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Critical Currents and Lower Critical Fields in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$

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Abstract

The influence of Fe substituted for Cu in $YBa_2Cu_3O_{7-\delta}$ on the intra- and intergrain properties has been studied. In the concentration regime $0 \leqslant x \leqslant 0.02$ the intragrain critical current density slightly increases with increasing concentration of iron, but for $x \geqslant 0.04$ it drops significantly. On the contrary, the intergrain critical parameters are gradually degraded with increasing x, for all concentrations of iron. It is, therefore, concluded that the part of iron under the form of impurity phases locates between grains and makes the intergrain transport properties worse.

1. Introduction

Since the early work of Xiao *et al.* [1] the problem of substitution for Cu in members of 1–2–3 family of compounds has attracted great attention. Quite a number of papers (see for example Refs. [2–5]) dealed with electric, magnetic and structural data in order to clarify the problem and, hence, the nature of the high-T_c superconductivity phenomenon. It is generally agreed that most of the substituted atoms (3*d*-elements as well as Ag, Ga and Al) at the Cu sites decrease the critical temperature. This seems to be reasonable because the replacement for Cu, which is strongly involved in the mechanism of high-T_c superconductivity, directly degrades the superconducting properties.

In the course of a systematic study, the case of Fe-substitution has revealed a few surprising facts: low temperature Mössbauer studies [6, 7] of samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ have shown the magnetic splitting in the spectra, which was interpreted in terms of existence of magnetic ordering over the Cu sites. Furthermore, structural studies have indicated the orthorhombic to tetragonal phase transition for $x_c = 0.02$–0.03, and this hypothetical tetragonal phase induced by Fe-dopants is superconducting, which is contrary to the tetragonal phase of pure $YBa_2Cu_3O_{7-\delta}$ with $\delta \geqslant 0.5$.

However, more detailed studies, with the aid of transmission electron microscopy, have revealed the complexity of the situation in the case of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. As has been shown in Ref. [8, 9], after doping of Fe atoms one deals with a microdomain structûre, with space symmetry that is orthorhombic, and the effect of tetragonalization was due to the effect of intereference of scattered waves from adjacent microdomains. In this picture, most of the doped Fe atoms would be located on the twin or microdomain boundaries and, hence, would cause any effects connected with the magnetic splitting of the Mössbauer spectra.

The modification of the structure of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ induced by doping allows to study the influence of structural changes on critical parameters, i.e. critical fields and critical currents. For example, early works dealing with the influence of twins on superconducting properties of $YBa_2Cu_3O_{7-\delta}$ proposed that the twin boundary region has a higher T_c than the matrix [10]. If this is the case, one may expect that the effect should be observable already for spacing less than 10–20 nm, since in pure $YBa_2Cu_3O_{7-\delta}$ the average twin spacing equals to 200 nm. Generally, twin boundaries play a very important role in some of the excitonic mechanisms proposed (see for example [11]). On the other hand, it was also suggested that boundaries act as strong pinning centers, which result in higher critical currents obtained in thin films [12]. Finally, Deutscher and Muller [13] argued that a significant depression of the superconducting order parameter could occur at twins and other planar defects in the high T_c oxides. In other words, these would be non- or weakly superconducting regions. The evolution of the $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ structure with increasing x directly allows us to check all these concepts.

In this work, the results of low field d.c. magnetization and a.c. susceptibility studies of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ for $0.0 \leqslant x \leqslant 0.12$ are presented. The analysis of the data is focused on the influence of Fe dopants on intra- and intergrain critical parameters. In the following physical properties related to both the grains and intergrain material will be distinguished by the suffixes G and J, respectively.

2. Experimental details

The samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ with $0.0 \leqslant x \leqslant 0.12$ were prepared by calcination of suitable amounts of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3 in a quartz boat at 940–950° C for 15 h in flowing oxygen. After cooling, the charge was powdered and pressed into pellets (3 mm in diameter and 5 mm in height), and the above process was repeated. The next cooling was stopped at about 400° C, and the samples were annealed for 2 days and then slowly cooled down to room temperature. All samples, as checked by X-ray powder diffraction, exhibited only a single phase.

