Flux pinning at grain boundaries in Bi-(Pb)-Sr-Ca-Cu-O ceramic superconductors

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For low magnetic-field amplitudes the imaginary part of the ac susceptibility, $\chi''(T)$, in ceramic high-temperature superconductors represents the intergranular bulk pinning loss. The loss peak at T_p shifts to lower temperature with increasing ac field and to higher temperature with increasing frequency. We have measured the shift of the χ'' peak in ceramic Bi-(Pb)-Sr-Ca-Cu-O samples. The Anderson flux-creep model in conjunction with the critical-state model for Josephson vortices is employed to explain quantitatively the dependence of T_p on frequency and ac field. The model allows the determination of the intergranular pinning potential, where pinning occurs at grain-boundary intersection points.

I. INTRODUCTION

When a magnetic field greater than the lower critical Josephson field is applied to a ceramic high-temperature superconductor, the field penetrates the intergranular weak-link network, generating a distribution of Josephson vortices inside the sample. Spatial variations of the Josephson coupling energy, disorder in the grain boundary junction array, and intersecting junctions produce a spatial variation of the vortex free energy which leads to intergranular flux pinning.[1,2] ac susceptibility measurements on high-T_c ceramic superconductors, using weak ac magnetic fields, are ideally suited to investigate the nature of the intergranular pinning mechanism because, in analogy with conventional superconductors, a critical state describes the magnetic behavior of these new granular superconductors.[2–6]

For ceramic $YBa_2Cu_3O_{7-\delta}$ it has been shown that the dependence of $\chi'(T)$ and $\chi''(T)$ on the ac magnetic field amplitude, H_{ac}, is determined by the pinning force density and that the dependence of the susceptibility on frequency f is determined by the value for the intergranular pinning potential.[7,8]

In this paper we report on $\chi''(T,H_{ac},f)$ measurements for a high-T_c phase Bi-Pb-Sr-Ca-Cu-O sample and a low-T_c phase Bi-Sr-Ca-Cu-O sample. A "finite-temperature" critical-state model for a granular superconductor, which considers the effects of intergranular flux creep, is employed in order to explain quantitatively the observed frequency and field dependence of χ''. Values for the intergranular pinning potential are determined and its functional dependence on magnetic field and temperature is discussed.

II. EXPERIMENTAL DETAIL

A $Bi_{1.84}Pb_{0.34}Sr_{1.91}Ca_{2.03}Cu_{3.06}O_{10}$ high-T_c phase sample (χ' onset at 107 K, zero resistivity at 103 K) was prepared by first forming a lead-free precursor by a solid-state reaction at 800–840 °C. After addition of the requisite quantity of Pb-O, sintering was performed at 860 °C for 14 h, followed by regrinding and final sintering at 850 °C for 66 h, all in air. The sample was cooled at 1 °C/min to 800 °C, then at 3 °C/min to 400 °C where it was annealed for 4 h in air. From x-ray diffraction it was established that the specimen consisted almost completely of single 2:2:2:3 phase. In addition, a $Bi_2Sr_2CaCu_2O_8$ low-T_c phase sample (χ' onset at 93 K, zero resistance at 73 K) was prepared using standard powder ceramic techniques. Final sintering was done at 860 °C for 5 h in air, followed by quenching in liquid nitrogen. Both samples were cut and filed into cylindrical shape, 11 mm long and 3 mm in diameter.

The ac susceptibility was measured using a Lakeshore-7000 susceptometer. A dual-phase lock-in amplitude was used to simultaneously measure the imaginary and real parts, χ' and χ'', of the susceptibility. The phase angle of the lock-in amplifier was readjusted for each frequency in order to zero the χ'' signal for a small measuring field at the lowest temperature. This phase adjustment was maintained at higher fields. A sinusoidal ac current was applied to the primary coil generating a homogeneous applied ac magnetic field and an induced voltage was measured across two nearly identical secondary coils in tandem. The pickup coils were compensated such that zero voltage was detected when no sample was present and thus the voltage was proportional to the time derivative of the sample's magnetization. The sample was placed in one of the secondary coils and aligned such that the cylinder axis was parallel to the applied field. Measurements were taken with temperature increasing at a rate of about 1 K/min for different fields, ranging from 0.01 Oe (0.8 A/m) to 10 Oe (800 A/m) and frequencies of 10, 100, and 1000 Hz. All fields are reported as rms values.

