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Effects of Cu substitution by Fe on the magnetic properties of $YBa_2Cu_3O_{7-y}$ single crystals

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We report magnetization measurements on single crystals in the system $YBa_2Cu_{3-x}Fe_xO_{7-y}$, with Fe concentration x up to 0.24. The relation between the superconducting properties and twin boundaries is discussed. Our results indicate that a model of higher-T_c regions in the twin boundaries seems incorrect. An anti-Meissner effect and crossover in the low-temperature inductive J_c measurements are observed, which indicate a possible pinning mechanism due to twin boundaries. A positive curvature to the H_{c1}-versus-temperature data suggests a strong temperature dependence of the Ginzburg-Landau parameters. No single pinning mechanism is dominant over the entire temperature and magnetic-field range in these oxide superconductors.

INTRODUCTION

Since the discovery of high-T_c superconductors,[1–3] a number of studies have concentrated on the mechanism of the superconductivity.[4] In $YBa_2Cu_3O_{7-y}$ and related systems, one of the most surprising results is the ability to substitute yttrium by other trivalent rare-earth elements with little effect on T_c. Specifically, superconductivity is not strongly affected by the large localized magnetic moments at the rare-earth sites.[5,6] Understanding of this insensitivity to the localized magnetic moments is based on the argument that the electrons responsible for the superconductivity are predominantly in the CuO planes. Hence, the exchange coupling between the conduction electrons and the rare-earth ions is weak. Secondly, superconductivity is sensitive to oxygen content in high-T_c superconductors, which is believed to be strongly related to the valence state of Cu at Cu(1) sites (chain sites).[7,8] In other words, the superconductivity of oxide superconductors is more sensitive to changes in the CuO plane, such as the concentration of free carriers or the appearance of magnetic moments. Therefore, substantial effects are anticipated when Cu is replaced by various transition elements, such as Fe and Co, and Al,[9,10] which make this substitution.

According to results on polycrystalline $YBa_2Cu_{3-x}M_xO_{7-y}$ (M=Fe, Ni, Zn, Co, and Al, etc.) samples published by many research groups,[9,10] the introduction of these dopants causes the degradation of superconductivity. T_c decreases almost linearly with increasing x and the transition width increases slightly with increasing x.[9,10] However, there is an interesting feature in these transition-metal substitution systems; namely, high-resolution transmission-electron imaging indicates that the twin boundary separation decreases as the impurity composition increases.[11,12] The formation of twins in $YBa_2Cu_{3-x}O_{7-y}$ is associated with the structural phase transformation in order to lower the elastic energy of internal stress. A minor replacement of Cu by Fe (x=0.06) in $YBa_2Cu_3O_{7-y}$ results in a reduced twin boundary separation from 200 to 20 nm. Simultaneously, the twin boundary thickness doubles from 1 to 2 nm. Furthermore, the twinning planes disappear for $x>0.1$, because of the structural transformation from the orthorhombic phase to the tetragonal phase.[13] These observations can be explained consistently if the substitution of Fe occurs primarily on the Cu chain sites.

To our knowledge, the effect of twin boundaries on the physical properties of oxide superconductors is not yet completely clear. Definitive experimental work on single crystals is critical since a number of valuable theoretical models regarding twin boundaries are under discussion. Fang *et al.* proposed the possibility of higher T_c in twin boundaries than in the matrix.[14] Chaudhari and Kes also suggested that twin boundaries can act as strong pinning centers for vortex lines.[15] In order to have a better understanding the role of twin boundaries in high-T_c superconductors and to test these theoretic models, direct measurements on transition element substituted $YBa_2Cu_3O_{7-y}$ single crystals are presented. In this study, we emphasize the magnetization measurement on $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystals.

EXPERIMENTAL DETAILS

The high-quality single crystals used in our experiments were grown by a modified self-flux technique.[16,17] Measurements were performed on a piece of $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal with typical dimensions of 0.8 mm×0.6 mm×0.4 mm. The iron component x varies from 0 to 0.24. Energy-dispersive x-ray (EDX) analysis was used to confirm that the substitute Fe was dissolved into the $YBa_2Cu_3O_{7-y}$ phase and to quantitatively identify the iron compositions.

