Fundamental and harmonic susceptibilities of YBa$_2$Cu$_3$O$_{7-\delta}$

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We have examined the complex harmonic magnetic susceptibilities $\chi_n' = \chi_n' - i\chi_n''$ ($n = 1, 2, 3, \ldots, 10$) of the sintered high-critical-temperature (high-$T_c$) superconductor YBa$_2$Cu$_3$O$_{7-\delta}$. The experimental variables for the measurements of $\chi_n$ were the sample temperature $T$ (10 $\leq T \leq 110$ K), the ac magnetic field amplitude $H_{ac}$ (1.4 $\mu$T $\leq \mu_0 H_{ac} \leq 8.5$ mT), frequency $f$ (7.3 $\leq f \leq 1460$ Hz), and the magnitude of a superimposed dc field $H_{dc}$ ($\mu_0 H_{dc} \leq 8.5$ mT). As functions of temperature, $\chi_n'$ and $\chi_n''$ depend on both $H_{ac}$ and $H_{dc}$. In particular, the $\chi_n'$ transition curve can shift to higher temperatures with increasing $H_{dc}$. Odd-harmonic susceptibilities were measured as functions of temperature below $T_c$ for zero $H_{dc}$; both even and odd harmonics were observed for nonzero $H_{dc}$. At fixed temperature, the odd-harmonic susceptibilities are even functions of $H_{dc}$, while the even-harmonic susceptibilities are odd functions of $H_{dc}$. We compared the experimental intergrain coupling characteristics of $\chi_n'$ and $\chi_n''$ with theoretical susceptibility curves based on magnetization equations derived by Ji et al. from a simplified Kim model for critical current density. The theoretical curves are in good agreement with the temperature- and field-dependent features of $\chi_n'$ and $\chi_n''$, and, therefore, the intergrain coupling component of a sintered high-$T_c$ superconductor behaves as a type-II superconductor.

I. INTRODUCTION

A measurement of the superconducting transition by means of complex ac susceptibility $\chi = \chi' - i\chi''$ typically shows, just below the critical temperature $T_c$, a sharp decrease in $\chi'$, a consequence of diamagnetic shielding, and a peak in $\chi''$, representing losses. This magnetic response was studied by Maxwell and Strongin, Ishida and Mazaki, Khoder, and Hein for conventional bulk superconductors.

Complex susceptibility is useful for characterizing high-critical-temperature (high-$T_c$) superconductors in conjunction with, or as an alternative to, resistivity, dc susceptibility, and specific heat. A sintered high-$T_c$ superconductor, such as YBa$_2$Cu$_3$O$_{7-\delta}$ (Y-Ba-Cu-O), can be modeled as a system in which the superconducting grains are weakly coupled. In such materials, $\chi$ has both intrinsic and coupling components. The coupling component is very sensitive to both temperature $T$ and the amplitude of the ac measuring field $H_{ac}$. Several experiments on the $H_{ac}$ dependence of $\chi$ versus $T$ have been reported.

For an ac magnetic excitation field, $H(t) = H_{ac}\sin(\omega t)$, at the fundamental frequency $\omega (\equiv 2\pi f_1)$, the harmonic susceptibility may be represented as $\chi_n = \chi_n' - i\chi_n''$, where $n = 1$ denotes the fundamental susceptibility. Bean's critical-state model for the magnetization of type-II superconductors, in which the critical current density $J_c$ was assumed to be independent of the local magnetic field, predicted the existence of odd harmonics of susceptibility.

Experimentally, Ishida and Mazaki used the fundamental and higher-harmonic susceptibilities to study a multiconnected low-temperature superconductor, which they modeled as a network of microbridge-type weak links. The model qualitatively described the temperature and $H_{ac}$ dependences of $\chi_2$ for a weakly connected superconductor. It predicted the emergence of odd-harmonic susceptibilities below $T_c$ and the proportionality of the magnitude of the third-harmonic susceptibility $|\chi_3|$ to $\chi_i^2$, in good agreement with experiment. Harmonic susceptibility was also used to characterize a synthetic one-dimensional superconductor. The Ishida-Mazaki conclusions are in good agreement with experimental data and some interpretations for high-$T_c$ superconductors.

Shaulov and Dorman compared $\chi_i^2$ and $|\chi_3|$ as functions of temperature and dc bias field for sintered Y-Ba-Cu-O. They detected a field-dependent transition temperature above which $|\chi_3|$ was zero but $\chi_i^2$ was not. They attributed this to a state of dissipative flux motion without pinning. Lam, Jefferies, and co-workers reported the nonlinear behavior of Y-Ba-Cu-O in a radio-frequency magnetic field. They modeled the system as a suitably averaged collection of flux-quantized supercurrent loops containing Josephson junctions and proposed a dynamic model for explaining the harmonic generation. A similar approach, with the addition of a field-dependent loop current, was presented by Xia and Stroud.

Harmonic susceptibilities of high-$T_c$ superconductors have been experimentally studied by others. Sato et al. reported the third-harmonic susceptibility $\chi_3' - i\chi_3''$ of sin-
tered Y-Ba-Cu-O and interpreted the harmonics as a superposition of the intrinsic and coupling contributions. Yamamoto et al. measured the third-harmonic susceptibility of single-crystal Y-Ba-Cu-O films in an ac magnetic field perpendicular to the film surface. Giovannella et al., Luccini et al., and Park et al. interpreted measurements of harmonic susceptibility using a superconductor glass model. Lera et al. measured the harmonic susceptibilities of sintered Y-Ba-Cu-O and used them to reconstruct the magnetic hysteresis loop. Okamoto et al. examined the third-harmonic content of the magnetic hysteresis loop as a function of dc bias field. Luzyanin et al. measured the low-field dependence of the magnitude of the harmonic magnetization. Xenikos and Lemberger measured the harmonic magnetization of single-crystal Y-Ba-Cu-O as a function of temperature just below $T_c$. They interpreted the results in terms of field- and temperature-dependent magnetoresistance.

