AC susceptibility harmonic response in YBCO single crystals with different oxygen contents

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Abstract

We measured up to the seventh harmonic response of the complex ac susceptibility ($\chi'' = j\chi''_{n}$; $n = 1–7$) vs. temperature, in YBCO single crystals with different oxygen contents ($6.5 \leq x \leq 7$). The ac field was applied in presence of an external dc field both parallel to the c-axis of the crystals. We show evidence that deoxygenation leads to a reduction of bulk pinning strength evidenced by a decrease in the value of the third, fifth and seventh harmonics. We compare our measurements with a numerical model that includes effects of flux creep and sample geometry where the activation barrier depends explicitly on temperature.

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1. Introduction

The complex ac susceptibility ($\chi = \chi' - j\chi''$) has been widely used to study the very rich vortex dynamics of high temperature superconductors in the mixed state. The imaginary component $\chi''$ of the fundamental ac susceptibility is a measure of the dissipation in the sample arising from vortex movement, while the real component $\chi'$ provides a measure of the screening of the impinging ac field into the sample [1].

High order harmonic susceptibilities are generated when the constitutive $E$–$j$ (electric field–current density) relationship is non-linear. The critical state model [2] accounts for the generation of high order harmonics but does not explain experimental observations where the peak heights of the harmonic susceptibilities strongly depend on ac field frequency [3]. Brandt [4] developed a numerical method to solve the non-linear diffusion-like equations which govern the spatial and temporal evolutions of the local magnetic field $B$, where the role of the flux diffusivity is played by the resistivity $\rho = E(J, T, B)/J(T, B)$ which is a function of the local current density ($J$), temperature ($T$) and the local magnetic field ($B$). This method includes magnetic relaxation and allows the calculation of the magnetic field and the current profiles in the sample, magnetic moment, hysteresis loops and ac...
susceptibility of superconductors with finite length in a perpendicular magnetic field [4]. Qin and Ong [5] have considered relaxation effects on higher order harmonics for a superconducting slab immersed in an ac magnetic field with a dc bias field, but the slab geometry is not appropriate to describe the widely used experimental arrays of a platelet sample in a magnetic field perpendicular to its surface.

Experimentally, the high order harmonics are used as a measure of the onset of irreversible magnetic behavior [6,7] and to test different aspects from theoretical models of the vortex dynamics [8–25].

In this work, the study of harmonic susceptibilities was applied to understand the phenomenological effect of oxygen doping in YBa$_2$Cu$_3$O$_{6+y}$ (YBCO) single crystals. It is well established that the oxygen content plays a significant role in the structure of YBCO single crystals [26,27]. Small variations in oxygen stoichiometry can change magnetic and transport properties of this compound. A reduction in the oxygen content has three major effects: first of all, there are changes in the density of current carriers which lead to a modification in the magnetic penetration depth and in the onset temperature of the superconducting transition ($T_c$), i.e. the temperature at which the sample begins to show a diamagnetic behavior [28]. Another effect is related to the anisotropy of the YBCO crystal, which can be controlled by the oxygen content. Oxygen doping changes the ratio of the effective masses $\gamma = (m_{ab}/m_c)^{-1/2} = (\xi_{ab}/\xi_c)$, where $\xi_{ab}$ and $\xi_c$ are the coherence lengths parallel and perpendicular to the Cu-O layers. As oxygen atoms are removed, $\xi_c$ decreases whereas $\xi_{ab}$ remains approximately constant, weakening the coupling between Cu–O layers, thereby driving the system more two dimensional [29–33]. The third effect is that as the oxygen atoms are removed the number of point defects (oxygen vacancies in the crystalline lattice) increases [34] and interestingly it has been recently shown that the overall deoxygenation effect is a reduction in the strength of bulk pinning [19,33–36].

In this work we measured up to the seventh harmonic response of the complex ac susceptibility vs. temperature ($\chi''(T) - j\chi''(T); n = 1–7$), in YBCO single crystals with different oxygen contents ($6.5 \leq x \leq 7$). The ac field was applied in presence of an external dc field, both applied parallel to the $c$ crystallographic axis. We show new evidence that deoxygenation leads to a reduction of bulk pinning strength which is evidenced by a decrease in the values of the third, fifth and seventh harmonics and a change in the ratio between the third and the fundamental harmonics response. We compare our measurements with a numerical model where the activation barrier depends explicitly on temperature.