The low-field dc magnetization was measured using a commercial superconducting quantum interference device (SQUID) magnetometer[18] between 6 and 120 K. A small single crystal with the typical mass of 0.1 mg was fixed in place by GE 7031 varnish inside a capsule. In order to have the flux lines parallel to twin boundaries, the specimen was prepared so that the applied magnetic field was perpendicular to the Cu-O plane. The gluing step is required to maintain proper orientation of the crystal with respect to the applied field. We obtained the shielding data by cooling the sample in zero field and then applying a low magnetic field of 5 Oe, followed by warming the specimen to the normal state. The perfect diamagnetism and extremely sharp transition indicate the sample quality is reliable. In our further discussion, we assume the variation of oxygen contents is very small in all of the single crystals. The degree of pinning can be determined from the zero-field-cooled (ZFC) Meissner effect and then verified by the remnant moment via the trapped flux effect. When the applied field is turned off, the shielding current disappears and only the trapped flux remains. If the flux lines are intrinsically pinned, the difference between the remnant moment and Meissner moment should be equal to the shielding moment, i.e.,

$$-M_{\mathrm{ZFC}}=M_{\mathrm{rem}}-M_{\mathrm{FC}} .$$

The inductive critical current density J_c is obtained through the hysteresis-loop measurement with magnetic fields between -5 and 5 Tesla. For the magnetic field aligned along the c axis, J_c is derived by using the Beam critical-state formula

$$J_c=20(M_+-M_-)/[b(1-b/3a)] .$$

Here, a is the larger dimension and b is the smaller dimension of the single-crystal plane. M_+ and M_- are the magnetizations for increasing and decreasing fields, respectively.

The lower critical field is determined by using a least-squares method to fit the magnetization data in the region around zero field to the expression

$$M=-H_a/[4\pi(1-D)] ,$$

where M is the volume magnetization, H_a is the external applied field, and D is the demagnetization factor. The magnetic field at which the magnetization starts to deviate from the fitting is defined the lower critical field H_{c1}.

EXPERIMENTAL RESULTS AND DISCUSSION

Our results show that the superconductivity is strongly dependent on the iron composition. The transition temperature drops approximately 40 K as x increases from zero to 0.24 and the 10–90 % inductive transition width broadens as the iron concentration increases (see Table I). Figure 1 displays the shielding effect in different iron composition single crystals with the magnetic field perpendicular to the Cu-O plane. The demagnetization factor (D) is strongly dependent on the shape of the sample and the relative orientation between the sample and the magnetic field. In our case, the values of D ranges from 0.84 to 0.90 for various kinds of shapes with the field applied perpendicular to the Cu-O plane. With the correction of the demagnetization factor, we found nearly perfect diamagnetism (>95%) in all of our iron-doped $YBa_2Cu_3O_{7-y}$ single crystals. There is a small diamagnetization near the onset temperature of superconductivity which extends over about 10 K, in particular, for high-iron-composition specimens. We are not sure at the current stage of research that this phenomenon is an intrinsic property of iron-doped $YBa_2Cu_3O_{7-y}$ or that it is due to the inhomogeneities.

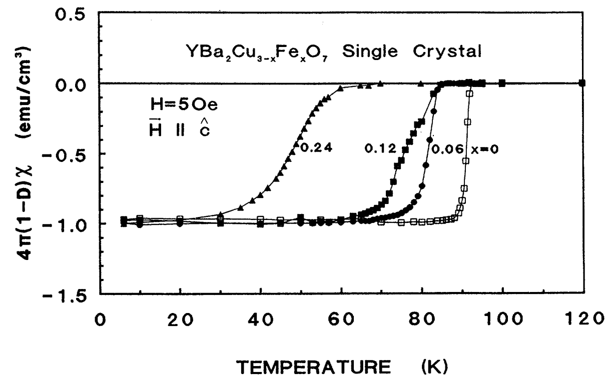

FIG. 1. Shield effect in $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal.

