Vibrating-reed studies on non-single-phase Bi-Ca-Sr-Cu-O superconducting ceramics

A. Gupta, P. Esquinazi, and H. F. Braun

Physikalisches Institut, Universität Bayreuth, D-8580 Bayreuth, West Germany

(Received 29 December 1988; revised manuscript received 8 March 1989)

The resonance frequency ω and damping Γ of two selected reeds of Bi-Ca-Sr-Cu-O ceramics were measured between 4.2 and 100 K in different applied magnetic fields up to 0.3 T. The samples showed large anomalies in ω and Γ at $\simeq 60$ and $\simeq 45$ K indicating the existence of different superconducting phases. These anomalies can be interpreted in terms of pinning and hysteretic motion of flux lines. Within experimental resolution x-ray-powder patterns resemble that of the 85-K superconductor $Bi_2CaSr_2Cu_2O_8$.

The existence of three superconducting phases in the quinary system Bi-Ca-Sr-Cu-O with critical temperatures near 10, 85, and 110 K is firmly established.[1] During a study of the rich phase diagram of this system,[2] we found that several samples showed strong diamagnetic features in ac susceptibility and resistive transitions near 45 and 60 K. Generally, such lower-temperature signals would be interpreted as inhomogeneity broadening of the higher superconducting transition or as weak-link lowering of the transition temperature. Since the signal seen in resistivity or even in ac susceptibility measurements is not representative for the superconducting volume fraction of a sample, and since lower-T_c material may be shorted out or shielded by higher-T_c material, we used the superconducting vibrating reed method as a sensitive means to detect superconducting phases. This method has proven valuable for the determination of superconducting properties in amorphous[3–7] and ceramic[7,8] superconductors.

In this paper we present the results of resonance frequency and damping measurements as a function of temperature T and applied magnetic field B_a in two non-single-phase Bi-based ceramic samples. Only the main results will be presented here, while details on irreversibility effects, structural analysis, and preparation conditions will be published elsewhere.[9]

The vibrating-reed technique has been extensively described in recent publications.[3,4] We summarize here the expected behavior of a thin and long superconducting reed performing flexural vibrations of small amplitude in a longitudinal magnetic field B_a.

(a) If B_a is less than the lower critical field $B_{c1}(T)$ the resonance frequency $\omega(B_a,T)$ has the ideal value $\omega_i(B_a)$, which increases monotonically with B_a.[3,7]

(b) If $B_a > B_{c1}(T)$, flux lines penetrate the material and the resonance frequency is reduced since the flux lines are not rigidly pinned; they are coupled to the pins elastically with an elastic constant $\alpha(B_a,T)$: the Labusch parameter. The resonance frequency is now

$$\omega^2(B_a,T) = \omega_i^2(B_a) - \omega_{\text{pin}}^2[\alpha(B_a,T),B_a] , \qquad (1)$$

where $\omega_{\text{pin}}^2 \propto 1/\alpha(B_a,T)$.[3,6] In both cases (a) and (b) the main contribution to the increase in $\omega(B_a,T)$ originates from the shielding of a small transversal field component $B_\perp = B_a \sin\phi$ when the reed is tilted by an angle ϕ.[3,6]

(c) If the reed is a composite or granular material the small transversal field component ($B_\perp \leq 0.1$ μT) can be shielded by intergrain currents or, if the superconducting intergranular links are destroyed due to the field distribution or high temperature, even by intragrain supercurrents.[10] For porous samples or samples with an amount of nonsuperconducting phases, the magnetic permeability increases,[11] affecting the shielding of the transversal field. Thus, with increasing B_a the measured resonance frequency may increase slower than expected, yielding a misleading low absolute value for α. In fields high enough to suppress superconductivity in most of the intergrain links and far enough above the lower critical field such that the permeability of the superconductor can be taken as constant, Eq. (1) may still be used to define an effective elastic constant $\alpha^*(B_a,T)$ with the same field and temperature dependence as the true α of the superconducting grains.

