Microwave loss and oxygen annealing in $YBa_2Cu_3O_x$ single crystals

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Reversible thermal annealing of $YBa_2Cu_3O_x$ single crystals in air has been studied by microwave loss measurements. Among the advantages of this contactless technique are the following: Crystals are kept in sealed capillaries throughout cycles of annealing and low-temperature measurement; features are resolved in loss versus temperature measurements that are not revealed by other techniques. Microwave loss is interpreted in terms of the Gittleman-Rosenblum model of fluxon motion in a viscous medium. Narrow temperature ranges are found for the formation of the 60- and 90-K phases. Optimal microwave response is obtained after but a few hours of annealing, indicating the importance of c-axis diffusion.

INTRODUCTION

Magnetic-field-dependent or differential microwave absorption bids to become an indispensible technique for the study of high-T_c superconductors.[1-7] The method, which for practical purposes senses only superconductivity, can detect submicrogram quantities and distinguish multiple T_c phases, as well as telling something about the quality of the superconducting state achieved. Uncertainty as to what this "something" is, is the major handicap the method suffers. Inherently dissipative, measurements cannot be directly related to conventional thermodynamic parametrizations, and the advancement of this promising technique awaits experimental verifications of conjectured dissipative mechanisms.

A remarkable feature of the chemistry of the 1:2:3 class of superconductors is the reversible insertion and removal of oxygen from the crystal lattice. Using a low-temperature zirconium getter technique, Cava *et al.* have shown the existence of two T_c plateaus for polycrystalline $YBa_2Cu_3O_x$, 90 K for $7 > x > 6.8$ and 60 K for $6.7 > x > 6.5$.[8] The variable oxygen sites lie on the copper oxide chains.[9,10] Less evident is how this transformation takes place, whether by mixed phases of discrete T_c's, a solution of variable T_c, or whatever.

This study has dual objectives. First, by means of differential microwave loss measurements we examine the variations in the superconductive response of single crystals at various stages in the oxygen annealing process. Microwave measurements are especially well suited for such an experiment as the small crystals can be kept in permanently sealed capillary tubes throughout the sequence of annealings and measurements. In brief, we find that the annealing windows for producing optimal superconductors are quite narrow. Second, we seek a better understanding of microwave loss itself. The essential points relevant to this work concern the crystalline regions probed by microwaves. To this end, we invoke a classic but rather general description of vortex displacements in a viscous medium that introduces the notion of vortex stiffness as a means for enhancing microwave penetration beyond the London distance.

EXPERIMENTAL

Crystals were grown from partially melted $YBa_2Cu_3O_7$-CuO mixtures, as described previously.[11] Growth was carried out in air, and samples were furnace quenched from a temperature below the melt solidification temperature ($\sim$880 °C). Crystals were mechanically separated from the solidified flux and stored under dry conditions at room temperature. Small rectangular platelets free of adherent flux were selected for this study.

Measurements of 9-GHz microwave loss were made with a computer-controlled electron-spin-resonance spectrometer modified for superconductor studies.[1] The sample was centered within a TE102 cavity in a helium dewar insert at a node of the microwave electric field. A static magnetic field was applied perpendicular to the microwave magnetic field at the sample and modulated at 100 kHz with a 10-G peak-to-peak amplitude. Differential microwave loss was then detected in the modulation of microwaves reflected from the cavity.

Detailed studies of two $YBa_2Cu_3O_x$ crystals, both about $1000 \times 500 \times 25$ μm^3, were carried out concurrently. The crystals were sealed in 1-mm quartz capillaries under air. Pockets at the capillary ends allowed the crystals to be oriented for loss measurements with the static field parallel to their c axes (normal to the principal surface). Estimates for residual oxygen enclosed give an eightfold excess for $\Delta x = 1$. A number of additional crystals were briefly studied to verify the conclusions presented herein.

Both crystals were simultaneously subjected to a series of heat treatments of varying temperatures and durations. In all cases the capillaries were moved in and out of the annealing furnace as quickly as possible. Measurements were then made with static fields of 20 and 100 G, cooling the crystals from above T_c at 5 K/min.[5] Each scan comprised 1000 discrete measurements of loss and temperature.

RESULTS

In general, the behaviors of both crystals versus temperature were quite similar and the same for fields of 20 and 100 G to within 10–20 %. Previous work with good single crystals has shown little dependence of differential loss at fields above 10 G.[1] This behavior contrasts with that of polycrystalline specimens, in which intergranular junctions are believed responsible for enhanced low-field losses. The similarity of 20 and 100 G results thus indicates junctions not to be a significant factor. For the sake of presentation, we show only data for one of the crystals at 100 G and, unless otherwise mentioned, it may be presumed that results are independent of the sample and measuring field.