The most interesting result in our magnetic response is the anti-Meissner effect found in some selected low-iron-composition samples. In the field-cooled (FC) situation, the single crystal is cooled from the normal state to the superconducting state under the same applied field (5 Oe). As shown in Fig. 2, the Meissner effect is 25% of the shielding signal in the pure $YBa_2Cu_3O_{7-y}$ specimen. With the field off at low temperatures, the remnant moment is equal to the difference between the shielding effect and the Meissner effect data. This result indicates that the pinning centers are inside the single crystal and superconductivity is a bulk property in our specimen. When the same situation is applied in the low-iron-composition samples, $x=0.06$ (Fig. 3) and 0.12, we obtain

TABLE I. Inductive transition temperature and width of $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal. Also shown are the demagnetization factor (D) of each specimen for the field aligned along the c axis.

x	T_c (onset)	T_c (50%)	T_c (10%)	T_c (90%)	dT_c	D
0	92.7	91.2	92.2	89.6	2.6	0.86
0.06	87.2	82.1	84.1	75.7	8.4	0.87
0.12	86.1	76.0	82.8	68.2	14.6	0.84
0.24	70.0	48.3	57.7	35.5	22.2	0.90

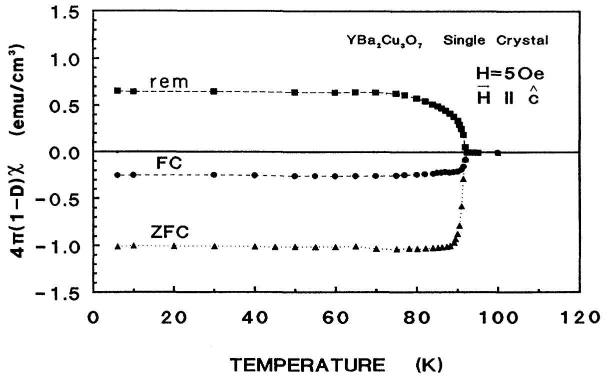

FIG. 2. Magnetic response in $YBa_2Cu_3O_{7-y}$ single crystal.

a negative Meissner to shielding ratio and an almost 100% remnant effect. This observation is reproducible and completely beyond our prior experience. In Table II, we list the ratios of the Meissner effect and the remnant effect to the shielding effect in different iron-doped $YBa_2Cu_3O_7$ single crystals. The anti-Meissner phenomenon, which is reproducible and field dependent, is correlated with the density of twin boundaries in our selected samples used in this report. Nevertheless, this phenomenon cannot be directly attributed to the twin boundaries. In investigations with various shapes of $YBa_2Cu_{3-x}Fe_xO_7$ single crystals, we found that the anti-Meissner effect does not occur in all low-iron-composition samples. Similar effects were also reported by other research groups in the Bi-Sr-Ca-Cu-O system[19] and La_2CuO_4-related systems which do not have any twinning. Therefore, this anti-Meissner effect must be related to some other effects, for example, the shape of the sample, various pinning mechanisms, vortex pair fluctuations,[19] or magnetic relaxation. At this stage, we cannot confirm the actual mechanism responsible for this phenomenon. Clearly, additional experimental research is required in order to determine the origins of the anti-Meissner effect.

TABLE II. Meissner ratio and remanent ratio of $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal (at $T=6$ K).

x	M_{FC}/M_{ZFC} (%)	M_{rem}/M_{ZFC} (%)
0	25	65
0.06	−10	100
0.12	−8	90
0.24	10	80

The critical current density basically decreases with increasing iron composition. As shown in Fig. 4, J_c gradually drops from 1.5×10^6 to 1.8×10^5 A/cm^2 with increasing x for $T=10$ K. The strong suppression of J_c in iron-doped $YBa_2Cu_3O_{7-y}$ systems occur for $T>10$ K. With the superconducting properties strongly dependent on the carrier concentration and the presence of local magnetic moments in the CuO plane. This suppression of J_c is understandable. However, a crossover occurs at $H=2$ Tesla for $T=5$ K. In Fig. 5, one observes that J_c in the $x=0.06$ sample is about 20% less than for the pure $YBa_2Cu_3O_{7-y}$ in low magnetic fields, but the reduced field dependence of J_c in low-iron-composition crystals yields higher J_c values than in pure $YBa_2Cu_3O_{7-y}$ in this high-magnetic-field range. In the low-temperature range, the uncertainty in the J_c measurement due to flux creep is small. With a conservative estimate, this experimental uncertainty is less than 5%.