A vibrating sample magnetometer (PAR model 155) was used to measure the low field dc magnetization of the samples. A self-made a.c.-susceptometer (for details of construction and measurement we refer to Refs. [14] and [15]) was used to collect the a.c.-susceptibility data. We have studied the following Fe-concentrations: 0.0 (reference), 0.01, 0.02, 0.04, 0.06, 0.08, 0.10 and 0.12.

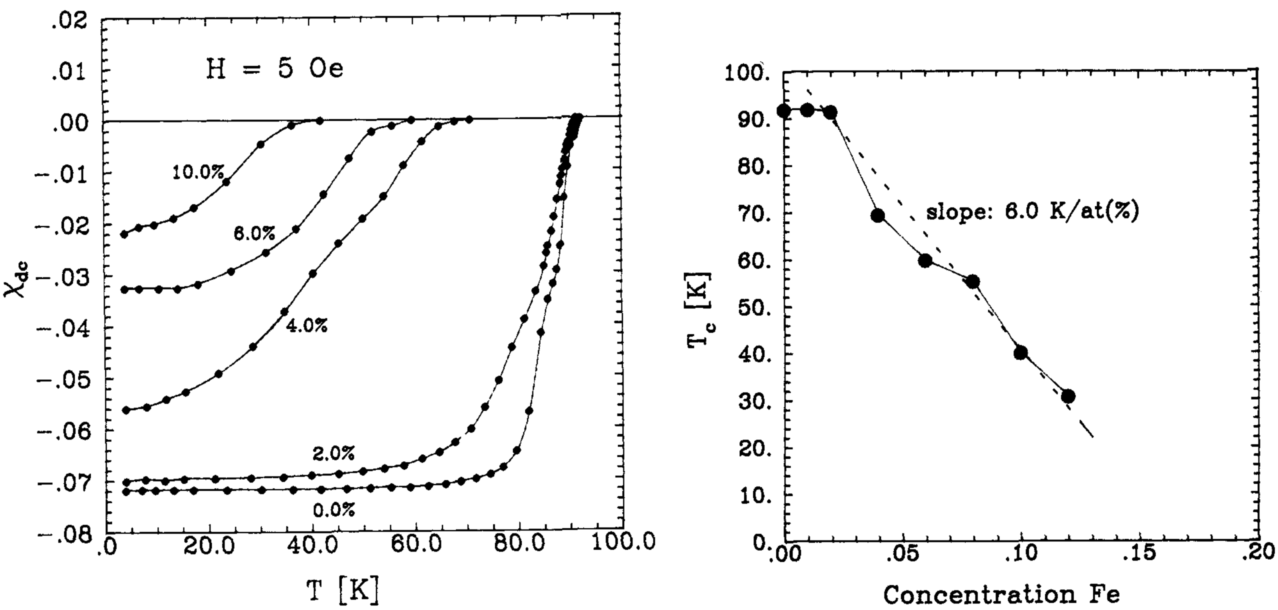


Fig. 1. (a) Diamagnetic shielding effect and (b) superconducting critical temperature for various iron concentrations in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$.

3. Results

3.1. *Intragrain properties*

The diamagnetic shielding effect for a few concentrations of Fe in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ is shown in Fig. 1(a), while the dependence of critical temperature, T_c^G (determined as the point of onset of diamagnetism), is illustrated in Fig. 1(b). One can notice that the difference in diamagnetic shielding between $x = 0.0$ and 0.02 is very small, and the diamagnetic signal in low temperatures is nearly equal to that of ideal screening, i.e. $\chi = -1/4\pi$. However, for higher concentrations, the degradation of superconductivity is evident. This fact may indicate that the fraction of the material which is superconducting decreases as the Fe concentration increases. Similarly to the effect of diamagnetic shielding, T_c^G is, in practice, unchanged up to $x = 0.02$ and starts to decrease for higher concentrations, with a slope of 6.0 K/at %. Such behaviour of both diamagnetic shielding and critical temperature may be attributed to a crossover from twin to microdomain structure observed for precisely the values of x of 2–3 at % [8].

