Low-field ac-susceptibility study of flux creep in metal-substituted $ErBa_2Cu_3O_{7-\delta}$

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Low-field ac-susceptibility studies of pure $ErBa_2Cu_3O_{7-\delta}$ and substituted samples of $ErBa_2(Cu_{0.995}M_{0.005})_3O_{7-\delta}$ (M=Fe, Co, Ni, Ga) have been carried out in the frequency range up to 1 kHz. The activation energy for flux creep in the case of the doped samples is considerably lower than that for the undoped sample. The analysis of the results within the framework of Müller's model [Physica C **159**, 717 (1989); **168**, 585 (1990)] shows that the intergrain critical current density gets considerably suppressed by the dopants. Employing a *SIS* junction model it is argued that this can be attributed to the reduction in the Fermi energy of the system due to the localization caused by the presence of the dopant atoms.

I. INTRODUCTION

The phenomenon of flux creep has received much attention in the case of high-T_c oxide superconductors. In these materials, the grain boundaries are weak links in which the flux can creep at a relatively lower field than in the grains. Moreover, because of the higher operating temperatures of the oxide superconductors, the thermal activation responsible for creep is easier in these materials. There have been several studies of flux creep in $YBa_2Cu_3O_{7-\delta}$, the so-called Y-123 system, in single crystal as well as bulk polycrystalline samples, and the activation energy for flux creep has been estimated by techniques such as dc magnetization, ac susceptibility, resistivity under applied field, etc.[1–11] The reported values of the activation energy vary widely depending upon the measurement technique and the microstructural features of the sample. It has been further found that some dopants like Fe, substituted in relatively low concentrations for Cu, aid flux pinning in the Y-123 system.[5]

ac susceptibility has been used to determine the flux creep activation energies in the Y-123 system.[1,9] A critical state model to determine the temperature and the ac field amplitude dependence of the complex susceptibility $\chi=\chi'-i\chi''$ in the case of granular superconductors was proposed by Müller.[12] In a further extension of the model by Müller[13] which incorporated Anderson's flux creep theory[14] it was possible to explain the observed increase of T_p, the temperature corresponding to the χ'' peak, with the frequency of the ac field.

It was further predicted that, for suitably higher magnetic fields, the smaller the grain size of the sample, the easier is the flux creep and stronger is the frequency dependence of T_p, which has also been confirmed experimentally.[9]

In this paper, we present the results of the frequency dependence of ac susceptibility studied in the range up to 1 kHz in pure Er-123 and also in the Fe, Co, Ni, and Ga substituted samples of $ErBa_2(Cu_{0.995}M_{0.005})_3O_{7-\delta}$ (M=Fe,Co,Ni,Ga). We have carried out these studies at an applied ac field amplitude (H_a) of 8 A/m. As will be discussed later, the main purpose of using a low field is that under this condition the activation energy for flux creep depends primarily on $I_0(0)$, the maximum intergrain current density at zero temperature or equivalently on the zero-temperature pinning potential of the sample. Consequently, we expect that there would be no significant effect due to other factors like the grain size, the penetration depth, T_p, etc. Thus the low-field frequency dependent ac-susceptibility study should provide a direct approach to probe the behavior of $I_0(0)$ of the sample which is a useful parameter required also for future studies involving high ac fields.

II. EXPERIMENT

Pure $ErBa_2Cu_3O_{7-\delta}$ (Er-123) and the doped samples $ErBa_2(Cu_{0.995}M_{0.005})_3O_{7-\delta}$ (M=Fe,Co,Ni,Ga) were prepared by the solid-state reaction route. Stoichiometric amounts of the metal oxides and carborates were mixed thoroughly within a mortar and pestle and compacted into circular pellets using a hydraulic press. The pellets were calcined at a temperature of 910 °C for a total period of 24 h with intermediate grinding and finally they were sintered in flowing oxygen for 24 h at 935 °C and 8 h at 600 °C followed by cooling to room temperature. Slab shaped samples (the dimensions of which are given in Table I) were cut from the circular pellets. These samples were characterized by resistivity vs temperature measurements employing a four-probe technique where the measuring system was hooked up to an IBM PC/AT system for automatic data control and acquisition. From the extrapolation of the normal parts of the R-T curves, the residual resistivities $\rho_0(0)$ of the samples at zero temperature were estimated. For the pure Er-123 sample $\rho_0(0)$ was found to be 0.05 m Ω cm. This is subtracted from the $T=0$ (observed) resistivities of the doped samples to get the contribution of the impurity [$\rho_{\rm imp}(0)$] to the residual resistivities of these samples. The single phase nature of the materials was confirmed by the powder x-ray diffraction patterns of the samples which were obtained using Siemens D-500 x-ray diffractometer.