2. Experimental

Good quality YBCO single crystals [37] (typical dimensions: 2 mm $\times$ 1 mm $\times$ 100 $\mu$m) were deoxygenated by annealing in controlled oxygen atmosphere for several days [38]. Samples were obtained with different final oxygen contents, $6.5 \leq x \leq 7$, which was estimated by comparing the onset of the superconducting transition $T_c(x)$ with previously published results [39,40].

The ac susceptibility measurements were made in a mutual inductance setup, consisting in a pair of secondary coils oppositely wound on a crystalline sapphire bar, and a primary coil wound over the secondaries. The excitation field ($B_{ac}$) was induced by an adjustable ac sinusoidal current flowing through the primary coil and a series high resistive load $R_1$ from the internal oscillator of a Lock-in Amplifier (Standford SR-850). The sample was glued with vacuum grease to the sapphire bar, with the $c$-axis parallel to the ac field. All the measurements were made in field cooled conditions, reducing temperature at a low rate (0.1 K/min), the ac field amplitude was fixed to 2 Oe, at a constant frequency of 10 kHz, while sequentially measuring with the Lock-in amplifier, in a single temperature run, the in-phase and out-of-phase voltages of the first seven harmonic responses ($\chi''(T) - j\chi''(T); i = 1–7$) for each sample.

The input of the primary was fed through a resistance in order to have a resistive load to fix the phase. The phase was adjusted to give $\chi'' = 0$ with the sample in the normal state a degree above $T_c$. At the lowest temperatures ($T \ll T_c$) it was
checked that \( \chi'' \approx 0 \). The error in the determination of the phase was less than 2°. We did not observe parasitic phase shifts due to reactances on the circuit. The dc field \( (B_{dc}) \), provided by a Nb–Ti superconducting coil, was also applied parallel to the c-axis. \( (B_{dc} = 600 \text{ Oe}) \).

3. Numerical calculations

We numerically studied the ac response for a superconducting strip in an ac magnetic field with a dc field both applied perpendicular to the strip, when the activation barrier \( U \) explicitly depends on the current density \( j \). We solved the equations following a method developed by Brandt [4] using parameters similar to those presented in a work from Qin and Ong [5]. We extended the study in Ref. [5] to the transverse geometry comparing our results with experimental observations.

The equation to be solved in a strip geometry [4] for the sheet current \( J = j \times d \) is

\[
\frac{1}{2\pi} \int_0^a \frac{\partial J(u,t)}{\partial t} \ln \left| \frac{y-u}{y+u} \right| \, du = \frac{E(y,t)}{\mu_0} - y \frac{\partial B_a(t)}{\partial t}
\]

(1)

where \( d \) is the thickness of the strip along the \( x \) direction, \( a \) is the width of the strip along the \( y \) direction. The magnetic field is applied in the \( x \) direction and currents flow in the \( z \) direction. The electric field induced by the flux motion is

\[
E = B \times v
\]

(2)

where the thermally activated flux velocity is given by

\[
v = v_0 \frac{J}{J_c} \exp \left[ - \frac{U(J)}{k_B T} \right]
\]

(3)

where \( v_0 = l \omega_m \), \( l \) is the hopping distance, \( \omega_m \) is the microscopic attempt frequency, \( k_B \) is the Boltzmann constant and \( J_c \) is the critical sheet current.

Eqs. (1)–(3) are discretized [4] and solved with a fourth order Runge–Kutta method with adaptive step size control.

The magnetization is

\[
M(t) = 2 \int_0^a y J(y,t) \, dy
\]

(4)

(5)

\[
\chi'' \approx \frac{1}{\pi B_{ac}} \int_0^{2\pi} \mu_0 M(t) \sin(n \omega t) \, \, d(\omega t),
\]

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\]

The applied magnetic field is given by the following expression:

\[
B_a(t) = B_{dc} + B_{ac} \sin(2\pi ft)
\]

(7)

where \( B_{dc} \) is the applied bias dc field, \( B_{ac} \) is the ac magnetic field amplitude, and \( f \) is the frequency of the ac magnetic field.

We tried several dependences for \( U(J) \) such as a low current divergent barrier \( U(J) = U_0(J_c/J) \) and the well known Anderson–Kim barrier \( U(J) = U_0(1 - J/J_c) \) as well as different dependencies for \( J_c(T,B) \) and \( U_0(T,B) \) corresponding to different pinning regimes [41]. We compared the different results and found that the temperature dependence of the higher harmonics response is well described for all the oxygen contents if we use

\[
U(J) = \frac{U_0}{\mu} \left[ \left( \frac{J_c}{J} \right)^2 - 1 \right]
\]