(d) The damping of a superconducting vibrating reed can be attributed to two main contributions both originating from flux-line motion:[12] (1) an amplitude and frequency-independent viscous damping $\Gamma_v(B_a,T) \propto \eta/\alpha^2(B_a,T)$ where η is the viscosity of the flux-line lattice, and (2) an amplitude and frequency-dependent hysteretic damping, which for a particular hysteresis loop model can be written as[3,6]

$$\Gamma_h(B_a,T) \propto u(1)/[\omega\alpha^2(B_a,T)] . \qquad (2)$$

Here $u(1)$ is the amplitude at the free end of the reed. At relatively high amplitudes of the reed and at fields $B_a \gg B_{c1}$ hysteretic damping is much larger than the viscous contribution.[4,6]

The two samples with nominal composition $BiCaSrCu_3O_y$ (sample 1) and $BiCa_{0.5}Sr_{1.5}Cu_2O_y$ (sample 2) and macroscopic density (4.5 ± 0.2) g cm^{-3} were prepared from high-purity oxides and carbonates. Both samples have x-ray-powder patterns typical for the 85-K superconductor $Bi_2CaSr_2Cu_2O_y$.[1] Only a few diffraction peaks due to impurity phases, characteristic of CuO and (Ca, Sr)Cu_2O_3 were detected. Scanning electron microscopy (SEM) and microprobe analysis reveal differences between both samples. The majority phase in sample 1 has well-defined grains with cationic composition Bi:Ca:Sr:Cu of 0.359:0.158:0.169:0.313. A minority phase with smaller grains has the composition $Bi_2CaSr_2Cu_2O_y$ of the 85-K superconductor.[1] Sample 2 has a homogeneouslooking majority phase with cationic composition 0.364:0.108:0.218:0.311. Embedded in this phase are grains of nonsuperconducting phases.

The resistive and ac susceptibility (20 Hz, field amplitude 0.1 mT, $B_a = 0$) transitions are shown in Fig. 1. Both samples show superconducting onsets, measured with both methods, near 80 K. The ac susceptibility shows two-stepped transitions with a second step beginning at 60 or 45 K.

For the vibrating-reed measurements we cut two slabs with length 7.4 mm (sample 2:8.3 mm), width 1.03 (1.23) mm, and thickness 263 (111) μm. In Figs. 2 and 3, we present the results for the resonance frequency ω and damping Γ. The curves shown are measured with increasing temperature on zero-field-cooled samples. Both ω and Γ reveal main transitions at $T_c \simeq 60$ K and $\simeq 45$ K for samples 1 and 2, respectively. For relative high fields the internal friction ($B_a = 0$) contribution to Γ is negligible, see Fig. 3. The increase in ω with field is a direct consequence of the pinning of flux lines in the samples [Eq. (1)]. The decrease of ω as T_c is approached from below indicates a decrease in α. As α approaches zero, the flux lines are more easily unpinned and the damping increases. When the sample becomes normal, flux lines no longer exist and the damping decreases, leading to the characteristic peak at T_c [or at $B_{c2}(T)$ if one increases field at constant temperature].[4,5] For comparison we plot in Fig. 3(a) the measured damping of a single-phase (within x-ray resolution) ceramic sample of $EuBa_2Cu_3O_{7-x}$ with T_c onset is equal to 87 K taken from susceptibility measurements. These results indicate that in both Bi-based samples a small volume fraction of the 80-K superconductor is present, in agreement with microprobe analysis. The transition at 80 K is not visible in the scale of Figs. 2 and 3, but is evident in the blown-up inset of Fig. 2(b). The presence of well-defined anomalies at different temperatures in the resonance frequency and damping is most naturally interpreted as signature of different superconducting phases with different T_c. At temperatures above 60 K (above 45 K in sample 2), flux lines exist only in the 80-K phase which occupies a small percentage of sample volume, contributing much less to $\omega(B_a,T)$ and $\Gamma(B_a,T)$ than the majority phase. In resistivity measurements, this small volume fraction appears to short out most of the sample. Even with ac susceptibility, the relative size of the transition steps is no indication for the amount of superconducting phase present. It is evident that the vibrating-reed method permits detection of low-T_c phases in the presence of high-T_c material.