We find that the lower critical field also has a strong dependence on iron composition. H_{c1} is corrected with the demagnetization factor drop from 2.86 to 0.5 kOe as x increases to 0.24 at $T=5$ K. The temperature dependence of H_{c1} in $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystals is illustrated in Fig. 6. Unlike conventional superconductors, we find that the temperature dependence of H_{c1} has a positive curvature over the entire temperature range. These upward curvatures were found by many research groups in direct critical-field measurements.[20,21] Our data of H_{c1} for $x=0$ and the field along the c axis are

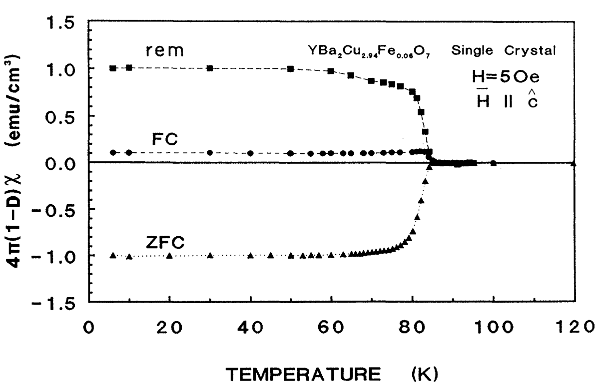

FIG. 3. Magnetic response in $YBa_2Cu_{2.94}Fe_{0.06}O_{7-y}$ single crystal.

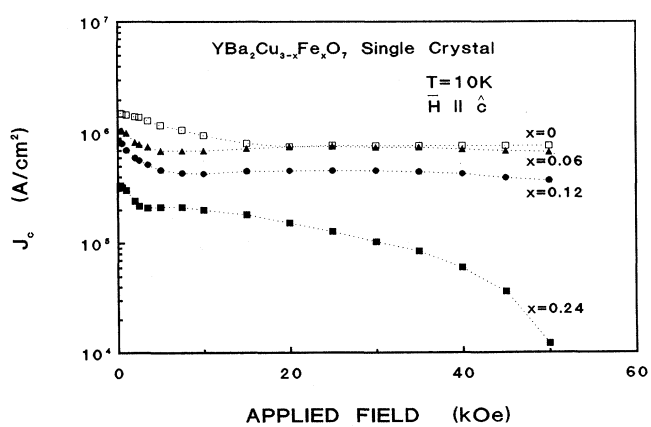

FIG. 4. Field dependence of critical current density in $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal at $T=10$ K.

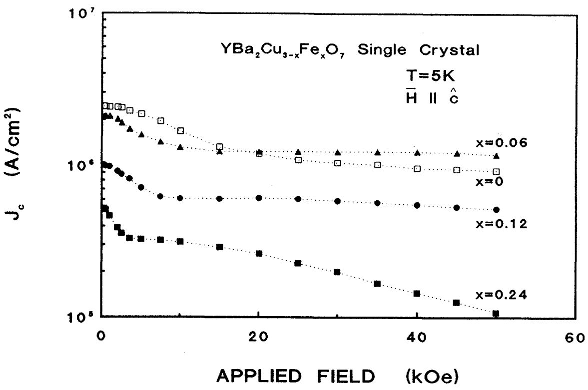

FIG. 5. Field dependence of critical current density in $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal at $T=5$ K.

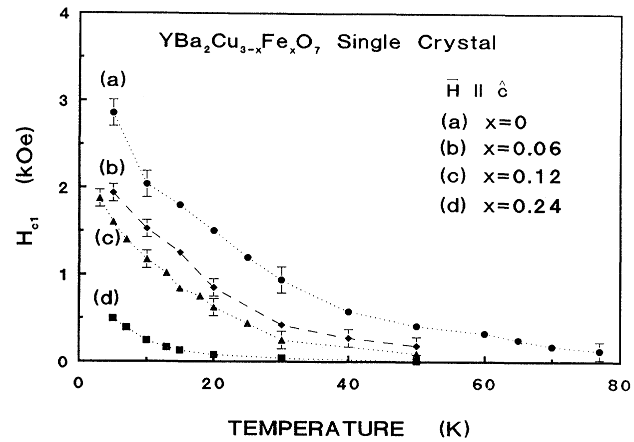

FIG. 6. Temperature dependence of lower critical field in $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal.