Unlike the Bean model, the critical-state model by Kim et al. assumes a critical current density $J_c$ that decreases with increasing local field $H$: $J_c = J_c(H) \propto H_0 + \int |H| dH$, where $k$ and $H_0$ are constants. Chen et al. computed the fundamental susceptibility based on Kim model equations for magnetization presented by Chen and Goldfarb. Müller calculated the temperature and field dependences of the fundamental susceptibility, including the intergranular contribution, using the Kim model and compared them to experimental results of Goldfarb et al. The Kim model has been shown to accurately predict many of the electromagnetic properties of the coupling component in sintered materials.

Müller and Ji et al. investigated the effect of a superimposed dc field on the generation of even harmonics, which are not predicted by the Bean model. Müller et al. compared $\chi_n$ obtained with a spectrum analyzer to theoretical results derived using the Kim model. Ji et al. used a simplified Kim model, in which $H_0$ was taken to be zero, and derived equations for the magnetic hysteresis loop around a dc bias field for a slab geometry. Using these equations, they numerically computed $\chi_n$ and compared experimental data obtained with a Fourier signal analyzer.

In this paper, we present a detailed investigation of the validity of the simplified Kim model by comparing experimental and theoretical complex harmonic susceptibility. We measured the dependences of both $\chi_n$ and $\chi_n'(n \leq 10)$ on temperature, ac field, and dc field using a lock-in amplifier rather than a signal analyzer. The higher harmonics result from hysteresis and nonlinearity of magnetization. We obtained good agreement of experimental data with the theoretical behavior deduced from the equations for magnetization of Ji et al.

Equations and results are expressed in SI units. Volume susceptibility is dimensionless, with full diamagnetism corresponding to a susceptibility of $-1$. Applied magnetic fields $H$ are given numerically as $\mu_0 H$, the flux density in free space, in units of teslas, where $\mu_0 = 4\pi \times 10^{-7}$ T/m. The conversion factor to cgs electromagnetic units is $10^{-4}$ T/G, where G is dimensionally and numerically equivalent to Oe.

II. EXPERIMENTAL MEASUREMENTS

A. Sample preparation

The YBa$_2$Cu$_{3-\delta}$O$_7$ samples were prepared by a solid-state reaction from Y$_2$O$_3$, BaCO$_3$, and CuO powders. The stoichiometric mixture was ground and reacted in air at 800°C for 19 h, 850°C for 9 h, 880°C for 22 h, and 800°C for 2 h. It was then cooled to room temperature in the furnace. It was reground, pelletized, and subsequently sintered in air at $800^\circ$C for 1 h, $900^\circ$C for 120 h, and cooled in the furnace.

The pellets were thoroughly oxidized in flowing oxygen at standard atmospheric pressure by using a programmable temperature controller. The temperature was increased linearly from 25 to 800°C in 2 h, held at 800°C for 22 h, decreased at a constant rate from 800 to 300°C in 48 h, kept at 300°C for 48 h, and decreased linearly from 300 to 25°C in 24 h. After the oxygen treatment, $\delta$ in the chemical formula decreased by approximately 0.025 based on the change in sample mass. We examined a 74%-dense Y-Ba-Cu-O specimen (9.2-mm diameter, 5.3-mm length, 1.658-g mass) by x-ray diffraction. The specimen was single phase and the lattice parameters were $a = 3.823 03 \pm 0.000 33$ Å, $b = 3.884 69 \pm 0.000 35$ Å, and $c = 11.661 51 \pm 0.000 09$ Å. The $c$ value corresponds to $\delta = 0.036$. The electrical resistivity of the Y-Ba-Cu-O sample was zero below 89.8 K.

We used this Y-Ba-Cu-O pellet for the measurement of the harmonic susceptibility. The demagnetization factor of the pellet was approximately 0.28 for ac and dc fields both applied perpendicular to the pellet axis, but, for consistency in computing the harmonic susceptibilities, we did not correct the susceptibility data for demagnetization factor.

B. Definition of harmonic susceptibility

The fundamental susceptibility $\chi_1$ has clear physical meaning. The real part $\chi_1'$ corresponds to the dispersive magnetic response and the imaginary part $\chi_1''$ corresponds to energy dissipation. $\chi_1$ reflects supercurrent shielding for superconductors. The external magnetic field $H(t)$ is

$$H(t) = H_{ac} \text{Im}(e^{i\omega t}) = H_{ac}\sin(\omega t),$$

where $\text{Im}(\cdot)$ denotes the imaginary part of the complex variable. We define the magnetization $M(t)$ as a function of $t$ by

$$M(t) = H_{ac} \sum_{n=1}^{\infty} \text{Im}(\chi_n e^{i\omega nt})$$

$$= H_{ac} \sum_{n=1}^{\infty} \left[ \chi_n'(\sin(n\omega t)) - \chi_n''(\cos(n\omega t)) \right],$$

