Flux creep and activation energies at the grain boundaries of Y-Ba-Cu-O superconductors

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We measured the ac susceptibility of sintered $YBa_2Cu_3O_{7-\delta}$ pellets as a function of temperature and ac magnetic-field amplitude and frequency. The imaginary part of the susceptibility χ'' exhibits two peaks. A narrow peak is located at the critical temperature of the grains. A broad peak at lower temperature is attributed to hysteresis losses at the grain boundaries. There is a small shift in this coupling peak to higher temperature as the frequency increases from 10 to 1000 Hz. We explain the shift in terms of Anderson flux creep on a time scale of milliseconds. The shift depends on the amplitude of the measuring field. The activation energy for flux creep ranges from 11.9 ± 1.0 eV in the zero-field limit [0.8 $A m^{-1}$ (0.01 Oe)] to 1.2 ± 0.3 eV at 800 $A m^{-1}$ (10 Oe). We extrapolate our data to find the value for an intergrain decoupling field of 1–2 $kA m^{-1}$ (13–25 Oe), above which flux creep presumably becomes flux flow at the grain boundaries.

I. INTRODUCTION

In addition to electrical resistivity, ac susceptibilty has been used to study the properties of high-critical-temperature (high-T_c) copper oxide superconductors. In particular, the susceptibility method is useful in determining the characteristics of the coupling component —variously referred to as weak links, Josephson junctions, bad component, grain boundaries, or intergranular component— in sintered, polycrystalline samples.[1–9]

We have measured the ac susceptibility of sintered $YBa_2Cu_3O_{7-\delta}$ pellets as a function of temperature and ac magnetic-field amplitude and frequency. Below the critical temperature, the imaginary part of susceptibility exhibits a broad peak that is attributed to hysteresis losses at the grain boundaries. There is a shift in this coupling peak to higher temperature with increasing frequency in the 10–1000 Hz range. This shift is very small, especially for fields of 80 $A m^{-1}$ (1 Oe) and below. Most groups measuring low-field ac susceptibility have reported no significant shift with frequency.[1–9] But shifts have been reported for relatively large ac fields,[10] and in Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O single crystals when large dc fields were superimposed upon small ac fields.[11–13]

The shift in the susceptibility curves may be interpreted as arising from flux creep at the grain boundaries. Flux creep was first predicted by Anderson, following the Abrikosov theory, in which the smallest possible breakdown of superconductivity is the motion of a quantum of magnetic flux. Anderson suggested that an energy barrier prevented the creep of flux lines.[14–17] In the presence of a current density **J**, the flux lines experience a Lorentz force per unit volume $\mathbf{J}\times\mathbf{B}$, which moves them sideways. **B** is the penetrated flux density. The flux motion is resisted by viscous drag and by inhomogeneities in the lattice that pin the flux. Once the Lorenz force exceeds the pinning force, electrical resistance is introduced because of flux flow. Even with pinning, the resistance is not exactly zero because thermally activated fluctuations can overcome pinning. This process is known as flux creep.

Flux creep is thought to be a small effect in conventional, hard superconductors, especially on a time scale of milliseconds. However, at the considerably higher temperatures of high-T_c superconductors, thermally activated flux creep can be a significant effect.[18] In this paper, we calculate the flux creep activation energies at the grain boundaries as a function of the applied magnetic field. The calculations are based on the temperature shifts with frequency of the coupling peak of susceptiblity.

II. EXPERIMENTAL DETAILS

The $YBa_2Cu_3O_{7-\delta}$ pellets were fabricated by mixing and grinding powders of Y_2O_3, $BaCO_3$, and CuO, 99.999% pure or better, calcining in flowing oxygen at 938 °C for 10 h, and then at 450 °C for 10 h. This was followed by pressing the powder into pellets, 6.3 mm in diameter and about 2 mm thick, at pressures of 100–1000 MPa. The pellets were annealed at 938 °C for 24 h and then at 450 °C for 10 h. Finally, the samples were cooled to room temperature.