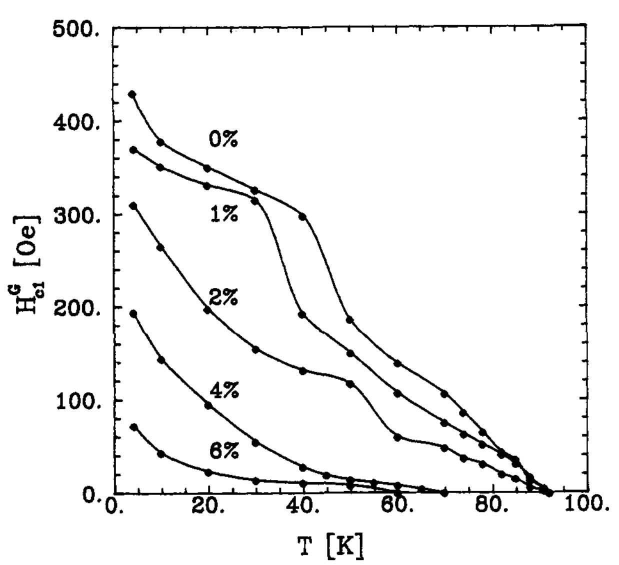


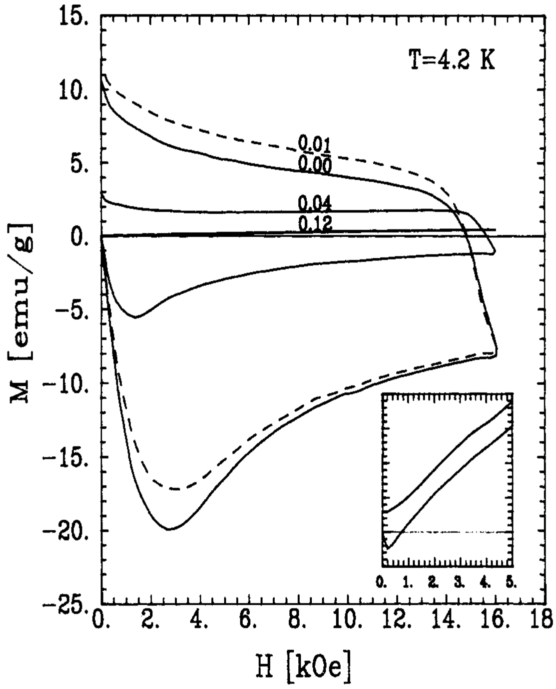
Fig. 2. H_{c1}^G of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ as a function of temperature for $0 \leqslant x \leqslant 0.06$.

Temperature dependence of lower critical field in grains, $H_{c1}^G(T)$, for a few concentrations of Fe is shown in Fig. 2. H_{c1}^G was determined from the isothermal high-field magnetization curves as illustrated in Fig. 3(a). The initial part of the magnetization curve is linear, and the point at which the deviation from the linearity begins correspond to H_{c1}^G [16]. With increasing concentration of Fe in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ this critical parameter is gradually degraded. The strong deviation from a simple parabolic temperature dependence of H_{c1}^G may be expected as a consequence of the strong anisotropy of critical fields in the $YBa_2Cu_3O_{7-\delta}$ phase and the polycrystalline nature of samples [17, 18].

The most interesting problem is connected with intragrain critical current densities, j_c^G. Utilizing hysteresis loops $M(H)$, it is possible to estimate the critical current density, $j_c(H)$, using the formula proposed by Fietz and Webb [19]:

$$j_c(H) = \frac{15|M^+(H) - M^-(H)|}{R}, \qquad (1)$$

where, respectively, M^+ and M^- are the values of measured magnetization for increasing and decreasing magnetic field branches, and R is the sample radius. However, as was recently shown by Chaddah *et al.* [20], this equation may provide an underestimation of j_c in the case of high-T_c superconductors. Figure 3(a) shows hysteresis loops obtained for different concentrations of Fe, while Fig. 3(b) presents the dependence of the intragrain critical current density, j_c^G, calculated from the above mentioned loops for $H = 10$ kOe and $T = 4.2$ K. From this dependence one can see that for concentrations lower than 0.02, j_c^G increases with increasing amount of Fe atoms. Such behaviour is expected because with increasing number of defects the movement of the flux line lattice is more strongly impeded, and the doped superconductor is able to sustain a current which is greater than that for an undoped sample. However, in this case, the situation is not simple. Following Hiroi *et al.* [8], the average twin spacing decreases from 200 nm for $x = 0$ to 10–20 nm for $x = 0.02$.