(1)

where $\chi_n = \chi_n' - i\chi_n'' (n = 1, 2, 3, \ldots).$ This form of the complex variable is consistent with the physical meaning of $\chi_1$, $\chi_n'$ and $\chi_n''$ can be calculated by

$$\chi_n' = \frac{1}{\pi H_{ac}} \int_0^{2\pi/\omega} M(t)\sin(n\omega t) d(\omega t),$$

(2a)
\[ \chi''_n = \frac{-1}{\pi H_{ac}} \int_0^{2\pi} M(t) \cos(n\omega t) d(\omega t). \tag{2b} \]

The same definition is used when a dc magnetic field is superimposed on the ac field. (See the Appendix for the experimental implications of an alternative definition for harmonic susceptibility.) The function \( M(t) \) consists of the appropriate equations for magnetization as a function of field \( M(H) \),\(^{34}\) in which \( H \) is expressed as \( H(t) = H_{ac}\sin(\omega t) \). For analytic evaluation, the integrals in Eqs. (2a) and (2b) are separated into intervals \( \pi/2 \) to \( 3\pi/2 \) and \( 3\pi/2 \) to \( 5\pi/2 \), corresponding to decreasing and increasing \( H(t) \).

C. Measurement of harmonic susceptibility

Experimentally, we observe a voltage, proportional to the time derivative of \( M(t) \), induced in a pickup coil,

\[ \frac{d[M(t)]}{dt} = H_{ac} \sum_{n=1}^{\infty} [n\omega \chi'_n \cos(n\omega t) + n\omega \chi''_n \sin(n\omega t)] . \tag{3} \]

We used a two-phase lock-in amplifier to separate the \( \cos(n\omega t) \) and \( \sin(n\omega t) \) parts. Consistent with our adopted sign convention, the lock-in reference was \( \sin(n\omega t) \) and the outputs had positive polarities.

We measured each \( \chi_n \) as a function of increasing temperature using a two-position ac susceptometer.\(^{41,42} \) Two-position measurements eliminate spurious contributions to the fundamental susceptibility signal from any pickup coil imbalance. The susceptometer was calibrated numerically and with standards.\(^{40} \) A high-permeability shield around the Dewar reduced the Earth's field to less than 0.5 \( \mu T \) in the measurement axis. The sample was cooled to \( \sim 5 \) K in zero field to minimize trapped flux in the superconducting sample. Instrument control and measurements were computerized. Susceptibility data were taken at temperature intervals of \( < 0.1 \) K as the temperature of the specimen increased at a rate \( < 0.4 \) K/min near \( T_c \).

The current to the primary field coil, proportional to \( \sin(\omega t) \), was generated by an ac constant-current amplifier driven by one channel of a two-channel synthesizer. Frequency accuracy was 5 \( \mu \)Hz. Second- and third-harmonic voltage distortion, measured with a signal analyzer across the susceptometer field coil, was less than 0.03\% of the fundamental voltage (\( -70 \) dBV). The second synthesizer channel provided a reference voltage, proportional to \( \sin(n\omega t) \), to the two-phase lock-in amplifier.

Correct phase adjustment is important for accurate separation of the real and imaginary parts of fundamental and harmonic susceptibilities. The procedure for each measurement of \( \chi_n \) was as follows. With both synthesizer channels at the intended harmonic frequency \( n f_1 \) and in phase, we adjusted the lock-in phase angle to null \( \chi''_n \) for a measuring field amplitude of 1.4 \( \mu T \) at \( \sim 7 \) K. (For small fields, there is perfect diamagnetic shielding and zero losses up to \( \sim 80 \) K.) The lock-in phase adjustment would be maintained for measurements at higher temperatures, higher ac fields, and with superimposed dc fields. We then set the excitation synthesizer channel to the fundamental frequency \( f_1 \), while the lock-in reference channel remained at \( n f_1 \). The relative phase between the two synthesizer channels was then adjusted to zero using Lissajous figures on an oscilloscope. With these adjustments, the two outputs of the lock-in amplifier were proportional to \( n\omega H_{ac} \chi'_n \) and \( n\omega H_{ac} \chi''_n \).

Some harmonic susceptibility measurements were made at constant \( H_{ac} \) and temperature (4 or 76 K) as a function of \( H_{dc} \) using the dc offset of the synthesizer. Lock-in phase adjustment was accomplished as described above. The sample was warmed to above 90 K and cooled in zero field before stepping \( H_{dc} \) from zero to either a positive or a negative maximum. This precaution avoided initial trapped flux in the sample. Due to instrument limitations, the steps in applied dc field were not entirely monotonic and likely caused minor magnetization hysteresis loops to be traced before the field stabilized at each higher value. The result, however, would be the same as with a smooth field sweep.

III. MODEL CALCULATIONS

A. Bean model

The harmonic susceptibilities \( \chi'_n - i\chi''_n \) can be evaluated analytically or numerically from magnetization \( M(t) \) as a function of field \( H(t) \). We approximate the superconductor sample disk as an infinite slab for purposes of applying the critical-state model. The harmonic susceptibilities for an infinite slab, when \( H_{ac} \) is less than the full penetration field \( H_p \), may be calculated analytically using the Bean equations for \( M(H) \):

\[ \chi'_1 = H_{ac}/2H_p - 1, \tag{4a} \]
\[ \chi'_n = 2H_{ac}/3\pi H_p, \tag{4b} \]
\[ \chi''_n = 0 \quad (n > 1), \tag{4c} \]
\[ \chi''_n = (-1)^n + 1/2H_{ac}/[H_p \pi(n - 2)n(n + 2)] \tag{4d} \quad (n \text{ odd}), \]
\[ \chi''_n = 0 \quad (n \text{ even}). \tag{4e} \]