Volume susceptibility was measured with a calibrated ac susceptometer. We used a dual-phase lock-in amplifier to simultaneously measure the imaginary (χ'') and real (χ') parts of susceptibility. The phase angle of the lock-in amplifier was adjusted for each measurement frequency to null χ'' for a small measuring field at 4 K. The phase adjustment was maintained for measurements at higher fields. Otherwise, inconsistencies in phase adjustment could give spurious frequency shifts in the susceptibility curves. A sinusoidal ac current was applied to a primary coil and an induced voltage was measured in the pick-up coil. The pick-up coil was compensated so that zero voltage was detected when no sample was present, and thus the induced voltage was proportional to susceptibility.[19]

Measurements were made with the magnetic field either parallel or perpendicular to the axes of the cylindrical pellets. The susceptibilities were corrected for a demagnetization factor. A high-permeability shield around the Dewar reduced the Earth's field to less than 0.4 $A m^{-1}$

(0.005 Oe) in the measurement axis. The sample was cooled to about 10 K with the primary coil shorted. Measurements were made with temperature increasing at a rate of 1 K/min or less in a range of fields from 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe) to 4.8 $\mathrm{kA\,m^{-1}}$ (60 Oe) for frequencies from 10 to 1000 Hz. All fields are reported as rms values. No dc bias field was applied. After we confirmed the frequency shift for all our pellets, we focused our measurements on a single pellet pressed at 250 MPa. The field was applied parallel to its axis. The pellet's density was 3.0 $\mathrm{g\,cm^{-3}}$, about 47% of the ideal x-ray density of 6.4 $\mathrm{g\,cm^{-3}}$.

III. RESULTS

In our measurements of ac susceptibility of sintered copper oxide superconductors we distinguish between the coupling (grain boundaries) and intrinsic (grain) components.[1-9] In the imaginary part (χ'') we observe two peaks that reflect energy dissipation [Fig. 1(a)]. As temperature increases towards T_c from below, flux lines and bulk shielding currents penetrate the material when the measuring field exceeds the lower critical field.[1] This creates losses that are primarily hysteretic in character. When the flux lines and shielding currents fully penetrate the material, the losses reach a maximum.[9,20] As temperature increases beyond T_c, the losses drop to zero. These same processes occur around T_c of the grains (intrinsic) or of the grain boundaries (coupling).

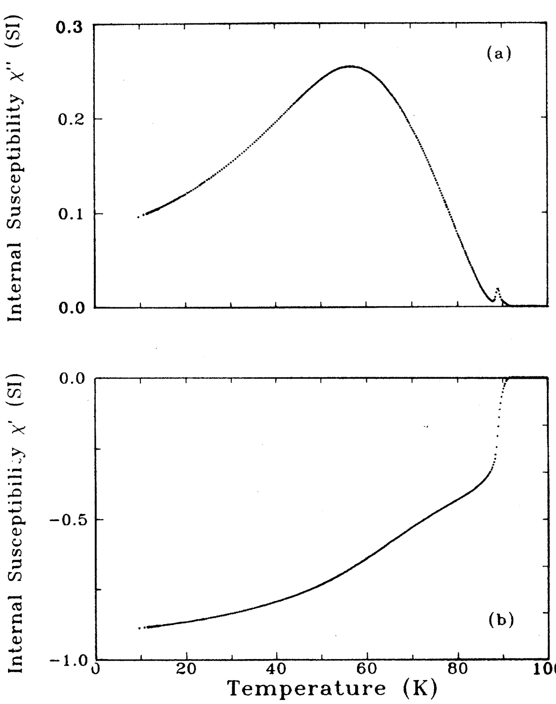

FIG. 1. Real (χ') and imaginary (χ'') parts of susceptibility for an applied magnetic field of 800 $\mathrm{A\,m^{-1}}$ (10 Oe) at 1000 Hz. Shown are (a) the coupling and intrinsic peaks in χ'' (the intrinsic peak considerably smaller in size), and (b) the intrinsic (steep) and coupling components of χ'.

The coupling peak is distinct for fields as low as 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe). At that field, the peak is positioned in temperature at about the intrinsic T_c of the grains. As the field amplitude is increased, the peak is shifted to lower temperatures and broadens. For temperatures above the peak, for a given measuring field, the grains are decoupled. Below the peak, the grains are coupled, which permits the real part (χ') of the susceptibility to reach -1 (SI) in small fields. For a field of 1.6 $\mathrm{kA\,m^{-1}}$ (20 Oe), χ'' peaks at 4 K. We call this the measured decoupling field for this sample.

