* single crystals of YBCO, which were produced in $BaZrO_4$ crucibles, became available recently. (Most of previous single crystals contained very small amounts of impurities from crucibles which appeared to tie up the oxygen vacancies which cannot be easily removed by heat treatments.)

For these new pure YBCO crystals, it was shown that the fish tail can by removed by fully oxidizing them in a high-pressure oxygen atmosphere. Conversely, the fish tail can be reintroduced by removing oxygen or by other appropriate treatments while keeping the same oxygen content [34]. Thus, it was conclusively shown that the fish tails in YBCO are due to very small regions of $YBa_2Cu_3O_{6.5}$ where oxygen vacancies ordered [35]. Earlier measurements of J_c in YBCO single crystals showing this effect indicated that the values of J_c achieved are relatively small, and may not be of practical interest, e.g., $J_c \sim 2 \times 10^4$ A/cm^2 at 3 T and 77 K [35]. Interestingly, more recent results indicate that the level of J_c from these very small 3-D pinning centers can be significantly higher than the earlier values as shown in Fig. 1 [36]. In this case, the deficiency in oxygen was reported to be 0.04 out of 7, i.e., $O_{6.96}$. It is quite remarkable that these precipitates are so effective in pinning the vortices. In terms of J_c, it is just below those for the heavy-ion-irradiated YBCO single crystal and very thin films of YBCO. (See Fig. 1.) Thus, the density of pinning centers in this specimen is likely to be very high and these may collectively pin the vortices quite effectively, particularly at relatively high fields.

Interestingly, this high value of J_c is very closed to that which was calculated for YBCO with the oxygen deficiency of 0.0265 by Vergas and Labalestier [35] based on the radius of the oxygen-vacancy ordered regions of ~ 1.0 nm and the interparticle distance of 25 nm. They also assumed that these ordered regions were formed by a spinodal decomposition of $YBa_2Cu_3O_{6.9735}$ to $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.5}$ with sizes significantly smaller than those, ~ 10 nm in the (010) and (001) directions, which can be estimated from electron diffraction of YBCO with $O_{6.7}$. Since the above oxygen deficiency $O_{6.9735}$ which was used for the J_c calculation, are so much less than the specimen where the measurements by TEM can be performed, these small sizes in YBCO with very small deficiencies may be reasonable values.

A number of other purposely introduced larger precipitates for enhanced vortex pinning are discussed in the literature. Among these, most studies are Y_2BaCuO_4, (211), precipitates in melt-textured YBCO. The additions of excess 211, which result in refinement of the precipitates, have been shown to increase critical-current densities of bulk YBCO [37,38]. The increase in values of J_c in this case was correlated with the increased densities of these rather large precipitates. Figure 1, however, shows one of the best values of $J_c(H)$ for H//c in these materials is still substantially lower than those for the films, or even less than those YBCO with the oxygen-vacancy ordered regions. It is noted that the size of the 211 precipitates (~ 1μm) and also the average interparticle distance are quite large. This means that the limitation in J_c is likely to be related to a less-effective pinning strength of these large precipitates and the large inter particle distances. The latter makes it difficult to pin the vortices against the Lorentz force because of limited rigidity of the line vortices in the superconductor.

In thin-film processing of YBCO by chemical vapor deposition, CVD, methods, it was shown that it was possible to introduce very fine precipitates of CuO [39] and Y_2O_3 [40]. The CuO precipitates are very thin platelets with dimensions of ~ 25 nm in diameter and ~ 0.5 nm in thickness. These are densely populated with an approximate inter-particle distance of 50 nm. Figure 1 shows that these precipitates were not effective in increasing the critical-current density of the film in comparison with other films. This may be due to the fact that the thickness of the CuO particles is very thin, thus making them very ineffective in pinning the flux lines against the line tension due to Lorentz force. It was also shown that dense, 10^{24} /m^3, precipitates of Y_2O_3 can be introduced in YBCO films by the CVD process. These precipitates are a few nm in diameter and ~ 10 nm apart. As shown in Fig. 1, the inclusion of these precipitates increased the film's critical-current density by a large factor in comparison with one without them. It appears that the difference in the attained J_c between these films with Y_2O_3 and CuO is that CuO precipitates are very thin in the c-direction while Y_2O_3 are more spherical leading to better pinning centers as pinning energy is proportional to the length along the vortices. What is quite striking is that the areal density of Y_2O_3 in this film and that which was used for the above calculation of J_c [35] for the oxygen-deficient YBCO, are approximately the same at ~ 10^{16}/m^2. Further, the calculated J_c , the measured J_c for $O_{6.96}$ by Kupfer *et al.* [35], and the J_c for the film with Y_2O_3 are all within a factor of 2 of J_c at high fields, H > 3 T. Thus, in order to achieve this level of high J_c, it requires the presence of small defects, ~ 1-2 nm, which are ~ 10 nm apart, and this is not always easy to do in the processing of practical conductors.