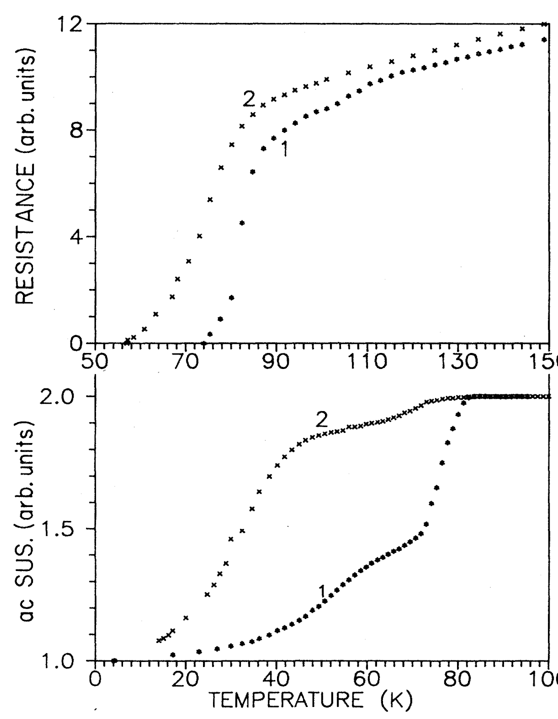

FIG. 1. Resistance and ac susceptibility for samples of $BiCaSrCu_3O_y$ (sample 1) and $BiCa_{0.5}Sr_{1.5}Cu_2O_y$ (sample 2) nominal compositions.

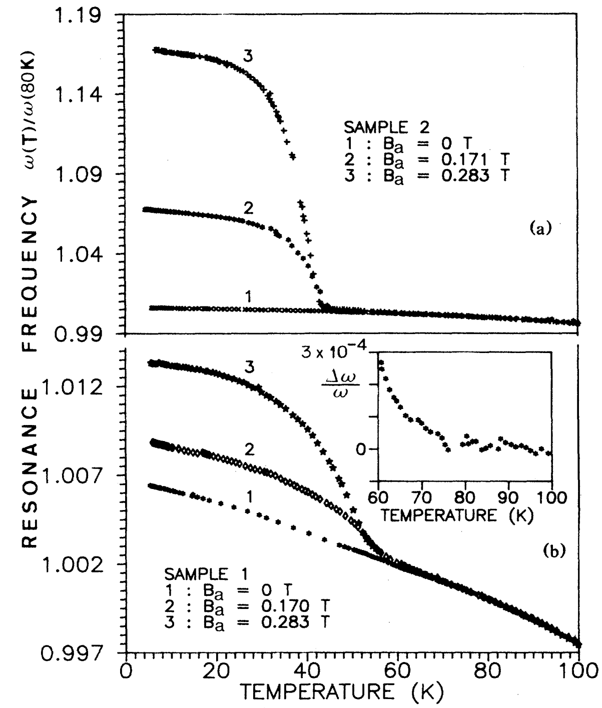

FIG. 2. Normalized resonance frequency as a function of temperature in different applied fields. ω (80 K) $= 2\pi \times 2030$ Hz ($2\pi \times 598$ Hz) for sample 1 (2). Inset: relative frequency shift $[\omega(B_a = 0.283\ \text{T}, T) - \omega(0,T)]/\omega(0,80\ \text{K})$ near 80 K.

The damping data of sample 1 clearly shows additional anomalies at 10 and 40 K, very likely indicating the presence of these superconducting phases. From irreversibility curves, i.e., the difference in signal between warming of zero-field-cooled samples and cooling at constant applied field, these anomalies are easily detected also in the frequency measurements.[9] Within the sensitivity of our method no 10- or 60-K transitions were seen in sample 2.

From the evidence presented, we may conclude the existence of two previously unrecognized phases in the Bi-Ca-Sr-Cu-O system, or at least on a Ca/Sr miscibility gap at our preparation conditions for a phase with higher