The ac-susceptibility measurements were made using

TABLE I. The dimensions, densities, T_c values, grain sizes, residual resistivity, and the estimated values of E_a (the activation energy for flux creep) for the pure Er-123 and 0.5 at. % Fe, Co, Ni, Ga (in place of Cu) substituted Er-123 samples.

Dopant	Sample dimensions (mm s)	Estimated density (g m s/cc)	T_c zero resistance (K)	T_c diamagnetic onset (K)	Grain size (μm)	Residual resistivity $\rho_{imp}(0)$ (mΩ cm)	Estimated values of E_a (eV)
Pure Er-123	12×2×2	4.6	92.8	92.5	2.2		10.00
Fe	10×2.5×1.5	5.0	88.5	88.7	2.0	0.55	3.77
Ni	6×2×1	4.6	89.1	89.0	2.6	0.31	8.50
Co	7×2.9×1.5	4.9	89.9	89.8	2.1	0.36	4.80
Ga	8×3×2	5.0	89.8	89.5	2.1	0.43	4.80

Lakeshore AC Susceptometer Model 7000. The samples were placed tightly in the sample holder and the ac field was applied parallel to the longest dimension of the samples. The measurements were made in the temperature range 65–100 K at ac field frequencies of 33.3, 333.3, and 1000 Hz, at a constant applied field of 8 A/m. The data were recorded at the intervals of 0.5 K. From the sample volume and the proper demagnetization factors taken from the instrument manual, absolute values of χ' and χ'' were calculated using the software provided with the instrument. The data points were fit with smooth curves to get the χ'' vs T plots from which T_p values were estimated.

The micrographs of the samples were obtained using a scanning electron microscope, model JOEL JSM 35 CF, from which grain sizes were estimated, which are listed in Table I. The densities of the samples, calculated on the basis of their weights and careful measurements of their sizes, are also listed in Table I.

III. RESULTS AND DISCUSSION

From the x-ray-diffraction patterns, it is found that all the samples $ErBa_2(Cu_{0.995}M_{0.005})_3O_{7-\delta}$ (M=Fe,Co, Ni,Ga) are of single phase with the Y-123 crystal structure. Owing to the low concentration of the dopants, there is no significant change in the lattice parameter values of the substituted samples when compared to those of the pure sample. Superconducting critical temperature T_c is, however, noticeably affected by doping.

The T_c values of the samples as determined by resistivity (ρ=0) and ac susceptibility (diamagnetic onset) measurements are listed in Table I. There is a good agreement between the T_c values determined by these two techniques. It is also seen that the T_c depression is maximum in the case of Fe substitution and minimum for Co and Ga substitutions. The T_c depression brought about by Ni doping lies between the above two values.

The variation of χ' and χ'' with temperature for the ac field frequencies 33.3, 333.3, and 1000 Hz for the above samples was recorded as mentioned earlier. The small applied ac field (8 A/m) resulted in small shifts of the susceptibility curves over this range of frequencies.

Nikolo and Goldfarb[1] defined the activation energy for flux creep (E_a) in terms of the frequency f of the ac field and the χ'' peak temperature T_p. The expression for E_a is

$$f = f_0 \exp\left[-\frac{E_a}{k_B T_p}\right], \tag{1}$$

where k_B is Boltzmann's constant and f_0 is a constant with the dimensions of frequency. E_a can be determined by the slope of the $1/T_p$ vs $\log_{10} f$ plots, which are straight lines, shown in Fig. 1.