(8)

which is characteristic of the vortex-glass collective creep model [42,43] where \( U_0 \) is the energy scale and \( \mu \) is a universal exponent. The temperature and field dependences of the critical current density and the apparent activation energy within the collective creep model are [5,41]:

\[
J_c(T,B) = J_{cl} \left[ 1 + \left( \frac{T}{T_c} \right)^2 \right]^{-1/2}
\]

\[
\times \left[ 1 - \left( \frac{T}{T_c} \right)^{2 \nu} \right]^{5/2} \frac{B_{dc}}{B + B_{dc}},
\]

(9)

\[
U_0(T,B) = U_{00} \left[ 1 - \left( \frac{T}{T_c} \right)^4 \right] \frac{B_{dc}}{B + B_{dc}}
\]

(10)

where \( B \) is the internal magnetic field evaluated along the sample.
4. Results and discussion

We measured the ac susceptibility response as a function of temperature up to the seventh harmonic in samples with different oxygen contents. The results for three of these samples up to the fifth harmonic are plotted in Figs. 1–3. Only odd harmonics are shown, as even harmonics were indistinguishable from the experimental noise. All the curves were normalized to the total step in $\chi'$.

We found that experimental curves for the oxygenated crystal (sample 1) were similar to those published in the work of Qin and Ong [5], but as we measure samples with different oxygen content we notice some differences in the experimental curves. We adjusted the parameters of the numerical model presented in Section 3, to obtain typical curves for the well oxygenated (sample 1) and for the highly deoxygenated sample (sample 3). The value of the parameters that were taken in accordance with the experimental setup are: $B_{dc} = 600 \text{ Oe}$, $B_{ac} = 2 \text{ Oe}$, $f = 10^4 \text{ Hz}$ (frequency of the applied $B_{ac}$ field), for a strip geometry of width $2a$ and thickness $d$: $a = 1 \times 10^{-3} \text{ m}$, $d = 1 \times 10^{-4} \text{ m}$.

The other parameters $j_{c0}$, $U_{00}/k_BT_c$, $v_0$ and $\mu$ are related to the mechanisms of pinning. The range of values for the oxygenated and deoxygenated samples was taken from the literature [5,50,52–54] and fitted comparing the curves obtained numerically with the experimental ones.

This set of parameters was adjusted to describe the results for an oxygenated sample and resulted

![Fig. 1. First harmonic ac susceptibility response. $\chi'$ and $\chi''$ vs. $t$ ($t = T/T_c$): (a) experimental results for samples with different oxygen content; (b) numerical simulation oxygenated and deoxygenated samples. The experimental curves progressively shift to lower temperature values and widen as oxygen content is reduced.](image-url)
Fig. 1 shows the real and imaginary components of the first harmonic response of the susceptibility as a function of reduced temperature ($t = T/T_c$) for samples with different oxygen contents (Fig. 1a) as well as numerical simulations for an oxygenated and for a deoxygenated sample (Fig. 1b). Even harmonics (not shown) from the numerical calculation are about two orders of magnitude smaller than odd ones. The main feature is that curves progressively widen in reduced temperature as oxygen content is reduced.

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The structure observed for the sample with $x = 6.9$ (sample 1) at $t < 0.98$ is probably due to an increasing coexistence of liquid and solid phases [44,45]. The change in the shape (shoulders) of the curves for this sample are not relevant in our analysis and will be disregarded. Also, as is shown below, not taking into account this feature in our numerical model does not lead to strong discrepancies between the experimental and the calculated curves of the higher harmonics.

In Fig. 2 we compare the real and imaginary components of the third harmonic response of the ac susceptibility as a function of reduced temper-
ature. There is an agreement in the shape of the experimental curves (Fig. 2a) with the calculated ones (Fig. 2b). This agreement is better for the oxygenated sample while certain features, as the minimum in the calculated imaginary component ($\chi''_5$) at high temperature ($t \approx 0.99$) vanishes in the experimental results as oxygen content is reduced. Note that a reduction by a factor of two in the magnitude of the third harmonic can be appreciated for samples with the lowest oxygen content (Fig. 2a, samples 2 and 3) from 0.05 to 0.025 at the positive peak of $\chi''_3$. This change is reproduced by the numerical simulation.

The temperature dependence of the fifth harmonic is shown in Fig. 3. There is an overall agreement between experimental results (Fig. 3a) and numerical calculations for the well oxygenated and the deoxygenated samples shown in Fig. 3b, in the shape of the curves and the changes in sign in both the real and imaginary components. The amplitude of the peaks and the temperature scale is also reproduced by calculations although features like the high temperature positive peak in the numerical calculations for $\chi''_5$ (see Fig. 3b) have not been observed experimentally. The seventh Fourier component (not shown) also shows a good agreement between experimental and numerical curves, is about five times smaller than the fifth harmonic, and contributes negligibly to the time dependence of the magnetization.