The intrinsic peak is barely visible until the applied field reaches about 800 $\mathrm{A\,m^{-1}}$ (10 Oe). Its height is several times smaller than that of the coupling peak [Fig. 1(a)]. Its position shifts very little in temperature as the field is increased from 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe) to 4.8 $\mathrm{kA\,m^{-1}}$ (60 Oe).

The real part of susceptibility (χ') shows a drop from 0 to as low as -1, depending on temperature and the field amplitude [Fig. 1(b)]. The drop has an inflection point. The intrinsic component corresponds to the steep drop at 90 K. The coupling component is the second segment that decreases less steeply in temperature. It is particularly distinct at fields of 80 $\mathrm{A\,m^{-1}}$ (1 Oe) and above.

The intrinsic component of χ' is nearly insensitive to the applied magnetic field. There is no shift in temperature as the field increases from 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe) to 1.6 $\mathrm{kA\,m^{-1}}$ (20 Oe). The coupling component, on the other hand, significantly shifts to lower temperature as the field is increased in this range.

As frequency was increased, the coupling components of χ' and χ'' showed slight shifts to higher temperature. As our reference point for specifying the temperature shift, we used the temperature of the peak in χ''. Since the measurements were made in increments of about 0.2 K, we fitted the three points near the maximum of χ'' with a parabola to get an improved value for the peak temperature. We estimate that the peak temperature determinations were precise within 0.1 K. The peak shift in temperature as the frequency increased from 10 to 1000 Hz ranged from 0.25 K at 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe) to 1.4 K at 800 $\mathrm{A\,m^{-1}}$ (10 Oe).

In Fig. 2 we plot $\ln f$ vs $1/T_p$ for a field of 80 $\mathrm{A\,m^{-1}}$ (1 Oe). Here f is the driving frequency and T_p is the temperature of the χ'' coupling peak. We obtain an approxi-

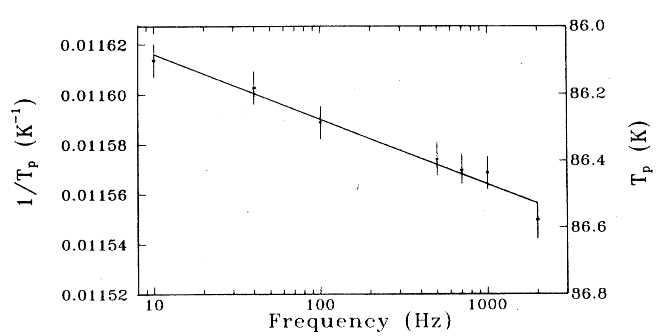

FIG. 2. Plot of $1/T_p$ vs $\ln f$ at 80 $\mathrm{A\,m^{-1}}$ (1 Oe). T_p is the temperature of the coupling peak and f is the driving frequency.

mately linear fit to the Arrhenius expression

$$f = f_0 \exp(-E_a/kT_p) ,$$

where E_a is the thermal activation energy, k is Boltzmann's constant, and f_0 is a characteristic frequency. E_a includes a barrier height and a field-dependent force term.[15,16]

From our Arrhenius plots for several driving fields we compute the activation energy as function of applied magnetic field. These are summarized in Fig. 3. We plot the data on a logarithmic scale to expand the low-field values. The energies vary from 11.9 eV at 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe) to 1.2 eV at 800 $\mathrm{A\,m^{-1}}$ (10 Oe). We estimate that the accuracy of the energies is within 1 eV at the lower fields and within 0.3 eV at the higher fields. The energy barrier in the zero-field limit is thus about 12 eV.