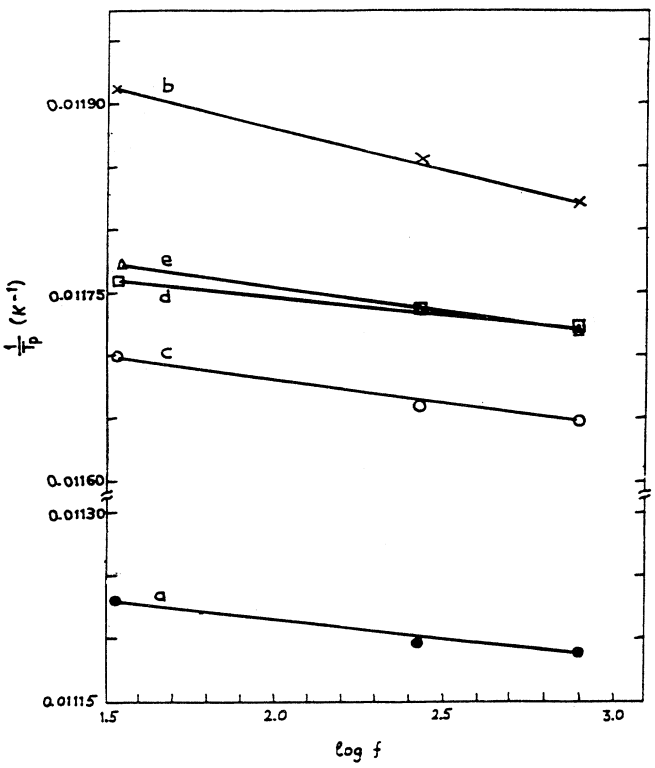

FIG. 1. Plots of $1/T_p$ vs $\log_{10} f$ (T_p is the χ'' peak temperature and f is the frequency of the applied ac field) at the ac field amplitude 8 A/m for the pure Er-123 and doped Er-123 samples. The notations (a)–(e) refer to the samples in the following manner: (a) Pure Er-123, (b) Fe doped, (c) Co doped, (d) Ni doped, and (e) Ga doped.

The values of E_a for different samples estimated by using Eq. (1) and Fig. 1 are listed in Table I. In the case of the undoped Er-123 sample the value of E_a is 10 eV which is comparable to the value obtained by Nikolo and Goldfarb for the Y-123 sample at a similar ac field amplitude.[1]

In the case of Fe, Co, Ni, and Ga substituted samples, the values of E_a are 3.7, 4.8, 8.5, and 4.8 eV, respectively, which are distinctly lower than the value for the undoped sample. In the case of Fe doped Y-123, a value of E_a close to that of a pure sample has been reported.[5] However, possibly the sample concerned had a high level of Fe content (5 at. %), leading to microstructural features like voids and normal regions which might help in flux pinning and raise the value of the activation energy for flux creep. Also, it has been found that,[15] when synthesized under special heat-treatment conditions such as annealing in N_2 gas, Y-123 samples with more than 2 at. % Fe contain clusters of Fe atoms which act as flux pinning centers. On the other hand, the scanning electron microscopy (SEM) picture of our Fe substituted Er-123 sample does not reveal any special microstructural features. This is expected in view of the low Fe content (0.5 at. %) of the sample and also due to the fact that the sample was not annealed in N_2 gas.

We shall now try to understand the results on the basis of Müller's model.[13] According to this model, the shift in T_p with ac field frequency indicates flux creep and T_p is implicitly given by the following expression:

$$-H_a+\left[\frac{a_pH_{op}}{b_p}\right]\ln\left[1+\frac{b_pH_a}{(b_p+a_p)H_{op}}\right]+\frac{b_pD}{2}=0\ . \tag{2}$$

Here the subscript p stands for χ'' peak. D is the sample thickness (or the diameter in the case of the cylindrical sample) and

$$a_p=\frac{\beta I_0(T_p)}{4\pi\bar{R}_g^2}\ , \tag{3}$$

$$b_p=\left[\frac{k_BT_p}{2\bar{R}_g^2\phi_0}\right]\ln\left[\frac{f}{f_0}\right]\ , \tag{4}$$

$$H_{op}=\frac{\phi_0}{4\mu_0\lambda(T_p)\bar{R}_g}\ . \tag{5}$$

In Eqs. (3)–(5) the parameters β, $I_0(T_p)$, $\bar{R}_g$, ϕ_0, μ_0, and $\lambda(T_p)$ have the following meanings. β is less than 1 and accounts for the effect of inhomogeneities in the complicated weak link network, $I_0(T_p)$ is the maximum Josephson-junction current at zero magnetic field at temperature T_p, $\bar{R}_g$ is the average grain size of the sample, ϕ_0 is the flux quantum, μ_0 is free space permeability, and $\lambda(T_p)$ is the London penetration depth at temperature T_p of the samples considered here.