We reconstructed ac magnetization loops [9,46] taking values of the fundamental susceptibility and
the harmonics at a fixed temperature determined at 10%, 50% and 90% of the superconducting transition on $\chi_1$. In Fig. 4 it is shown that the loops become smoother and rounded as the oxygen content is reduced, the saturation arising from strong pinning vanishes resulting in a more elliptic shape. This is due mainly to a change in the ratio between the amplitudes of the third and first harmonics at a given temperature; the ratio controls the shape of the ac hysteresis loop and the change in the shape suggests that the deoxygenated samples have a lower bulk pinning strength. This effect is clearly reproduced in the simulations.

A reduction in $U_0/k_BT_c$ makes thermal relaxation more relevant as the vortex system approaches the flux flow regime. The reduction in the magnitude of the higher harmonics in our samples as the oxygen content is decreased, leads to the changes in the reconstructed ac magnetization loops and might suggest that as oxygen content is reduced the behavior of the vortex system shifts gradually away from critical state behavior.

Fig. 4. Reconstructed magnetization ac loops from the values of the harmonics at a fixed temperature. 10%, 50% and 90% of the superconducting transition: (a, b) Experimental results for samples with different oxygen contents; (c) numerical simulation oxygenated sample; (d) numerical simulation deoxygenated sample. The loops become smoother and rounded as the oxygen content is reduced, the saturation arising from strong pinning vanishes resulting in a more elliptic shape.
towards flux flow regime. It is worth to note that the measured maximum of the dissipation \( \chi''_1 \) lies for all samples between the predicted values for a disk in critical state \( \chi''_1 = 0.24 \) [5,17,47] and in flux flow \( \chi''_1 = 0.44 \) [48,49] but we did not find a clear monotonic dependence of the peak amplitude with oxygen content. However, the decrease in the higher harmonic response seems more sensitive to the increasing creep rate with decrease of oxygen content. This is observed in the numerical simulation where the chosen value \( U_{\text{ff}}/k_B T_c = 2 \) gives a higher dissipation peak (\( \chi''_1 \)) but a lower value of the higher harmonics and a better resemblance between the experimental and the simulated magnetization loops. An increase in the value of \( U_{\text{ff}}/k_B T_c \) gives a lower dissipation peak but a lesser resemblance of the other curves.

The calculated values for the critical current density and energy scales that better reproduce our experimental results show clearly a decrease in the effective bulk pinning strength for the deoxygenated sample. The decrease of \( j_{\text{c0}} \) in one order of magnitude for the deoxygenated sample is in agreement with previously published experimental measurements [50].

We tried several values for the exponent, \( \mu \), which are present in the literature for different pinning regimes [49]. We found that our results were better described for the oxygenated sample taking \( \mu = 0.6 \) according to Qin and co-workers [5, 51–54] and a value of \( \mu = 1/7 \) for the deoxygenated sample. This might indicate a change in the dynamic regime of the vortex lattice from small bundles to single vortex pinning which could happen because the superconducting transition occurs at lower temperature for the deoxygenated sample or be a result of a better accommodation of the vortex lattice due to an enhancement in the number of pinning centers after deoxygenation.

The fitted vortex velocity scale \( v_0 \) decreased from \( v_0 = 1 \) m/s for high oxygen content [5] to \( v_0 = 5 \times 10^{-2} \) m/s for low oxygen content. A plausible interpretation of the reduction of the electrical field by reducing the parameter \( v_0 \) may indicate a reduction in the hopping distance between pinning sites due to the enhancement of the oxygen vacancies density by the deoxygenation.

The chosen expression for the dependence of \( U(T, B) \) does not reflect the linear behavior expected at high temperatures (\( \chi''_1 \rightarrow 0 \)) because \( U \) diverges as \( J \rightarrow 0 \). For a vortex liquid with low pinning it is expected a finite value for the activation barrier in the small current limit [49]. Therefore, further work is needed in order to take both types of \( U(J) \) relationships at low and high temperatures into account.

5. Conclusions

In summary, in this work we measured the higher harmonic response of the complex ac susceptibility vs. temperature, in YBCO single crystals with different oxygen contents (6.5 \( \leq x \leq 7 \)). We found that there is a reduction in the magnitude of the higher harmonics as the oxygen content is reduced beyond a certain value. This suggests that deoxygenation reduces the bulk pinning strength. Our results were compared with a numerical model which takes into account relaxation effects and supports this interpretation.

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