III. THE MODEL

The imaginary part of the ac susceptibility, χ'', is proportional to the area of the normalized hysteresis loop, $\langle B \rangle / H_{\mathrm{ac}}$ versus H_a/H_{ac}, where $\langle B \rangle$ is the spatially averaged flux density in the sample, H_a the applied magnetic field and H_{ac} the ac field amplitude.[9] The critical-state model shows that as the temperature approaches T_p, where χ'' peaks, the flux penetrates deeper and deeper into the sample, which cause the normalized hysteresis loop to widen. The loop area is found to be largest at T_p where the flux fully penetrates the sample. For temperatures above T_p, flux pinning weakens such that flux easily penetrates the sample and $\langle B \rangle$ is close to "equilibrium" with H_a. This causes a decrease of the hysteresis loop area. A critical-state model for a granular superconductor, where superconducting grains are weakly Josephson-coupled, was described in Ref. 7, where the calculated $\chi'(T,H_{\mathrm{ac}})$ and $\chi''(T,H_{\mathrm{ac}})$ were shown to be in excellent agreement with experimental data for ceramic $YBa_2Cu_3O_{7-\delta}$.

In order to understand the frequency dependence of the ac susceptibility, it is necessary to employ a "finite-temperature" critical-state model, which accounts for the influence of thermally activated flux creep on the critical-state profiles. A model which considers flux creep in an approximate way was already described in Ref. 8. Here, we improve this model by taking backwards hopping of flux lines into account and reducing the number of model parameters.

In the case of a long cylindrical sample with radial coordinate r, where the applied field is parallel to the cylinder axis, the critical-state equation for the intergranular magnetic field profile, H, is

$$\frac{dH(r)}{dr} = \pm \frac{F_P}{|B(r)|} , \tag{1}$$

where F_P is the intergranular pinning force density of Josephson vortices. Using the Anderson flux creep model,[10] one obtains for the pinning force density

$$F_P = \frac{kT}{V_b r_p} \operatorname{arcsinh} \left[\frac{\nu_h}{\nu_0} \exp \frac{U(T,H)}{kT} \right] , \tag{2}$$

where $U(T,H)$ is the average intergranular pinning potential, r_p the potential range, V_b is the flux bundle volume, ν_0 the attempt frequency for hopping, and ν_h is the "minimal-observable" flux-line hopping rate.

It has been shown that for an isolated Josephson vortex in a two-dimensional (2D) array of grains the pinning potential range, r_p, is equal to the grain radius, R_g, and the depth of the pinning potential, $U(T,H=0)$, is proportional to I_0, the maximum Josephson-junction current flowing across a grain boundary.[11] In the case of magnetically overlapping vortices, we assume that I_0 decreases with magnetic field, H, according to a Fraunhofer-like pattern.[12] Because in real materials a broad grain size distribution exists, the pronounced dips in the Fraunhofer pattern disappear for the averaged $I_0(T,H)$, which has the approximate form

$$I_0(T,H) = I_0(T,0) \frac{H_0/2}{|H| + H_0/2} , \tag{3}$$

where

$$H_0 = \frac{\Phi_0}{4\mu_0 \lambda_L(T) \overline{R}_g} . \tag{4}$$

Here, Φ_0 is the flux quantum, $\overline{R}_g$ the average grain radius, and λ_L the London penetration depth for the grains (ignoring anisotropy), $\lambda_L(T) = \lambda_L(0)[1-(T/T_c)^4]^{-1/2}$. Because of Eq. (3) the intergranular pinning potential can be factorized as

$$U(T,H) = U_0(T) \frac{H_0/2}{|H| + H_0/2} . \tag{5}$$

It was assumed that $U_0(T)$ has the simple form

$$U_0(T) = U_0(0)(1 - T/T_c)^{\alpha} . \tag{6}$$

For *SIS*-type grain boundary junctions one would use $\alpha = 1$, and for *SNS*-type,[12] $\alpha = 2$. The intergranular flux bundle volume V_b in Eq. (2) was taken as

$$V_b = \frac{\Phi_0}{|B|} 2\overline{R}_g , \tag{7}$$

where the correlation length along an intergranular flux line, which meanders around grains, was assumed to be equal to the average grain size $2\overline{R}_g$.