By extrapolation, $E_a = 0$ at 1–2 $\mathrm{kA\,m^{-1}}$ (13–25 Oe). We call this the extrapolated decoupling field. It is comparable to our measured decoupling field of about 1.6 $\mathrm{kA\,m^{-1}}$ (20 Oe), where the data show the disappearance of the coupling peak in χ''. For fields below 80 $\mathrm{A\,m^{-1}}$ (1 Oe), E_a is large and frequency shifts are minimal. This could explain the frequency independence of the susceptibility curves reported in other papers.[1-9]

Finally, we examined the frequency dependence of the intrinsic peak in χ'', corresponding to grains. There was no detectable frequency dependence at fields of 2.4 $\mathrm{kA\,m^{-1}}$ (30 Oe) and below. It was not until a field as large as 4.8 $\mathrm{kA\,m^{-1}}$ (60 Oe) was used that there was a distinct shift in temperature of 0.47 K as the frequency increased from 10 to 1000 Hz. That corresponds to an activation energy of 6.2 eV. Our experimental apparatus did not allow us to work with higher ac fields. We expect the intrinsic activation energy to decrease as fields increase beyond 4.8 $\mathrm{kA\,m^{-1}}$ (60 Oe).

Several determinations of flux-creep activation energies have been reported for single crystals. Those measurements were made with large dc bias fields[11-13] or by studying relaxation of high-field magnetization on a time scale of minutes.[21] Our activation energies are not directly comparable for the following reasons: (1) We use a simple Arrhenius expression to model thermal activation.

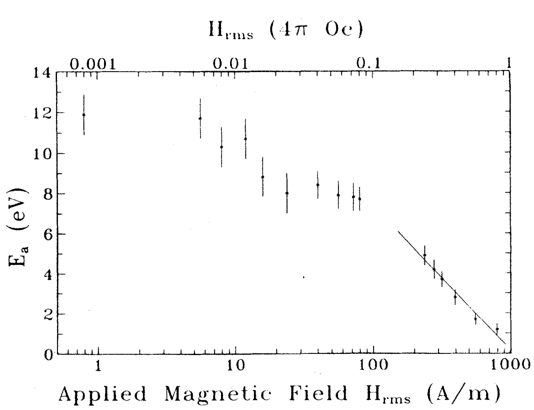

FIG. 3. Plot of the thermal activation energy E_a at the grain boundaries vs the applied magnetic-field amplitude.

(2) Except for the intrinsic activation energy for the grains mentioned above, our work refers to the grain boundaries. (3) Our measurements are for small ac fields with no dc bias field.

IV. DISCUSSION

In this paper, we explain the frequency shift of the χ'' coupling peak in terms of flux creep. The effect is small and depends on the magnitude of the measuring field. Most of the losses seen in χ'' are hysteretic and frequency independent, originating from the viscous motion of flux lines and the irreversible penetration of bulk shielding currents over the field cycle. In addition to hysteresis loss, there is thermally activated flux creep that is frequency dependent. The frequency range 10–1000 Hz implies flux creep on a time scale of milliseconds. At a given temperature near the coupling peak, higher frequencies allow less time for flux to penetrate the intergranular component. This tends to improve its shielding ability.

Flux creep at the grain boundaries was measured for fields as small as 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe). As the field increases, the Lorentz force $\mathbf{J} \times \mathbf{B}$ increases, the thermal activation energy decreases, and more flux vortices get depinned during the field cycle. When the field reaches a decoupling value of 1–2 $\mathrm{kA\,m^{-1}}$ (13–25 Oe), the activation energy drops to zero, and flux creep presumably becomes flux flow at the grain boundaries.

At the grain boundaries, the $YBa_2Cu_3O_{7-\delta}$ may be degraded and have a different stoichiometry.[22-24] This would impair flux pinning and enhance flux creep in this region compared to the interior of the grains. The intrinsic behavior of the grains is expected to follow the flux-creep model as well, but at higher applied fields.

V. CONCLUSION

Flux creep at the grain boundaries should be considered for sintered high-T_c superconductors. The coupling component of susceptibility has a small temperature shift with frequency in the range 10–1000 Hz. In a field of 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe), the shift was only 0.25 K. At 800 $\mathrm{A\,m^{-1}}$ (10 Oe), the shift was 1.4 K. We interpreted the shift in terms of flux creep at the grain boundaries. Depending on the value of the applied magnetic field, the activation energies ranged from 1.2 eV at 800 $\mathrm{A\,m^{-1}}$ (10 Oe) to 11.9 eV at 0.8 $\mathrm{A\,m^{-1}}$ (0.01 Oe).