2.2.2 *Linear Defects*

Among the defects in crystals, dislocations are linear and therefore offer the possibility of providing effective pinning centers since the core and the region within the radius of a few lattice parameters are highly stressed and likely to be either normal or very weakly superconducting. The dislocations in these superconductors tend to lie in the *a-b* plane and it is very difficult to align them along the *c*-direction. One special case for which this happens is at the low-angle [001] tilt boundaries. As in the classical picture of a low-angle tilt boundary, the boundary is formed by the insertion of equally spaced edge dislocations along the [001] direction in the plane of the boundary. The spacing *d* of the dislocations are determined by the misorientation angle θ between the adjacent crystals. Very recently, taking advantage of this special dislocation arrangement, Diaz *et al.* demonstrated that the equally spaced dislocations at a low-angle grain boundary can act as pinning centers if the field is aligned parallel to the dislocations [29].

Another interesting observation associated with a high-angle (001) tilt grain boundary in bulk bicrystals is the fact that the boundary consists of a periodic facet structure, and electron microscopy of the boundary revealed that the corners of the facet are highly stressed. Since the facet is periodic, these stressed regions are periodically aligned along the *c*-axis in the boundary plane. Thus, it may be possible to match the vortex lattice with this periodic stress field, as was found as the values of J_c peaked when the vortex lattice parameter was matched with the period of the stress field [30].

2.2.3 *Planar Defects*

Unfortunately, it is very difficult to arrange these linear defects internal to the grain of a superconductor to make them useful in increasing J_c even though the above linear pinning centers are very interesting to study. Other commonly observed defects in YBCO are twin boundaries which are formed in the bulk of YBCO grains since these are formed as the result of the structural phase transformation from a tetragonal to an orthorhombic structure during the oxygen absorption process. Twins are formed to accommodate the volume change due to the transition, and it was shown that the boundary, which forms along the (110) and equivalent planes, has a displacement (of an order of 1/4 of the (110) lattice parameter) along the plane [41]. The thickness of the distorted region is estimated to be ~ 1 nm in fully oxygenated YBCO [42,43]. It is expected that this distortion makes the twin boundary region weak or nonsuperconducting, and thus may act as strong pinning sites. In the earlier studies, although it was observed that the boundary can pin the vortices in a resistivity measurement [44], the critical-current densities of the bulk YBCO are not usually very high. This is likely due to the large spacing, ≥ 0.1 μm, between the boundaries in most of the bulk YBCO and to the very large lateral dimensions. Also, in the thin films, it is, in many cases, difficult to see the effect of the twin boundaries on critical-current densities in spite of the fact that the spacing, 20 - 50 nm, and the length, ~ 200 - 2,000 nm, of the boundaries in the films are very small. This is due to the fact that the in situ deposited thin films, particularly those by a laser ablation technique, generally have very high densities of grown-in defects and these defects dominate the vortex pinning providing very high critical current densities as shown in Fig. 1 as an example.

More recently, fabrication of thick YBCO films on metallic substrates has gained considerable attention due to the interest using these tapes in electrical power applications. In general, the values of J_c in these thick films are about an order of magnitude lower than those for the best thin films or the heavy-ion-irradiated YBCO shown in Fig. 1. They are nearly the same as the CVD-processed YBCO film with Y_2O_3. It was shown that it is possible in some cases to see the contribution of the twin boundaries to J_c when that the values of J_c are reduced to this level. The possible contribution from the twin boundaries are assumed from the fact that the angular dependence of J_c in an applied field exhibit a maximum when the boundary is parallel to the field [27,28]. However, what is not clear yet is how vortices are pinned at the boundaries while the currents have to cross the boundary.