As noted by Ji et al.,\(^{37} \) no even harmonics appear in the framework of the Bean model, neither when \( H_{ac} > H_p \) nor when there is a superimposed dc field. The hysteresis loop corresponding to these harmonic susceptibilities is lenticular.\(^{11,25,26} \) Total loss per unit volume per field cycle is\(^{43} \)
\[ W = \pi \mu_0 H_{ac} \chi''_1. \]
Losses are solely hysteretic in the critical-state model; Eq. (4b) represents hysteresis loss, as may be verified by comparing the equations for \( \chi'_1 \) and \( W \).\(^{33,44} \)

B. Ishida-Mazaki model

Ishida and Mazaki\(^{12,13} \) gave expressions for the harmonic susceptibilities of a multiconnected Josephson network. They are equivalent to the formulation of Rollins and Silcox\(^{45} \) for a bulk superconducting surface sheath. The equations are
\[ \chi' = \frac{1}{\pi} \left( \frac{\sin 2\alpha - 2\alpha}{\pi} \right) \]

\[ \chi'' = \frac{1}{\pi} \left( \sin 2\alpha / \pi \right) \]

\[ \chi'' = \frac{\sin(n+1)\alpha}{n+1} - \frac{\sin(n-1)\alpha}{n-1} \] \quad (n odd), \hspace{1cm} (5c)

\[ \chi'' = \frac{\cos(n+1)\alpha - 1}{n+1} - \frac{\cos(n-1)\alpha - 1}{n-1} \] \quad (n odd), \hspace{1cm} (5d)

\[ \chi' = 0 \quad (n \text{ even}) \]

\[ \chi'' = 0 \quad (n \text{ even}) \] \hspace{1cm} (5f)

where \( \alpha = 2 \sin^{-1} \left( H_m / H_{ac} \right)^{1/2} \) and \( H_m \) is the magnetic field which would induce a current equal to the critical current of the weak-link loop. The sign convention adopted here requires the factors \((-1)^n (n+1)/2\) in the expressions for \( \chi' \) and \( \chi'' \). The Ishida-Mazaki model describes the essential features of the temperature and ac field dependences of \( \chi' \) and \( \chi'' \) for high-\( T_c \) and other multiconnected superconductors. Reconstruction of the magnetic hysteresis loop using the harmonic susceptibilities gives a rhomboid. The model indicates nonzero \( \chi'_n \) for \( n > 1 \) but, as in the case of the Bean model, it does not predict the even harmonics in a dc bias field.

### C. Kim model

To account for the even harmonics and nonzero \( \chi'_n \), Ji et al.\(^{37} \) derived equations for sample magnetization as a function of field

\[ H(t) = H_{dc} + H_{ac} \sin(\omega t) \]

using a simplified Kim model, \( J_c = k / |H_x| \), where \( k \) is a constant, and \( H_t \) is the local magnetic field. Although this form is discontinuous at \( H_t = 0 \), the integrations used to determine \( M \) are finite.\(^{37} \) Susceptibility could then be obtained using Eqs. (2). For an infinite slab of thickness \( 2a \), the full penetration field \( H_p \) is \( (2ka)^{1/2} \). The equations depend on the relative magnitudes of \( 2H_p^2 \) and \( \Delta^2 \), where

\[ \Delta^2 = [H_p^2 \sgn(H_a) - H_p^2 \sgn(H_b)] \]

\[ H_a \equiv H_{dc} + H_{ac}, \quad H_b \equiv H_{dc} - H_{ac}, \]

\( \sgn(x) = x / |x| \), for \( x \neq 0 \), and \( \sgn(x) = 0 \) for \( x = 0 \).

Because we used them in our analysis, the equations derived by Ji et al. are reproduced here for a sample cooled in zero field and never exposed to fields greater than \( H(t) \).

For the case \( \Delta^2 > 2H_p^2 \), the magnetization \( M(t) \) for \( H(t) \) decreasing is

\[ M(t) = \frac{2}{(3H_p^2)} \frac{1}{|H(t)|^3} [H(t)^2 \sgn[H(t)] + H_p^2 \sgn[H_a] - H_p^2] \] \quad (6a)

when \( H_a > H(t) > H_p^2 \sgn[H_a] - 2H_p^2 \sgn[H_a] - 2H_{ac}^2 \), and

\[ M(t) = \frac{2}{(3H_p^2)} [H(t)^2 \sgn[H(t)] + H_p^2 \sgn[H_a] + H_{ac}^2] \] \quad (6b)

when \( H_p^2 \sgn[H_a] - 2H_p^2 \sgn[H_a] - 2H_{ac}^2 > H(t) > H_b \). The magnetization \( M(t) \) for \( H(t) \) increasing is

\[ M(t) = \frac{2}{(3H_p^2)} [H(t)^2 \sgn[H(t)] + H_p^2 \sgn[H_b] + H_{ac}^2] \] \quad (6c)

when \( H_b < H(t) < H_p^2 \sgn[H_b] + 2H_p^2 \sgn[H_b] + 2H_{ac}^2 \), and

\[ M(t) = \frac{2}{(3H_p^2)} [H(t)^2 \sgn[H(t)] - H_p^2 \sgn[H_b] - H_{ac}^2] \] \quad (6d)

when \( H_p^2 \sgn[H_b] + 2H_p^2 \sgn[H_b] + 2H_{ac}^2 < H(t) < H_a \).