The "minimal-observable" hopping rate, ν_h, for an applied steady magnetic field, is the inverse of the measuring time. In the case of a long cylindrical sample with radius R and an applied magnetic ac field of amplitude H_{ac} and frequency f, one finds for the minimal-observable hopping rate

$$\nu_h \simeq \frac{8\Phi_0 H_{\mathrm{ac}} \overline{R}_g^{\,2}}{RkT} f . \tag{8}$$

Equation (8) was derived by equating the time derivative of the applied field, averaged over the first half of an ac cycle, to the time derivative of the decaying field inside the sample, where the field inside was assumed to decay with time t as $\sim [1-(kT/U_0)\ln(t\nu_0)]$. The attempt frequency ν_0 was related to the relevant dimensions of V_b and the velocity of sound $c_s \simeq 3\times 10^3$ m s^{-1}.

Equation (1) with the boundary condition $H(R,t) = H_{\mathrm{ac}}\cos(2\pi f t)$ was solved in a similar way as outlined in Ref. 7, where the effect of flux creep had been neglected ($F_P = U/V_b r_p$). The spatially averaged intergranular flux density $\langle B \rangle$ was then used to calculate χ'' as defined in Refs. 7 and 9, and the χ''-peak temperature, T_p, was determined as a function of the ac field amplitude, H_{ac}, and frequency f. The results were compared with the experimental data.

IV. RESULTS AND DISCUSSION

In order to calculate $T_p(H_{ac},f)$, values for the material parameters $\lambda_L(0)$, $\bar{R}_g$, $U_0(T=0)$, and α [Eq. (6)] had to be chosen. For the London penetration depth at zero temperature, $\lambda_L(0)$, we used 0.4 μm. The average grain size, $\bar{R}_g$, was estimated using polarized light microscopy on polished areas of the samples. A rough estimate led to $\bar{R}_g \simeq 2-4$ μm for the high-T_c phase sample and $\bar{R}_g \simeq 3-8$ μm for the low-T_c phase sample. The intergranular potential depth at zero magnetic field, $U_0(T=0)$, and the exponent α in Eq. (6) were chosen such that $T_p(H_{ac})$ at $f=100$ Hz agreed best with the experimental data.

Figure 1 shows experimental and calculated values of T_p for the high-T_c phase sample as a function of H_{ac} at the fixed frequency of $f=100$ Hz. For the calculation $\bar{R}_g=3$ μm, $U_0(T=0)=18$ eV, and $\alpha=1.5$ were used. Figure 1 illustrates that the experimental data and the calculation agree within 1 K. It was found that the tempeature shift of T_p, as the frequency increases from 10 to 1000 Hz, ranged from 0.6 K at 0.01 Oe to 2.1 K at 10 Oe for the high-T_c phase sample and from 3.7 K at 0.01 Oe to 9 K at 1 Oe for the low-T_c phase sample. The experimental curves for T_p^{-1} as a function of $\ln(f)$ at different amplitudes, H_{ac}, were linear and could be fitted by an Arrhenius expression, $f=f_0\exp(-E_a/kT_p)$, where the energy E_a depends on the amplitude H_{ac}. A similar behavior was previously found for ceramic $YBa_2Cu_3O_{7-\delta}$.[13] The calculation for T_p^{-1} also showed a linear dependence on $\ln(f)$. The energy E_a as a function of H_{ac} is shown in Fig. 2 for the high-T_c phase sample. Values for E_a vary from 7.0±1.0 eV at 0.01 Oe to 1.5±0.3 eV at 10 Oe. The solid line represent the results of the model calculation. It can be seen that the shift of the χ'' peak with frequency for different ac field amplitudes is correctly predicted by the model with the exception of E_a at the very low field of 0.01 Oe, where the experimental determination of E_a is made difficult because of instrumental noise. It is important to recognize that only two "free" material parameters, $U_0(0)$ and α, were used to fit our $T_p(H_{ac}, f=100$ Hz) measurement and that for the calculation of $E_a(H_{ac})$, which characterizes the effect of flux creep on the ac susceptibility, no new or additional parameters were needed.