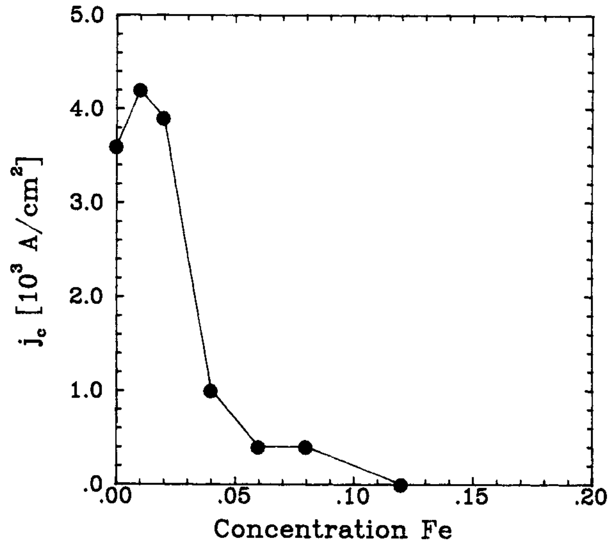


Fig. 3. (a) Hysteresis loops of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ at $T = 4.2$ K, for $x = 0, 0.01, 0.04$ and 0.12, and (b) intragrain critical current density, j_c^G, as a function of x.

If, according to Chaudhari *et al.* [12], the twin boundaries are strong pinning centers for flux lines, one should observe rather the linear correlation between twin spacing and j_c^G but, as can be noticed from our measurements, it was not established – the twin spacing increases 10 times, whereas the critical current density is only 20% greater for $x = 0.02$ in comparison with $x = 0$. One should take into account that the effect of increasing j_c^G may be depressed because of the existence of iron impurities, acting as Cooper pair breakers. However, other intragrain critical parameters, T_c^G and H_{c1}^G, are only slightly degraded in the concentration regime $0.0 \leqslant x \leqslant 0.02$. Thus, one can draw the following conclusion: twin boundaries may play a minor though detectable role in flux lines pinning in $YBa_2Cu_3O_{7-\delta}$. This explanation would be consistent with the results of Dinger *et al.* [21], who studied the dependence of critical current density upon twin spacing in single crystals of $YBa_2Cu_3O_{7-\delta}$. For concentrations higher than $x \geqslant 0.04$, j_c^G drops significantly, and this fact seems to be caused by the microdomain structure, which probably depresses the critical current inside the grains. Another interesting effect observed in these samples for $x = 0.10$ and 0.12 is the coexistence of independent superconductivity and paramagnetism [see insert in Fig. 3(a)].

3.2. *Intergrain properties*

Recently critical Josephson currents between single grains in $YBa_2Cu_3O_{7-\delta}$ thin films were measured by Mannhart *et al.* [22]. Strong Fraunhofer diffraction-like dependence of the critical current, $j_c^J(H)$, and similarity of the temperature dependence of the zero field critical current [22] to the Ambegaokar–Baratoff [28] formula strongly suggests that there are insulating barriers between grains. In spite of the attainable intragranular current densities of the order of 10^7 A/cm^2, the real transport currents are depressed 3 to 4 orders of magnitude by the existence of weak links between the grains.

The dependence of $H_{c1}^J(T)$ for a few chosen concentrations of Fe in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ is shown in Fig. 4. In analogy to H_{c1}^G, H_{c1}^J was determined from the isothermal low-field magnetization curves as the point at which the deviation from the initial linearity begins [see Fig. 5(a)]. One can notice a gradual degradation also of this critical parameter with increasing concentration of iron.