quite consistent with the values published by Krusin-Elbaum *et al.*[22] for the temperature range higher than 35 K. In the low-temperature region, our data show a much stronger temperature dependence in comparison with the BCS prediction. In addition, a straight application of the Ginzburg-Landau relation, which is valid at all temperatures in the dirty limit, can be used;[23–25] namely,

$$H_{c2}=(2\kappa^2/\ln\kappa)H_{c1} ,$$

where κ is the ratio of the penetration depth to the coherence length. However, this argument ignores any temperature dependence for κ and ignores paramagnetic limiting arising from the spins of the conduction electrons. The twin boundaries might also limit the spatial extent of the vortices; therefore, the upper critical field of the Ginzburg-Landau expression has to be modified by $H_{c2}\propto\phi_0/(\xi\cdot s)$, where ϕ_0 is the flux quantum, s is the spacing between the twin planes, and ξ is the superconducting coherence length.[26] Through either relation, the upper critical field has the similar curvature in the H_{c2} versus T graph as found in $H_{c1}(T)$. The coherence length derived from the upper critical fields is expected to be strongly temperature dependent, even for the temperature much less than the critical temperature. In Kes and van den Bergs' paper,[27] they point out that crystal defects which include twin boundaries give rise to local inhomogeneities which then couple to the normal vortex cores. That core interaction is the major mechanism of flux pinning in $YBa_2Cu_3O_{7-y}$ and related systems. Moreover, the most effective pinning occurs when the defect size is the same order as the coherence length. Due to the increasing twin thickness and strong temperature dependence of the coherence length in the low-iron-composition specimens, the crossover observed in the low-temperature J_c measurement is believed to be caused by the match of the twin thickness and coherence length.

The other possible pinning centers in a $YBa_2Cu_{3-x}Fe_xO_{7-y}$ single crystal include impurity phases, dislocation, growth-flux inclusions, or oxygen-vacancy clusters. From our limited measurements, we cannot tell which defect is dominant in various temperature and field ranges. However, twin boundaries seem to play an important role in the pinning process, at least in the low-temperature range, in the low-iron-composition $YBa_2Cu_{3-x}Fe_xO_{7-y}$ systems. This conclusion may not be valid for the pure $YBa_2Cu_3O_{7-y}$ system because the thickness of the twin boundary does not match the coherence length. Liu *et al.* measured the magnetic crystal current density before and after detwinning.[28] In the case of the applied magnetic field parallel to the c axis, their results suggest that twin boundaries are not the primary pinning centers responsible for high J_c at 6 K in the pure $YBa_2Cu_3O_{7-y}$ single crystal. The various types of macroscopic defects must play different role of pinning centers in different temperature and field ranges. Clearly the pinning mechanism is more complicated in high-T_c superconductors because of the strong temperature dependence of Ginzburg-Landau parameters.

CONCLUSION

In conclusion, we have studied the magnetic properties of iron-doped $YBa_2Cu_3O_{7-y}$ single crystals. The superconducting properties, such as transition temperature, transition width, lower critical field, and critical current density, are suppressed as the iron composition increases. The suggestion of stimulated superconductivity in twin boundaries seems incorrect. The field-dependent anti-Meissner effect observed might indicate some dynamic flux pinning. The crossover of the critical current density at low temperature occurs in low-iron-composition samples, suggesting that flux lines can be pinned effectively by twin boundaries. Due to the characteristics of short coherence length in oxide superconductors, the superconducting behavior shows great sensitivity to crystal disorders. The defect size relative to the coherence length is a very important factor in determining the pinning mechanism. From our critical-field measurements, the positive curvature of H_{c1} versus temperature indicates the

Ginzburg-Landau parameters, such as coherence length and penetration depth, are strongly temperature dependent in the low-temperature region. Therefore, we conclude that no single mechanism can dominate the flux-pinning effect in the whole superconducting range.

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