The parameter b_p in Eq. (4) specifies the flux creep effect and relates the value of T_p with the frequency f of the ac field. The Josephson current $I_0(T_p)$ depends on the nature of the junction, i.e., whether it is of *SIS* type or *SNS* type. Müller[13] found that *SIS* junctions, which follow $I_0(T)=I_0(0)[1-T/T_c]$, provide a more suitable representation of the T dependence of $I_0(T)$; in the present analysis we employ this relation. In Eq. (5), the parameter $\lambda(T_p)$ also depends upon temperature, given by the relation[13]

$$\lambda(T_p)=\bar{\lambda}(0)\left[1-\left[\frac{T_p}{T_c}\right]^4\right]^{-1/2}\ . \tag{6}$$

Using Eqs. (5) and (6), H_{op} may be expressed by

$$H_{op}=\frac{\phi_0}{4\mu_0\bar{R}_g\bar{\lambda}(0)}\left[1-\left[\frac{T_p}{T_c}\right]^4\right]^{1/2}\ . \tag{7}$$

For the pure Y-123 sample,[13] $\bar{\lambda}(0)=5000$ Å.[13] The grain size of the pure Er-123 sample used in our studies is found by SEM to be 2.2×10^4 Å (Table I). Using $T_p=89.3$ K and $T_c=92.8$ K (Table I) and Eq. (7), we obtain $H_{op}=156$ A/m. This implies that, for the pure system, $H_a\ll H_{op}$ (since $H_a=8$ A/m).

For the doped samples, $\bar{\lambda}(0)$ is not expected to be enhanced significantly because the dopant concentration (Fe,Co,Ni,Ga) is only 0.5 at. %. The grain size of the doped samples shows that $\bar{R}_g$ in this case is not much different from that of the undoped sample (the variation in $\bar{R}_g$ is within a factor of 1.2; see Table I). Moreover, numerical calculations show that the relative magnitude of H_{op} cannot be very sensitive to the T_p values unless T_p differs from T_c by less than about 6 mK. This is certainly not the case in the present observations. Thus, on the basis of $\bar{\lambda}(0)$, $\bar{R}_g$, and T_p/T_c, we do not expect much change in H_{op}. So, for the doped samples also we expect $H_{op}\gg H_a$. Therefore, only the first term in the series expansion of the logarithmic function in Eq. (2) will be significant. Equation (2) is simplified to

$$-H_a+\frac{a_pH_a}{b_p+a_p}+\frac{b_pD}{2}=0\ . \tag{8}$$

Solving this equation for b_p, and using Eq. (1), we obtain

$$E_a=\frac{\beta I_0(0)\phi_0}{2\pi}-\frac{4H_a\bar{R}_g^2\phi_0}{D}\ . \tag{9}$$

Here the first and the second terms are of the order of 10 and 10^{-3} eV, respectively. This means that, at the ac fields of the order of 8 A/m used in the present investigation, the major effect on the activation energy E_a arises from the factor $\beta I_0(0)$, the maximum Josephson current at zero magnetic field at zero temperature, or equivalently, the pinning force density $\alpha_J(0)$, the zero-temperature pinning potential of the sample. Thus the activation energies obtained in the present investigations give an estimate of the changes in the zero-temperature pinning potential brought about by Fe, Co, Ni, and Ga substitutions (0.5 at. % at Cu site) in the Er-123 system with respect to the undoped sample. The zero-temperature intergranular pinning potential is reduced by a factor of 2.8, 2.1, 1.2, and 2.1 by Fe, Co, Ni, and Ga substitutions, respectively.

Thus, in small applied fields, the main effect of the dopants Fe, Co, Ni, and Ga in the Er-123 system appears

to cause a reduction in the pinning potential, or the maximum intergrain current at zero temperature [$I_0(0)$]. We may examine now the reason for this decrease for the doped samples. Flux dynamics and pinning in high-T_c superconductors have been reviewed by Nikolo.[16] In these materials the microstructural features, such as grain boundaries, twin boundaries, inhomogeneities in composition, normal regions, voids, and cracks can act as effective pinning centers provided the size of these features is comparable to the coherence length; otherwise, they have a decoupling effect, whereby they serve as weak links. Our samples had been synthesized under identical processing conditions and do not show any noticeable variation in their microstructures. Of course, the densities of the samples (Table I) vary in the range 2–9 %. Though the bulk superconducting properties are dependent on the density of the sample,[17] the density variation in our samples is too small to give rise to any significant changes in the flux pinning characteristics, especially at low fields. Hence the decreased flux pinning and the lower values of the activation energy for flux creep in the doped samples has to be understood on the basis of the intrinsic effect of the dopants on the intergranular current and the pinning potential of the samples.