The initial differential loss versus temperature measurement for this crystal is shown in Fig. 1(a). Behavior appears complex, with two well-resolved, field-independent peaks at 57 and 59 K, plus a broad background extending up to 80 K, and an intervening region of negative differential loss. Similar results have been found for many as-grown crystals, although the precise structure is unique to each crystal. In one instance, six well-resolved peaks were seen clustered about 55 K (Fig. 2). Negative differential loss is a pathological feature not infrequently encountered with crystals of dubious character. In this sample it disappeared with the first anneal and did not reoccur subsequently, so we shall not speculate on its origins.

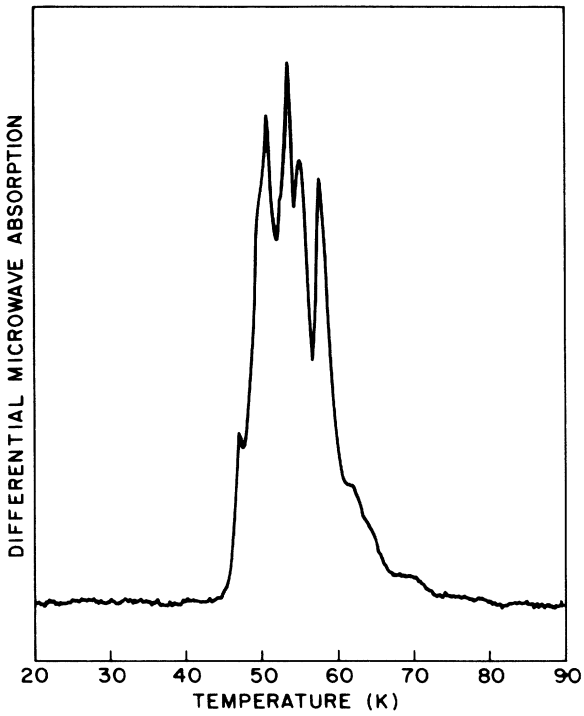

FIG. 2. Differential microwave loss for another as-grown crystal illustrating the detail observable by such measurements. The intensity and pattern were nearly independent of applied fields between 20 and 1000 G.

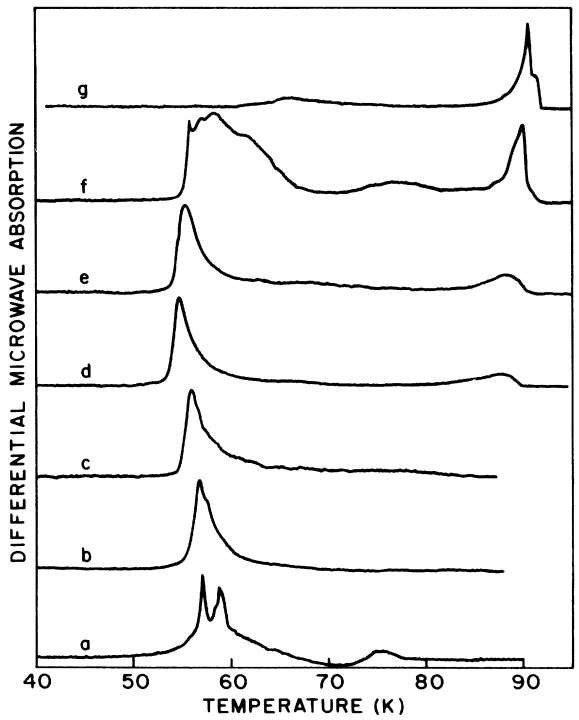

FIG. 1. Differential microwave loss vs temperature for a $YBa_2Cu_3O_x$ single crystal: (a) as grown; (b) after 1 h at 650 °C; (c) 200 °C, 30 min; (d) 300 °C, 30 min; (e) 350 °C, 30 min; (f) 400 °C, 30 min; and (g) 450 °C, 30 min.

The crystals were first subjected to a 60-min. anneal at 650 °C [Fig. 1(b)]. This treatment sharpened the response to a 57-K peak, with some indications of additional features at slightly higher temperatures. These "shoulders" are not vagaries of temperature fluctuations or junction resonances as they were reproduced in a following scan at a different field. The details of this structure are, however, unique to each crystal. It may be further noted that most of the changes between Figs. 1(a) and 1(b) occurred during the first 10 min. of annealing.

The remaining plots in Fig. 1 show the consequences of annealings at temperatures from 200 to 450 °C. One observes a progressive decline in 60-K response, with some broadening towards higher temperatures, plus a regular increase in 90-K features that become quite sharp after annealing at 450 °C. It seems evident that the crystal is inhomogeneous over this range, with coexistent 60- and 90-K phases, and that T_c is not changing continuously. It is perhaps remarkable that even a brief 30 min. anneal at 200 °C produces discernible superconductivity changes. In subsequent experiments we have found overnight annealing at 450 °C (18 h) sufficient to transform small BaYCuO crystals into sharp 90-K phases, with differential loss restricted to the 85–90-K region and no detectable 60-K response. Some structure to the 90-K phase, with resolved peaks less than 1 K apart, can be seen in Fig. 1. Such features are not uncommon, although again they are crystal specific.