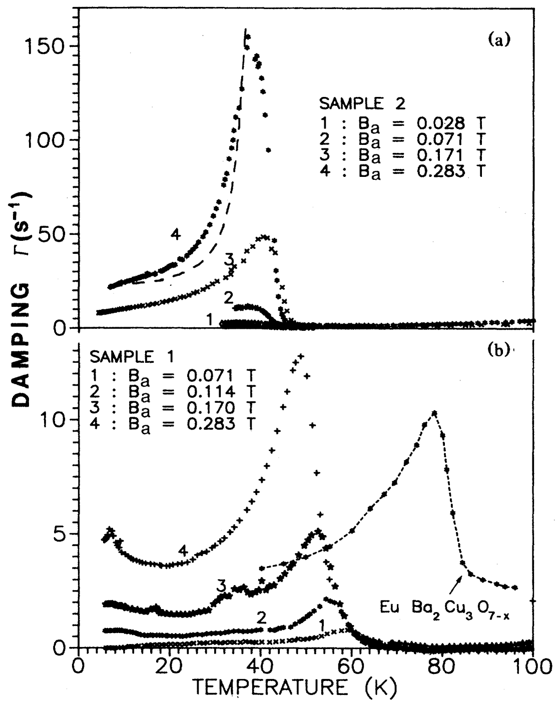

FIG. 3. Damping as a function of temperature for different applied fields. For comparison the damping of $EuBa_2Cu_3O_{7-x}$ (ceramic) taken at $B_a=0.081$ T [$\omega(80\text{ K})=2\pi\times1330$ Hz] is also shown. For convenience and only for sample 1 the background damping $\Gamma(B_a=0,T)$ has been subtracted. The dashed line (top figure) is a one-parameter fit to Eq. (2), taking into account the difference between Γ defined at the resonant amplitude (experimental values) and as the half-width at $u(1)/2^{1/2}$ (see Refs. 3,4, and 6).

Bi/Cu ratio than the established superconductors in this system. The similarity of the powder x-ray patterns may indicate an intergrowth-type structure variant, difficult to distinguish with x-ray methods even on single crystals. Such intergrowth variants have been observed with high-resolution electron microscopy (HREM) in the related Tl-based system.[13] Alternatively, the existence of an extended homogeneity range of the phase with ideal composition $Bi_2Sr_2CaCu_2O_y$ and with substitutional disorder between Sr/Ca and Bi cannot be ruled out.[14]

One could argue that, in spite of the scanning electron microscopy and microprobe data, the observed transitions at 45 and 60 K are a result of thermal activation assisted flux flow, a phenomenon which explains the shift in T_c with frequency observed in susceptibility measurements.[15] However, in our case T_c measured at 20 Hz (ac susceptibility) and $B_a=0$ is equal to that measured with the vibrating reed at 590 and 2300 Hz in different applied fields. Moreover, with the vibrating reed we were not able to see, within hours, any time effect. It is likely that, because of the dissipative vibration, flux motion is accelerated such that a (metastable) equilibrium is reached more rapidly than in magnetization measurements.

The larger relative increase in $\omega(B_a,T)$ in sample 2 compared to 1 is due to the different sample geometry. The difference in the absolute values of $\Gamma(B_a,T)$ in both samples can be attributed mainly to the different values of resonance frequency, provided that hysteretic losses [Eq. (2)] are the main contribution to damping. We show below that this assumption is justified.[16] From Eq. (1) we calculate $\alpha(T)/\alpha(5\text{ K})$ for sample 2 at $B_a=0.283$ T (Fig. 4). The total pinning-force density is

$$F_p=j_cB_a\simeq\alpha s_p\ , \tag{3}$$

where j_c is the critical current density and the length s_p is typically of the order of $a_0/2\pi$ [$a_0=(\phi_0/B_a)^{1/2}$ is the flux-line spacing], depending on the pinning mechanism.[5,17] Thus, $j_c(t)/j_c(5\text{ K})$ is also represented by Fig. 4. The inset shows the magnetic field dependence of (effective values) α^* and j_c^* at 5 K, derived using Eqs. (1) and (3). Note that α^* increases roughly linearly in B_a, while j_c^* is rather constant. Using this temperature and field dependence of α^* and measured values of $u(1)$ and $\omega(B_a,T)$, we calculate $\Gamma_h(B_a,T)$ using Eq. (2), i.e., assuming a hysteretic-loss mechanism. We obtain a quadratic dependence of Γ on B_a in agreement with experiment and we can roughly reproduce the observed temperature dependence using only one free parameter $\alpha(B_a,T)/\alpha^*(B_a,T)=20$. As an example, the dashed line in Fig. 3 represents the calculated $\Gamma_h(B_a,T)$ at $B_a=0.283$ T. Note that the peaks in Γ are located at temperatures several degrees below the critical temperatures. This might be just due to the relatively broad-transition width common in ceramic samples. Nevertheless, preliminary measurements[9] in other samples indicate that an intrinsic dissipation mechanism could contribute to the shift of the damping peak.