We now try to see how the considered dopants or impurities in the Er-123 system can bring about a decrease in $I_0(0)$. As mentioned earlier the grain boundaries in the present case seem to be of *SIS* type, for which the maximum supercurrent varies linearly with the transmission coefficient T_j. In fact,[18]

$$I_0(0)=\frac{eh}{m^*\xi_0}T_j\approx\frac{ek_BT_c}{m^*v_F}T_j\ , \tag{10}$$

where ξ_0, the coherence length at 0 K in the clean limit, is, in the first approximation, expressed in terms of the BCS value, given by $\xi_0=hv_F/k_BT_c$. Here v_F is the carrier velocity, e is the electronic charge, h is the Planck's constant, and m^* is the effective mass of the carrier hole. In Eq. (10), ξ_0 and T_j are affected by the dopants or the impurities. In the cuprate superconductors, ξ_0 increases with the impurity concentration[19] presumably because of ensuing decrease in T_c with doping.[20] Hence, according to Eq. (10), increase in ξ_0 causes $I_0(0)$ to decrease. But this decrease is small as ξ_0 is expected to increase by less than 10% for 0.5 at. % impurity concentration of the samples used in the present studies. Thus the major reason for the decrease of $I_0(0)$ in the case of doped samples is expected to be the decrease in the transmission coefficient T_j.

An expression for the transmission coefficient T_j can be obtained by treating the insulating part of the *SIS* junction as a square potential barrier of height G and width a. The required expression for T_j has been given by Landau and Lifshitz.[21] In this expression, we replace k_1^2 by $2m^*E_f$ and k_2^2 by $2m^*(E_f-G)$, where E_f is the Fermi energy. Thus the transmission coefficient may be written as

$$T_j=\left[1+\frac{G^2}{4E_f(E_f-G)}\sin^2(Aa\sqrt{E_f-G}\,)\right]^{-1}. \tag{11}$$

Here $A=2m^*/\hbar$ with $\hbar=h/2\pi$.

According to Eq. (11) the variation of T_j is governed by G, E_f, and a. For the Y-123 or Er-123 superconductor, $E_f\approx1$ eV while $G\approx k_BT_c\approx10$–50 meV. Numerical calculations suggest that T_j is not very sensitive to small variations in G; but small variations in a may lead to significant changes in T_j values.

From Eqs. (10) and (11), it follows that $I_0(0)$ is affected by the changes in the Fermi energy E_f of the system. Phenomenologically E_f decreases with the impurity concentration,[22] which can be understood as follows. When introduced into the pure Er-123 system, the impurities will start to bring about localization effects in the carrier states. The localized states will be separated from the extended states by the mobility edge E_c (Ref. 23). More clearly, the states lying within E_c from the top or bottom of the conduction band will correspond to the localized states and will not take part in conduction. Thus the carrier density will be reduced effectively with the introduction of impurities in the pure system. The Fermi energy E_f which increases with the increase in the carrier density will thus get reduced due to the presence of the dopants in the Er-123 system. This is in the general conformity with the resistivity behavior and in particular the residual resistivity data of the present samples (Table I).

According to Eq. (11), for decreasing E_f and for appropriate values of the barrier width a, T_j will decrease. The quantitative difference in the reduction of T_j or E_a for different (doped) samples is expected to be due to different changes in E_f and a by Fe, Co, Ni, and Ga doping.

IV. CONCLUSIONS

In conclusion, we have studied the frequency dependence, in the range up to 1 kHz, of the low-field ac susceptibility of pure Er-123 and 0.5 at. % Fe, Co, Ni, and Ga doped Er-123 samples. The dopants are found to significantly decrease the activation energy for flux creep in the system. Within the framework of Müller's model the main reason for this behavior turns out to be the suppression of the integrain critical current density. In a *SIS* boundary system, this can be attributed to the decrease of the Fermi energy E_f in the doped Er-123. The decrease of E_f is reasonably characterized in terms of the residual resistivity of the doped samples.

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