For the case \( \Delta^2 < 2H_p^2 \), the magnetization \( M(t) \) for \( H(t) \) decreasing from \( H_a \) to \( H_b \) is

\[ M(t) = \frac{2}{(3H_p^2)} [H(t)^2 \sgn[H(t)] + H_p^2 \sgn[H_a] - H_p^2] \] \quad (7a)

The magnetization \( M(t) \) for \( H(t) \) increasing from \( H_b \) to \( H_a \) is

\[ M(t) = \frac{2}{(3H_p^2)} [H(t)^2 \sgn[H(t)] + H_p^2 \sgn[H_b] - H_p^2] \] \quad (7b)

The magnetic hysteresis loops obtained from these equations are minor loops, centered about any field, within the envelope of the symmetric astroid-shaped magnetization loop.\(^{33,38} \) A comparable but more protracted analysis using the complete Kim model was described by Müller.\(^{34} \)

We numerically obtained \( \chi'_n \) and \( \chi''_n \) using Eqs. (2) for various combinations of \( H_{ac}, H_{dc}, \) and \( H_p \). The integrals were evaluated using fast Fourier transforms (FFT) and double-precision variables. For the calculation, we sequentially generated 128 discrete values of \( M(t) \) for one period of

\[ H(t) = H_{dc} + H_{ac} \sin(\omega t) \]

using Eqs. (6) and (7).
D. Temperature dependence of susceptibility

The temperature dependence of susceptibility comes from that of \( J_c \), \( k_c \), or \( H_p \). Ji et al.\textsuperscript{37} assumed the two-fluid-model temperature dependence of \( J_c \):

\[
J_c \propto \left[ 1 - (T/T_c)^2 \right] \left[ 1 - (T/T_c)^k \right]^{1/2}.
\]

Müller\textsuperscript{34} used a different temperature dependence:

\[
J_c \propto \left[ 1 - (T/T_c)^2 \right]^2 \text{ for the intergranular coupling component and }
J_c \propto \left[ 1 - (T/T_c)^k \right]^2 \text{ for the intrinsic intragrain component.}
\]

In fact, it is not necessary to assume a temperature dependence for \( J_c \) to describe the essential features of \( \chi''_c \). In this work, we simply express the temperature dependence of \( \chi''_c \) and \( \chi''_c \) in terms of \( H_p(T) \). \( H_p \) is zero at \( T_c \). As \( T \) decreases from \( T_c \), \( H_p \) increases monotonically. For \( H_p \leq 0 \), \( \chi''_c \equiv 0 \). We find that \( H_p \) is a good proxy for temperature.

IV. RESULTS AND DISCUSSION

In this section we compare measured susceptibilities as functions of temperature to model calculations with the full penetration field \( H_p \) as the dependent variable. We also compare experimental and theoretical susceptibilities as functions of a superimposed dc field \( H_{dc} \).

A. Fundamental susceptibility

Fundamental susceptibilities \( \chi' \) were measured with the excitation field and the lock-in amplifier reference both at 73 Hz. We examine ac- and dc-field effects.

1. Effect of ac field

In Fig. 1, we show the fundamental susceptibility (\( \chi' \) and \( \chi'' \)) at 73 Hz of the Y-Ba-Cu-O pellet as a function of temperature for three ac-field amplitudes (\( \mu_0 H_{ac} = 0.0424, 0.424 \), and 2.12 mT) in zero dc field. The data in this figure, as in all the figures, represent the external susceptibility, not corrected for demagnetization factor. Demagnetization correction would cause \( \chi' \) to approach \(-1 \) at low temperature.

These experimental curves have intrinsic granular components and intergranular coupling components. \( \chi' \) shows two peaks corresponding to the intrinsic and coupling components. As \( H_{ac} \) increases, the height and breadth of the two peaks increase as they move to lower temperature. For \( \mu_0 H_{ac} = 0.424 \) mT, the intrinsic and coupling components happen to form a composite curve. A further increase of \( H_{ac} \) causes a two-step structure in \( \chi' \) and a shoulder in \( \chi'' \). These features are well known.\textsuperscript{5–10}

For comparison of theory and experiment, we concentrate on the intergranular coupling component because it dominates the curves in Fig. 1. (The comparison could be made for the intrinsic grains by using much larger fields \( H_{ac}, H_{dc} \), and \( H_p \).) Figure 2 shows model calculations of \( \chi' \) and \( \chi'' \) as functions of \( H_p \) for three ac fields (\( \mu_0 H_{ac} = 0.0424, 0.424 \), and 2.12 mT) in zero dc field. The curves are consistent with the calculations by Chen et al. in the slab limit.\textsuperscript{32} Use of the complete, rather than simplified, Kim model would reduce the height of the \( \chi'' \) peaks in Fig. 2 (see Müller\textsuperscript{34}). As discussed above, \( H_p \) is a monotonically decreasing function of increasing tem-

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**FIG. 1.** Real and imaginary parts of fundamental susceptibility, \( \chi'_1 \) and \( \chi''_1 \), of the Y-Ba-Cu-O pellet as a function of temperature for three different \( H_{ac} \) (\( \mu_0 H_{ac} = 0.0424, 0.424 \), and 2.12 mT), \( H_{dc} = 0 \), \( f_1 = 73 \) Hz. The data are not corrected for sample demagnetization factor.