In order to estimate the intergranular current densities, $j_c^J(H)$, in samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$, d.c. as well as a.c. methods have been utilized. In the d.c. method, by registering hysteresis loops in a magnetic field below H_{c1}^G [a sample of such a loop is shown in Fig. 5(a)], it is possible to estimate $j_c^J(H)$ in the following manner: $j_c^J(H)$ is determined by deconvoluting the intergrain contribution to the M'–H curve from the real M–H curve using expression [23]:

$$M' = (M - \chi H)/(1 - 4\pi\chi), \quad (2)$$

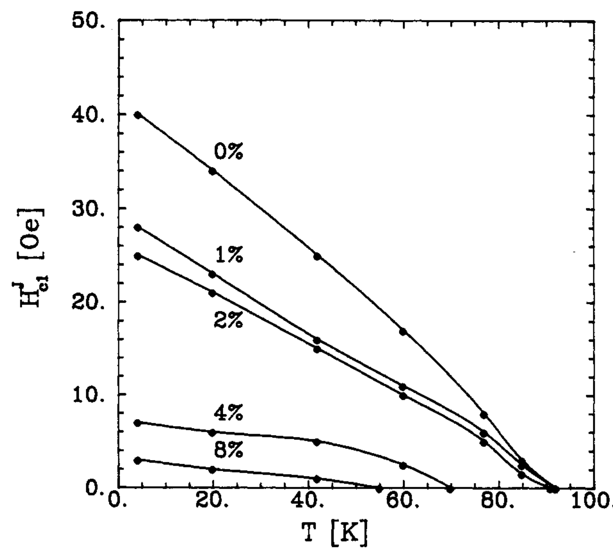


Fig. 4. H_{c1}^J of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ as a function of temperature for $0 \leqslant x \leqslant 0.08$.

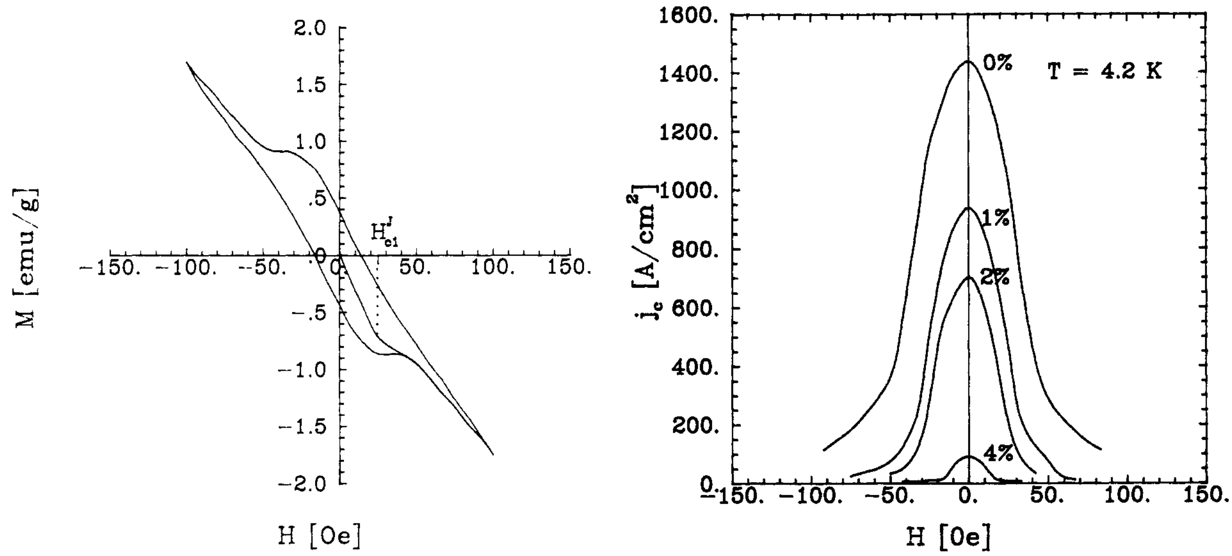


Fig. 5. (a) A typical low field hysteresis loop and (b) intergranular critical current density, j_c^J, of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ as a function of magnetic field for $0 \leqslant x \leqslant 0.04$.

where M' denotes magnetization connected only with intergrain volume, M represents total magnetization of the whole sample, χ is the susceptibility of the grains (usually $\chi = -0.68/4\pi$), and H denotes magnetic field. The M'–H curve thus obtained from the low field M–H loop was similar to the intragrain one [see Fig. 3(a)]. From the M'–H loop we estimate $j_c^J(H)$ using the formula of Fietz and Webb [eq. (1)]. The dependencies of $j_c^J(H)$, estimated in this way, are shown in Fig. 5(b). One can notice that these dependencies are qualitatively (in shape) the same as the dependencies of $j_c^J(H)$, for an array of disordered Josephson junctions [15] (thus the Fraunhofer diffraction-like dependence is "smeared out").