Figure 3 shows the intergranular pinning potential $U(T,H)$ of Eq. (5) at three different temperatures and for magnetic fields up to 10 Oe. The large value of the average intergranular pinning potential found here does not contradict the low intergranular transport current density commonly measured in sintered ceramic samples as the critical current density is not determined by the pinning potential alone but by the pinning force density which is $F_p \simeq U/V_b r_b$. In the model $V_b r_p = 2\bar{R}_g^2 \Phi_0/|B|$, which is large compared to typical values of $V_b r_p$ for conventional Abrikosov vortex pinning at defects. A large intergranular pinning potential was also determined by Maley *et al.*[14] who measured the rate of magnetic flux creep through a wall of a hollow cylinder of ceramic $YBa_2Cu_3O_{7-\delta}$. They observed a logarithmic time dependence of the magnetic field in the center of the tube for an outside applied steady field of 28 Oe at 75 K and extracted an intergranular potential depth of 1.55 eV.

The measured energies E_a for the low-T_c phase sample were 0.4±0.1 eV at 0.01 Oe, 0.2±0.05 eV at 0.1 Oe, and 0.02±0.005 eV at 1 Oe. The calculation gave E_a(0.01

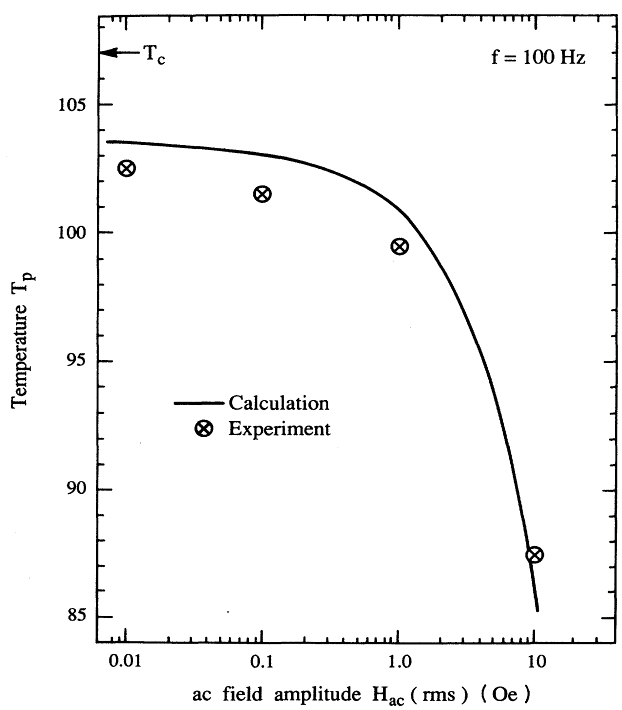

FIG. 1. Measured and calculated χ''-peak temperature, T_p, as a function of the applied ac magnetic field amplitude, H_{ac}, at 100 Hz for the high-T_c phase sample.