**FIG. 2.** Model calculations of the real and imaginary parts of fundamental susceptibility, \( \chi'_1 \) and \( \chi''_1 \), for a superconductor as a function of full penetration field \( H_p \) for three different \( H_{ac} \) (\( \mu_0 H_{ac} = 0.0424, 0.424 \), and 2.12 mT), \( H_{dc} = 0 \), \( f_1 = \) arbitrary. \( H_p \) is a monotonically decreasing function of increasing temperature.
FIG. 3. Fundamental susceptibilities $\chi_1$ and $\chi_2''$ of the Y-Ba-Cu-O pellet as a function of temperature for five different $H_{dc}$ ($\mu_0 H_{dc} = 0$, 0.424, 0.993, 2.98, and 8.48 mT), $\mu_0 H_{ac} = 0.424$ mT, $f_1 = 73$ Hz. Note the decrease in $\chi_2''$ coupling peak height for applied dc fields.

The figure is scaled to demonstrate similarity with the coupling components in Fig. 1. The model does not explain the change in height of the $\chi_2''$ peaks with $H_{ac}$ seen experimentally.

2. Effect of dc field

In Fig. 3, we show $\chi_1$ and $\chi_2''$ of the Y-Ba-Cu-O pellet as functions of temperature for five dc bias fields

FIG. 4. Model calculations of the fundamental susceptibilities $\chi_1$ and $\chi_2''$ as a function of $H_{dc}$ for five different $H_{ac}$ ($\mu_0 H_{ac} = 0$, 0.424, 1.00, 3.00, and 8.48 mT), $\mu_0 H_{dc} = 0.424$ mT, $f_1 = 73$ Hz. For an applied dc field, the $\chi_1$ peak decreases in height and the $\chi_2''$ transition shifts to lower temperature.

For $\mu_0 H_{dc} = 0$, 0.424, 0.993, 2.98, and 8.48 mT, for $\mu_0 H_{ac} = 0.424$ mT and $f_1 = 73$ Hz. The $\chi_1$ curves decrease as a function of decreasing temperature in a two-step manner at higher $H_{dc}$. This is similar to the effect of higher ac fields in Fig. 1. The peak height of $\chi_2''$ decreases appreciably for a dc field of 0.424 mT and above. This is not the case for the ac-field dependence in Fig. 1.

In Fig. 4, we show calculated curves of $\chi_1$ and $\chi_2''$ as

FIG. 5. Fundamental susceptibilities $\chi_1$ and $\chi_2''$ of the Y-Ba-Cu-O pellet as a function of temperature for four different $H_{dc}$ ($\mu_0 H_{dc} = 0$, 0.861, 1.722, and 3.179 mT), $\mu_0 H_{ac} = 2.12$ mT, $f_1 = 73$ Hz. The relatively large ac field makes apparent the shift in the $\chi_1$ coupling transition to higher temperature with increasing dc field.

FIG. 6. Model calculations of the fundamental susceptibilities $\chi_1$ and $\chi_2''$ as a function of $H_{dc}$ for four different $H_{ac}$ ($\mu_0 H_{ac} = 0$, 0.861, 1.722, and 3.179 mT), $\mu_0 H_{dc} = 2.12$ mT, $f_1 = 73$ Hz. For an applied dc field, the $\chi_1$ peak decreases in height and the $\chi_2''$ transition shifts to lower temperature.
FIG. 7. Odd-harmonic susceptibilities $\chi_1'$ and $\chi_n''$ ($n = 1, 3, 5, 7$) of the Y-Ba-Cu-O pellet as a function of temperature. The measurement parameters were $\mu_0 H_{ac} = 0.424$ mT, $H_{dc} = 0$, and $f_1 = 73$ Hz.

FIG. 8. Model calculations of the odd-harmonic susceptibilities $\chi_1'$ and $\chi_n''$ ($n = 1, 3, 5, 7$) of a superconductor as a function of $H_p$, $\mu_0 H_{ac} = 0.424$ mT, $H_{dc} = 0$, $f_1 = \text{arbitrary}$.

FIG. 9. Odd-harmonic susceptibilities $\chi_1'$ and $\chi_n''$ ($n = 1, 3, 5, 7$) of the Y-Ba-Cu-O pellet as a function of temperature for a superimposed dc magnetic field. The measurement parameters were $\mu_0 H_{ac} = 0.424$ mT, $\mu_0 H_{dc} = 0.424$ mT, and $f_1 = 73$ Hz.

FIG. 10. Model calculations of the odd-harmonic susceptibilities $\chi_1'$ and $\chi_n''$ ($n = 1, 3, 5, 7$) of a superconductor as a function of $H_p$, $\mu_0 H_{ac} = 0.424$ mT, $\mu_0 H_{dc} = 0.424$ mT, $f_1 = \text{arbitrary}$.
functions of decreasing \( H_p \) for similar conditions as in Fig. 3. As the dc field is applied, the \( \chi'_1 \) peak height decreases as in the experimental curves in Fig. 3 and as modeled by Müller. However, the transition in theoretical \( \chi'_1 \) initially shifts to higher temperature. We explore this phenomenon further in Figs. 5 and 6. In Fig. 5 we show experimental \( \chi'_1 \) and \( \chi''_1 \) for a relatively large ac field \( \mu_0 H_{ac} \) of 2.12 mT at 73 Hz, with dc fields \( \mu_0 H_{dc} \) ranging from 0 to 3.18 mT. We note a positive shift in the coupling transition in \( \chi'_1 \) with increasing \( H_{dc} \), more emphasized than in Fig. 4. In Fig. 6, theoretical curves as functions of decreasing \( H_p \) for the corresponding parameters show the same effect. These curves, of course, refer to a single-component superconductor. Gomory and Lobotka and Giovannella et al. reported the dc-field dependence of \( \chi'_1 \) and \( \chi''_1 \) as functions of temperature. They did not examine the reduction of \( \chi''_1 \) peak height or the positive shift in \( \chi'_1 \) as \( H_{dc} \) increases.