We have also used a.c. susceptibility measurements to investigate the intergrain properties of the $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ samples. The results of $\chi'(T)$ and $\chi''(T)$ ($\chi_{a.c.} = \chi' - j\chi''$) dependencies, obtained in a measuring frequency of 7 kHz with the a.c. field amplitude $H_{a.c.} = 0.25$ Oe, are shown in Fig. 6. According to the Bean's critical state model [25], the maximum in the $\chi''(T)$ dependence occurs at a well defined temperature, in which the a.c. field penetrates into the exact, geometrical center of the long, cylindrical specimen [24–26], and the Josephson critical supercurrent at this temperature is given by the following:

$$j_c = \frac{10}{4\pi} H_{a.c.}/R, \quad (3)$$

where j_c is in [A/cm²], $H_{a.c.}$ in [Oe], and the radius of the sample, R, is in [cm]. Since the temperature, at which the maximum of $\chi''(T)$ appears, depends upon the a.c. field amplitude $H_{a.c.}$, one may obtain the dependence $j_c^J(T)$ by applying different amplitudes $H_{a.c.}$.

The temperature dependence of $j_c^J(T)$ for $x = 0.01$, close to T_c, is shown in Fig. 7 (left-hand scale). This dependence was obtained by registering $\chi''(T)$ curves for different amplitudes, $H_{a.c.}$. The $j_c^J(T)$ dependence is quite linear at

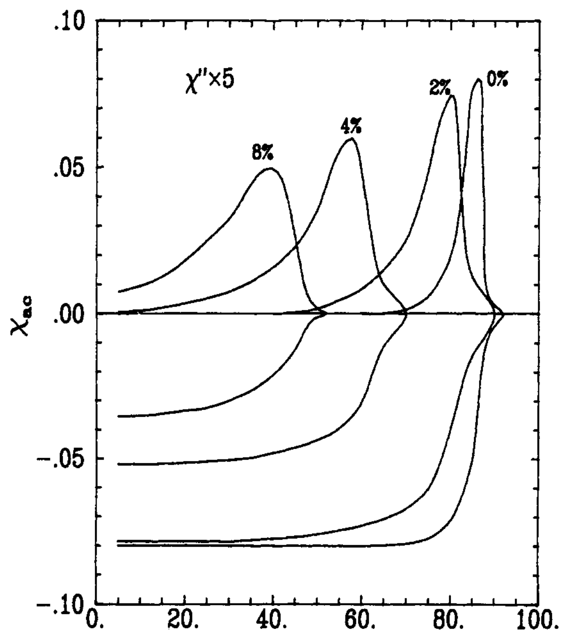


Fig. 6. Temperature dependence of the real and imaginary parts of complex susceptibility of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ for $x = 0, 0.02, 0.04$ and 0.08.

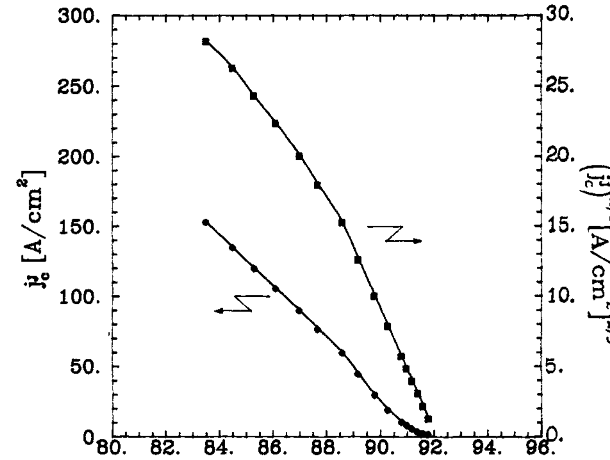


Fig. 7. Temperature dependence of j_c^J determined from χ'' peaks (left-hand scale) and plot of $(j_c^J)^{2/3}$ (right-hand scale).