2.2.4 *Thin Films*

In the above discussions, we have often referred to the very high values of J_c attained in thin (< 1 μm) YBCO films [21] and it is shown in Fig. 1, as an example. Although a number of TEM examinations were carried out by a number of people, it is still not clear what type(s) of defects makes them to carry such high J_c. It is generally believed that there are small grown-in defects in the film since these high J_c are generally observed in the films which are deposited at relatively low temperatures, e.g., 750° C or below. When the films are grown much thicker, due to the extended time required for the film to stay at high temperature, some of these defects are annealed away and correspondingly, J_c decreases by approximately an order of magnitude. However, the details of this are not satisfactorily understood yet.

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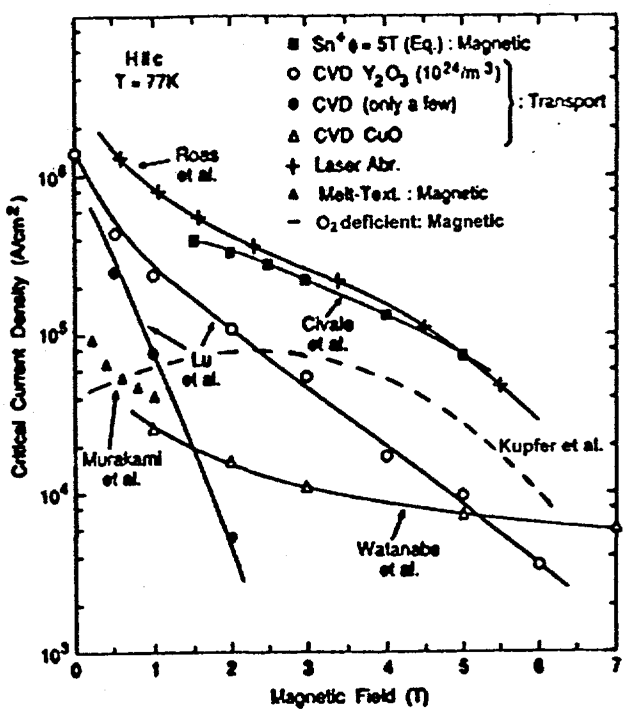

Fig. 1. Comparison of critical current densities of $YBa_2Cu_3O_7$ at 77 K and H//c: (a) thin films by a laser ablation process and CVD processes, (b) a single crystal irradiated by high energy Sn ions to an equivalent fluence of 5 T, (c) a melt-textured crystal with 211 precipitates, and (d) an oxygen deficient $YBa_2Cu_3O_{6.94}$ single crystal.

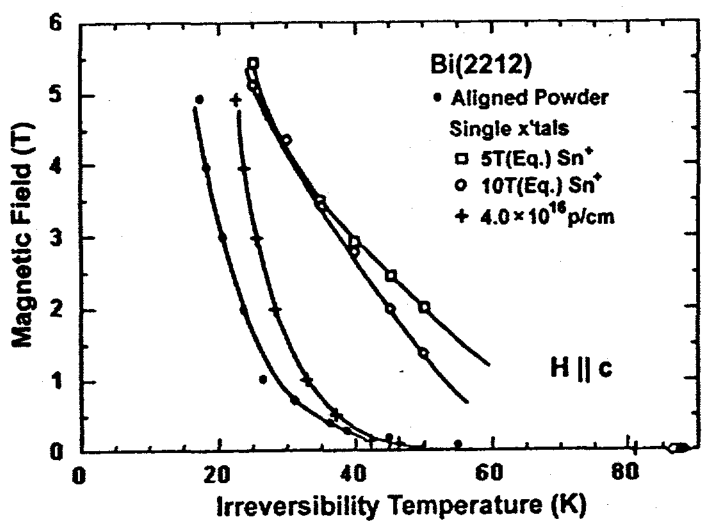

Fig. 2. Comparision of the irreversibility temperatures for virgin, a proton irradiated, and a heavy ion irradiated Bi(2212)