B. Higher-harmonic susceptibility

Unlike the fundamental susceptibilities, the higher-harmonic real parts \( \chi'_n \) and imaginary parts \( \chi''_n \) are not constrained to negative and positive values, respectively. The superposition of a dc field permits the even harmonics.

FIG. 11. Even-harmonic susceptibilities \( \chi'_n \) and \( \chi''_n \) \( (n = 2, 4, 6, 8) \) of the Y-Ba-Cu-O pellet as a function of temperature for a superimposed dc magnetic field. The measurement parameters were \( \mu_0 H_{ac} = 0.424 \) mT, \( \mu_0 H_{dc} = 0.424 \) mT, and \( f_1 = 73 \) Hz.

FIG. 12. Model calculations of the even-harmonic susceptibilities \( \chi'_n \) and \( \chi''_n \) \( (n = 2, 4, 6, 8) \) of a superconductor as a function of \( H_p \), \( \mu_0 H_{ac} = 0.424 \) mT, \( \mu_0 H_{dc} = 0.424 \) mT, \( f_1 \) = arbitrary.

1. Odd harmonics in ac field

In Fig. 7, we show experimental odd-harmonic susceptibilities \( \chi'_n \) and \( \chi''_n \) \( (n = 1, 3, 5, 7) \) of the Y-Ba-Cu-O pellet as functions of temperature for an ac field \( \mu_0 H_{ac} = 0.424 \) mT at \( f_1 = 73 \) Hz. The ninth harmonic was measured but is not shown. There was no applied dc field. There is good qualitative correspondence with theoretical curves shown in Fig. 8. Quantitative agreement could be improved by using the complete Kim model, as discussed above. As noted by Lucchini et al., the fine structure in the higher-order harmonics is due to intrinsic granular and intergranular coupling critical transitions.

2. Even harmonics in ac field

Even harmonics were detected for zero \( H_{dc} \) at the \( 10^{-3} \) level in susceptibility. In principle, the appearance of these small harmonic susceptibilities could be attributed to even-harmonic content of \( H_{ac} \), a slight dc offset in the constant-current amplifier, or residual ambient dc fields. Even harmonics are not expected for symmetric hysteresis loops centered at zero field.

3. Odd and even harmonics in superimposed ac and dc fields

In Fig. 9, we show the odd-harmonic susceptibilities \( \chi'_n \) and \( \chi''_n \) \( (n = 1, 3, 5, 7) \) of the Y-Ba-Cu-O pellet as func-
FIG. 13. Odd-harmonic susceptibilities $\chi'_s$ and $\chi''_s$ ($n = 1, 3, 5, 7$) as functions of $H_{ac}$; $T = 76 \text{ K}$, $\mu_0H_{ac} = 2.121 \text{ mT}$, $f_1 = 73 \text{ Hz}$. The curves were obtained by cubic-spline smoothing.

FIG. 14. Model calculations of odd-harmonic susceptibilities $\chi'_s$ and $\chi''_s$ ($n = 1, 3, 5, 7$) as functions of $H_{ac}$; $\mu_0H_{ac} = 4.243 \text{ mT}$, $\mu_0H_{ac} = 2.121 \text{ mT}$, $f_1 = \text{arbitrary}$.

ctions of temperature for an ac field $\mu_0H_{ac} = 0.424 \text{ mT}$ at $f_1 = 73 \text{ Hz}$. The ninth harmonic is not shown. There was a superimposed dc field $\mu_0H_{dc} = 0.424 \text{ mT}$. The theoretical curves are shown in Fig. 10. They are quite different from the theoretical curves for $H_{dc} = 0$ in Fig. 8.

In Fig. 11, we show the even-harmonic susceptibilities $\chi'_n$ and $\chi''_n$ ($n = 2, 4, 6, 8$) of the Y-Ba-Cu-O pellet as functions of temperature for an ac field $\mu_0H_{ac} = 0.424 \text{ mT}$ at $f_1 = 73 \text{ Hz}$. The tenth harmonic is not shown. There was a superimposed dc field $\mu_0H_{dc} = 0.424 \text{ mT}$. The theoretical curves are shown in Fig. 12.

The signs of the harmonics depend on the polarity of the superimposed dc field. We observed, for example, that the curves of second harmonic susceptibilities $\chi'_2$ and $\chi''_2$ as functions of $T$ both shift phase by $\pi$ (change their sign) for a negative dc bias field.

4. Field and frequency dependences of third-harmonic susceptibility

The third-harmonic susceptibilities $\chi'_3$ and $\chi''_3$ are the strongest and the most easily measured of the higher harmonics. We measured the third-harmonic susceptibilities $\chi'_3$ and $\chi''_3$ of the Y-Ba-Cu-O pellet as functions of temperature for different ac fields $H_{ac}$. The shift of the coupling transition with increasing ac field is similar to the behavior of the fundamental (Fig. 1). The increase in magnitudes of $\chi'_3$ and $\chi''_3$ with increasing $H_{ac}$ reflects the increase in nonlinearity, including hysteresis, in the magnetization as a function of field.