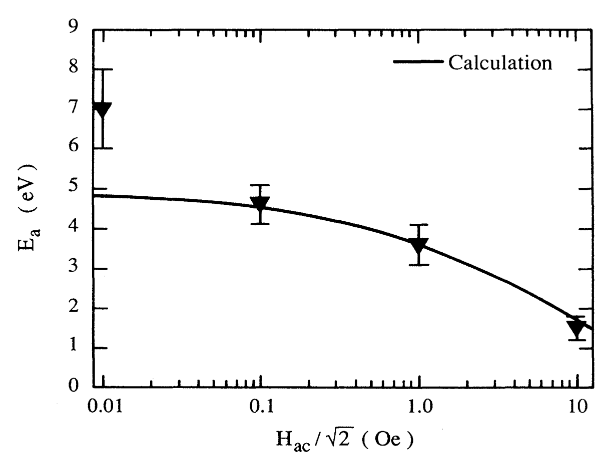

FIG. 2. Measured and calculated energy E_a obtained from the Arrhenius expression $f \sim \exp(-E_a/kT)$ as a function of the applied ac magnetic field amplitude, H_{ac}, for the high-T_c phase sample.

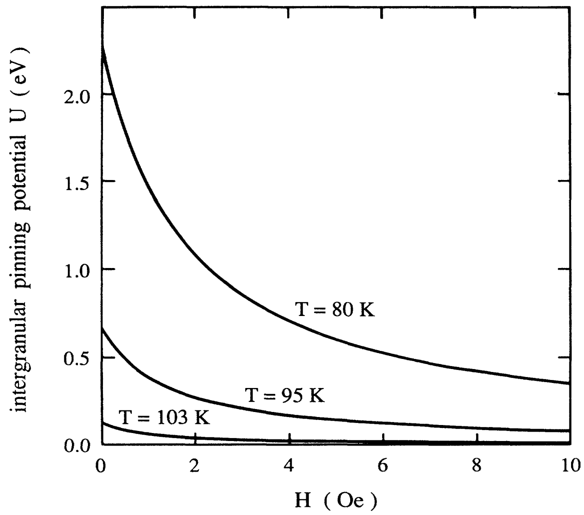

FIG. 3. The intergranular pinning potential, U, as a function of the local magnetic field, H, at different temperatures for the high-T_c phase sample.

Oe)$=$0.25 eV, $E_a(0.1\ \text{Oe})=0.22$ eV, and $E_a(1\ \text{Oe})=0.039$ eV, which predicts the shift of the χ'' peak with frequency reasonably well. Again, the material parameters were chosen to obtain best agreement with the experimental data of T_p versus H_{ac} at $f=100$ Hz. The parameters for the low-T_c phase sample were $\overline{R}_g=7$ μm, $U_0(T=0)=0.25$ eV and $\alpha=1$. The relatively small value for the intergranular pinning potential U_0 reflects the fact that the χ'' peak for an rms amplitude of 1 Oe appears at the low temperature of $T_p \simeq 25$ K, in contrast to $T_p \simeq 100$ K for the high-T_c phase. Because of the very weak intergranular pinning force density of the low-T_c phase sample, a χ'' peak for $2^{-1/2}H_{ac}=10$ Oe is not present above 4.2 K.

It is interesting to notice that in the special case of $\alpha=1$ (linear decrease of U_0 with temperature) the energy $E_a(H_{ac}\simeq 0)$ is equal to $U_0(T=0)$ so that the shift of χ'' with frequency is a direct measure for the pinning potential depth at zero temperature and zero field. This was also outlined in the discussion in Ref. 8.

V. CONCLUSIONS

A "finite-temperature" critical-state model for intergranular Josephson vortices was employed in order to explain the functional dependence of the χ''-peak temperature, T_p, on ac magnetic field amplitude, H_{ac}, and frequency f. Good agreement with experimental data for a Bi-Pb-Sr-Ca-Cu-O and a Bi-Sr-Ca-Cu-O ceramic sample was obtained, assuming that (i) the intergranular flux lines meander between grains where they are pinned at grain boundary intersection points, (ii) the flux-line correlation length is equal to the average grain size, and (iii) the pinning potential decreases with the local magnetic field like $(H_0/2)/(|H|+H_0/2)$. This last assumption reflects the strong field dependence of the Josephson current across grain boundaries. For the low-T_c phase sample a *SIS* junction temperature dependence was found while for the high-T_c phase sample the exponent α, which characterizes the temperature dependence, lies between that of *SIS* and *SNS* junctions.

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