Table I. *Superconducting transition temperature T_c, crossover temperature T_x, and intergrain critical current density j_c^J at $T = 0$ K, for various iron concentrations*

Concentration	T_c [K]	T_x [K]	j_c^J ($T = 0$) [A/cm^2]
0.00	92.0	90.2	880
0.01	92.0	88.0	650
0.02	91.5	86.5	510
0.04	70.0	64.5	115
0.06	60.2	55.6	90
0.08	55.3	46.5	40
0.10	40.1	≈25	15 ± 5

temperatures lower than $T \approx 88$ K, and such a behaviour is consistent with the Ambegaokar-Baratoff theory of the critical Josephson current close to the superconducting transition temperature. The deviation from linearity in the vicinity of T_c may be connected with the suppression of the order parameter inside grains in the Ginzburg–Landau region, where the correlation length, ξ, between electrons forming Cooper pairs becomes larger than the average distance between grains [24, 27]. In the Ginzburg–Landau region, the temperature dependence of the critical current should be of the following type:

$$j_c \propto (T_J - T)^{3/2}, \quad (4)$$

where T_J is connected with the occurence of the Josephson-type superconductivity [15, 24]. A plot of $[j_c^J(T)]^{2/3}$ is shown also in Fig. 7 (right-hand scale), and it is clearly seen that in the temperature range in which $j_c^J(T)$ is nonlinear, the dependence of $[j_c^J(T)]^{2/3}$ is linear. Hence, the crossover temperature, T_x, between these two regions can be determined and is listed in Table I for different x in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. By applying the Ambegaokar–Baratoff [28] formula to the temperature dependence of the critical current close to T_c (for linear part only),

$$\left.\frac{dj_c}{dT}\right|_{T=T_c} = -2.67 j_c(0)/T_c, \quad (5)$$

one can determine $j_c^J(0)$; the values of $j_c^J(0)$ obtained in this way are listed in Table I. However, the results of d.c. and a.c. measurements of intergrain currents allow only a qualitative comparison of the influence of iron on the transport properties of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$, because Bean's model only approximately applies in this case. More accurate values can be obtained from resistivity measurements.

On the basis of the results of intergrain critical parameter measurements, one can draw the following conclusions: the gradual degradation of critical field, $H_{c1}^J(T)$, and critical current, $j_c^J(T)$, with increasing concentration of iron is evident. This fact is in contrast to the case of intragrain current, $j_c^G(x)$, which is higher for $x = 0.01$ and 0.02, as compared with that at $x = 0$. The high resolution electron microscopy studies, even for pure $YBa_2Cu_3O_{7-\delta}$, identified various grain boundary phases [29]; among them were CuO, CuO_2, $BaCO_3$ and Y_2BaCuO_5. It is possible that in Fe-doped samples, a small number of impurity phases containing Fe locate in the vicinity of grain boundaries or between grains, acting in a destructive way on superconducting transport properties. These additional phases would go undetected by X-ray as well as neutron diffraction because of their variety and relatively small number. It has been already reported that to such impurity phases may belong Fe_2O_3 [30], $BaFeO_3$ [31], or $YBaCuFeO_5$ [32]. The increasing number of impurity phases between grains must, undoubtely, cause the degradation of intergrain critical parameters.

4. Conclusions

In summary, magnetic studies of intra- and intergrain critical parameters of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ were carried out for a series of samples with $0.0 \leqslant x \leqslant 0.12$. Concerning the intragrain properties, our results indicate that the twin boundaries are not effective pinning sites, because the significant increase of density of twins leads only to small enhancement of j_c^G. On the other hand, the gradual degradation of all intergrain parameters may be attributed to the increasing number of impurity phases containing iron. Since the intergrain critical current is limited by poor coupling of the grains, the increasing number of impurity phases located in the vicinity of grain boundaries decrease j_c^J.

Acknowledgment

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