The obtained field and temperature dependence of j_c ($\simeq 20j_c^*$) are qualitatively similar to those obtained in single- and polycrystalline samples but the absolute value of j_c is lower by 5 orders of magnitude. Low values for $\alpha(B_a,T)$ and j_c have been obtained for other ceramics with the vibrating-reed technique.[8] A low value for α may point out that the three-dimensional almost amorphous array of flux lines in the reed with a large amount of

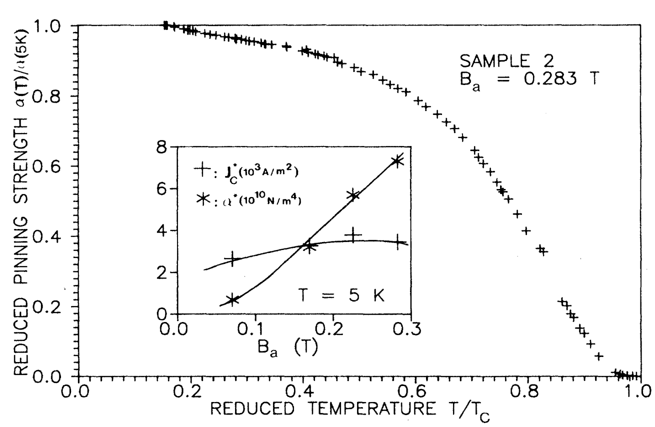

FIG. 4. Temperature dependence of the Labusch parameter $\alpha(T)$ normalized to 5 K for sample 2. Inset: calculated effective Labusch parameter and critical current density as a function of applied field at $T=5$ K. The lines are guides to the eye.

strong pinning centers moves in an effectively flat pinning potential; in this case the simple relation (3) is not applicable. Instead, new hysteretic-loop models with possibly different amplitude and pinning-force dependence as those described in Ref. 3 have to be considered. Clearly, experimental data on single crystals are needed for a better understanding of the anomalous low α values obtained in ceramic materials.

Our interpretation of the damping peaks in terms of hysteretic losses may be important for the understanding of similar features observed recently in single crystals and interpreted as an evidence of a flux-lattice melting effect.[18] The existence of superconducting phases with similar x-ray patterns could lead to misinterpretation of the experimental data even in so called "single" crystals where their presence would be very difficult to detect.

We thank E. H. Brandt for a critical reading of the manuscript. The support and collaboration of F. Pobell and D. Rainer is gratefully acknowledged.

---

[1]See, for example, J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, Phys. Rev. B **38**, 8885 (1988).

[2]A. Gupta and H. F. Braun, Physica C **153**, 904 (1988).

[3]E. H. Brandt, P. Esquinazi, H. Neckel, and G. Weiss, Phys. Rev. Lett. **56**, 89 (1986); J. Low Temp. Phys. **63**, 187 (1986).

[4]P. Esquinazi, H. Neckel, G. Weiss, and E. H. Brandt, J. Low Temp. Phys. **64**, 1 (1986).

[5]P. Esquinazi, J. Luzuriaga, and C. Durán, Phys. Rev. B **37**, 3689 (1988).

[6]P. Esquinazi and E. H. Brandt, Jpn. J. Appl. Phys. **26**, 1513 (1987).

[7]C. Durán, P. Esquinazi, J. Luzuriaga, and E. H. Brandt, Phys. Lett. A **123**, 465 (1987).

[8]P. Esquinazi and C. Durán, Physica C **153**, 1499 (1988).

[9]A. Gupta, P. Esquinazi, and H. F. Braun (unpublished).

[10]In the extreme case of completely isolated superconducting grains, an enhancement in ω with B_a should still be observable due to tilt modulus c_{44} contribution (Ref. 3), provided the grains perform a non-negligible rotation relative to B_a or, if the grains are very small, the field distribution in the sample is not homogeneous.

[11]A. M. Campbell, Supercond. Sci. Technol. **1**, 65 (1988).

[12]A possible third source for dissipation in ceramics could come from the shielding surface ac currents through resistive intergrain junctions.

[13]M. Verwerft, G. von Tendeloo, and S. Amelinckx, Physica C **156**, 607 (1988).

[14]G. Grader, E. Gyorgy, P. Gallagher, H. O'Bryan, D. Johnson, S. Sunshine, S. Zahurak, S. Jin, and R. Sherwood, Phys. Rev. B **38**, 757 (1988).

[15]J. van den Berg, C. J. van der Beek, P. H. Kes, J. A. Mydosh, M. J. V. Mencken, and A. A. Menovsky, Supercond. Sci. Technol. (to be published).

[16]The amplitude dependence of the damping has been experimentally verified. For a detailed discussion of these results, see Ref. 9.

[17]E. H. Brandt, J. Low Temp. Phys. **53**, 41 (1983).

[18]P. L. Gammel, L. F. Schneemeyer, J. V. Waszczak, and D. J. Bishop, Phys. Rev. Lett. **61**, 1666 (1988); E. H. Brandt, P. Esquinazi, and G. Weiss, Phys. Rev. Lett. **62**, 2330 (1989).