Analysis of the thermal activation energies leads to the concept of a grain decoupling field. As the magnetic field is increased, flux creep becomes easier. When the magnetic field reaches a decoupling value of 1–2 kA/m (13–25 Oe) the activation energy vanishes. In terms of the susceptibility curves, the coupling peak in χ'' vanishes.

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[1]R. B. Goldfarb, A. F. Clark, A. I. Braginski, and A. J. Panson, Cryogenics **27**, 475 (1987).

[2]D.-X. Chen, R. B. Goldfarb, J. Nogués, and K. V. Rao, J. Appl. Phys. **63**, 980 (1988).

[3]H. Mazaki, M. Takano, R. Kanno, and Y. Takeda, Jpn. J. Appl. Phys. **26**, L780 (1987).

[4]H. Mazaki, M. Takano, Y. Ikeda, Y. Bando, R. Kanno, Y. Takeda, and O. Yamamoto, Jpn. J. Appl. Phys. **26**, L1749 (1987).

[5]J. García, C. Rillo, F. Lera, J. Bartolomé, R. Navarro, D. H. A. Blank, and J. Flokstra, J. Magn. Magn. Mater. **69**, L225 (1987).

[6]R. Renker, I. Apfelstedt, H. Küpfer, C. Politis, H. Rietschel, W. Schauer, H. Wühl, U. Gottwick, H. Kneissel, U. Rauchschwalbe, H. Spille, and F. Steglich, Z. Phys. B **67**, 1 (1987).

[7]H. Küpfer, I. Apfelstedt, W. Schauer, R. Flükiger, R. Meier-Hirmer, and H. Wühl, Z. Phys. B **69**, 159 (1987).

[8]D.-X. Chen, J. Nogués, N. Karpe, and K. V. Rao, Kexue Tongbao (Beijing, English edition) **33**, 560 (1988).

[9]F. Gömöry and P. Lobotka, Solid State Commun. **66**, 645 (1988).

[10]K. V. Rao, D.-X. Chen, J. Nogués, C. Politis, C. Gallo, and J. A. Gerber, in *Proceedings of the Symposium on High Temperature Superconductivity,* edited by D. U. Gubser and M. Schluter (Materials Research Society, Pittsburgh, 1987), Vol. EA-11, p. 133.

[11]A. P. Malozemoff, T. K. Worthington, Y. Yeshurun, F. H. Holtzberg, and P. H. Kes, Phys. Rev. B **38**, 7203 (1988).

[12]T. K. Worthington, Y. Yeshurun, A. P. Malozemoff, R. M. Yandrofski, F. H. Holtzberg, and T. R. Dinger, in *Proceedings of the International Conference on Magnetism, Paris, 1988* [J. Phys. (Paris) Colloq. (to be published)].

[13]J. van den Berg, C. J. van der Beek, P. H. Kes, J. A. Mydosh, M. J. V. Menken, and A. A. Menovsky, Supercond. Sci. Technol. **1**, 249 (1989).

[14]P. W. Anderson, Phys. Rev. Lett. **9**, 309 (1962).

[15]P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. **36**, 39 (1964).

[16]M. R. Beasley, R. Labusch, and W. W. Webb, Phys. Rev. **181**, 682 (1969).

[17]M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975), Chap. 5.

[18]D. Dew-Hughes, Cryogenics **28**, 674 (1988).

[19]R. B. Goldfarb and J. V. Minervini, Rev. Sci. Instrum. **55**, 761 (1984).

[20]J. R. Clem, Physica C **153–155**, 50 (1988).

[21]Y. Yeshurun, A. P. Malozemoff, T. K. Worthington, R. M. Yandrofski, L. Krusin-Elbaum, F. H. Holtzberg, T. R. Dinger, and G. V. Chandrashekhar, Cryogenics **29**, 258 (1989).

[22]Y. M. Chiang, J. A. S. Ikeda, and A. Roshko, in *Ceramic Superconductors II,* edited by M. F. Yan (American Ceramics Society, Westerville, Ohio, 1988) p. 607.

[23]S. E. Babcock, T. F. Kelly, P. J. Lee, J. M. Seuntjens, L. A. Lavanier, and D. C. Larbalestier, Physica C **152**, 25 (1988).

[24]P. Dubots and J. Cave, Cryogenics **28**, 661 (1988).