There were subtle frequency effects in the range $7.3 \leq f_1 \leq 1460 \text{ Hz}$. These appeared as slight changes in the shapes of $\chi'_3(T)$ and $\chi''_3(T)$. In addition, there were small shifts in the temperature position of the coupling peak in $|\chi'_3|$ of similar magnitude to frequency shifts seen in the $\chi''_3$ coupling peak.57 The Kim model, and other critical-state models, do not predict frequency-dependent susceptibilities.

C. Effect of dc field at constant temperature

We measured the dc-field dependence of harmonic susceptibility with the sample immersed in liquid nitrogen at 76 K. The odd harmonics were even functions of dc field.
and the even harmonics were odd functions of dc field. This was also true in measurements at 4 K. By selecting the appropriate ac-field amplitude $H_{ac}$, and modeling with a full penetration field $H_p$ twice as large, we are able to reproduce the key features of all the experimental curves.

Figure 13 shows the odd harmonics for $\mu_0H_{ac}=2.121$ mT and $-4.5<\mu_0H_{dc}<4.5$ mT. The theoretical curves in Fig. 14 are similar, but show more detail. Figures 15 and 16 show the experimental and theoretical even harmonics. Good quantitative agreement was obtained for $n<5$.

V. CONCLUSION

We investigated the intergrain coupling characteristics of sintered Y-Ba-Cu-O by means of the harmonic susceptibilities $\chi'_n$ and $\chi''_n$. Like the fundamental $\chi'_1$, the higher harmonics are manifestations of hysteresis and nonlinearity of the magnetization. (As pointed out by Shaulov and Dorman,\textsuperscript{15} $\chi''_1$ could also result from hysteretic but linear behavior.) We compared the experimental results with theoretical susceptibility curves based on equations derived by Ji \textit{et al.} from a simplified Kim model for critical-current density. The theoretical curves are in good agreement with the temperature- and field-dependent features of $\chi'_n$ and $\chi''_n$. This is evidence that the intergrain coupling component has all the features of a type-II superconductor with reduced $J_c$, $H_p$, and $T_c$. Based on the results of experiments in which the coupling component is shown to disappear upon powdering,\textsuperscript{48-50} we surmise that coupling is achieved by the proximity effect or by microbridges. In principle, agreement with the model for intrinsic intragrain properties could be tested using a high-field ac susceptometer.

The simplified Kim model tends to exaggerate the magnetization near zero field,\textsuperscript{33} magnifying $\chi''_1$ and $|\chi_1|$. Numerical agreement between experiment and theory is improved if the complete Kim model is used, as was done by Müller \textit{et al.} for $\chi'_1$ and $\chi''_1$ as functions of temperature\textsuperscript{14} and for $|\chi_n|$ at a fixed temperature.\textsuperscript{36} Alternative approaches, such as dynamic-loop,\textsuperscript{16-19} and nonlinear-magnetoresistance\textsuperscript{20} models have been used with some success to explain the harmonic power spectrum, $|\chi_n|$.
By comparing theoretical and experimental susceptibility curves and using a realistic model for the magnetization process, one could deduce $H_p(T)$ and $J_x(T)$. The experimental behavior of the higher harmonics, particularly the complex form $\chi'' - i\chi''$, serves as an important test of the Kim critical-state model or other models.

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APPENDIX: ALTERNATIVE DEFINITION FOR HARMONIC SUSCEPTIBILITY

In this paper, we defined the applied magnetic field as

$$H(t) = H_{ac} \text{Im}(e^{i\omega t}) = H_{ac} \sin(\omega t),$$

where $\text{Im}(\cdot)$ denotes the imaginary part of the complex variable. An alternative definition of the harmonic susceptibility is for an applied field

$$H(t) = H_{ac} \text{Re}(e^{i\omega t}) = H_{ac} \cos(\omega t),$$

where $\text{Re}(\cdot)$ denotes the real part. In this case, the magnetization $M(t)$ is

$$M(t) = H_{ac} \sum_{n=1}^{\infty} \text{Re}(\kappa_n e^{i\omega t})$$

$$= H_{ac} \sum_{n=1}^{\infty} \left[ \kappa'_n \cos(n\omega t) + \kappa''_n \sin(n\omega t) \right]. \quad (A1)$$

The harmonic susceptibilities $\kappa_n = \kappa'_n - i\kappa''_n$ ($n = 1, 2, 3, \ldots$) can be evaluated by

$$\kappa'_n = -\frac{1}{\pi H_{ac}} \int_0^{2\pi} M(t) \cos(n\omega t) dt, \quad (A2)$$

$$\kappa''_n = -\frac{1}{\pi H_{ac}} \int_0^{2\pi} M(t) \sin(n\omega t) dt.$$

The physical meanings of $\kappa'_1$ and $\kappa''_1$ are preserved by this definition.

We can relate $\chi_n$ to $\kappa_n$ as

$$\chi'_m - 3 = \kappa'_m - 3, \quad \chi''_m - 3 = \kappa''_m - 3,$$

$$\chi'_4 = \kappa'_4, \quad \chi''_4 = \kappa''_4,$$

where $m = 1, 2, 3, \ldots$. In complex notation, $\chi_n = (-1)^{3n+1}/2\kappa_n$, $n = 1, 2, 3, \ldots$. Note that the real and imaginary parts are interchanged for even harmonics, but $|\chi_n|$ is always equal to $|\kappa_n|$ for all $n$. These relations should be kept in mind for interlaboratory comparisons of the harmonic susceptibilities as well as for theoretical calculations.