Figure 3 continues the changes observed as annealing temperatures were progressively raised to 650 °C. The

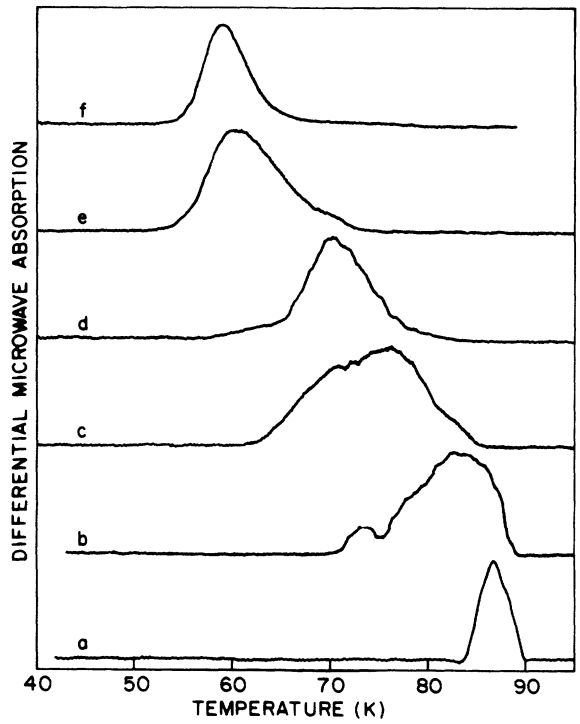

FIG. 3. Continuation of the annealing experiment in Fig. 1. (a) 500 °C, 40 min; (b) 550 °C, 30 min; (c) 575 °C, 30 min; (d) 600 °C, 30 min; (e) 625 °C, 30 min; and (f) 650 °C, 30 min.

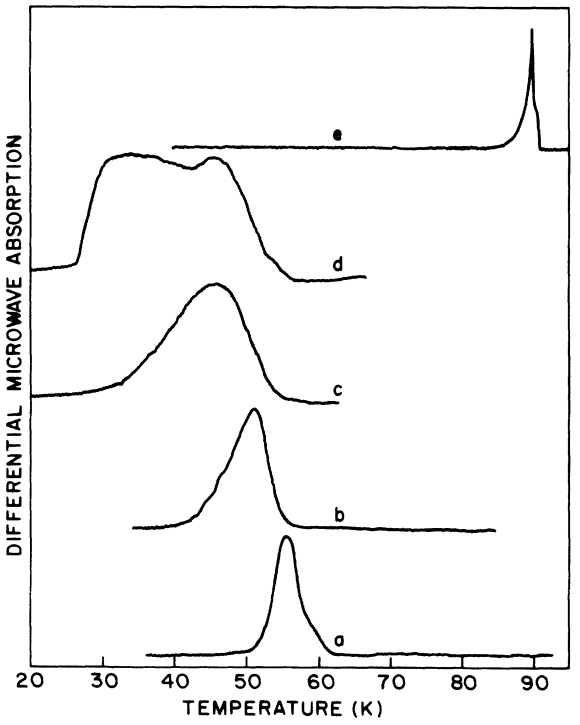

FIG. 4. Continuation of the annealing experiment in Fig. 3. (a) 700 °C, 30 min; (b) 750 °C, 30 min; (c) 800 ° C, 30 min; (d) 850 °C, 30 min; and (f) 450 °C, 18 h.

90-K feature first broadens towards lower temperatures, eventually reaching the 60-K region and then coalescing into a relatively narrow peak at a temperature coincident with that of the previous 650 °C anneal [Fig. 1(b)]. Clearly, the bimodal pattern of Fig. 1 is not retraced, and behavior suggests a more intimate mixture or continuous distribution than occurs at lower temperatures. The previously observed 60-K structure is not recovered, although it may be buried beneath the broader response curve.

Finally, Fig. 4 shows the changes occurring as the annealing temperature is raised above 650 °C. Initially there is a modest shift of the peak to lower temperatures but the plots broaden considerably above 800 °C, extending from 25 to 55 K after a 30 min. anneal at 850 °C. At this point the crystal was annealed overnight at 450 ° C and the concluding plot in Fig. 3 shows a complete recovery of the 90-K response, including the aforeseen structure.

From this series of experiments, two temperatures stand out for annealings in air, 450 and 650 °C. In subsequent experiments with many other crystals we have found that alternating cycles of 18 h at 450 °C and 1 h at 650 °C can reversibly toggle crystals between states, giving the sharpest differential microwave loss features at 90 and 60 K, respectively.

DISCUSSION

Oxygen stoichiometry studies of polycrystalline $YBa_2Cu_3O_x$ show two well-defined T_c plateaus at 90 and 60 K for $7 > x > 6.8$ and $6.7 > x > 6.5$, respectively.[8] These temperatures are identical with those found in this work, so we presume that the plots in Fig. 1 show oxygen insertion with x increasing from 6.5 to 7, those in Fig. 3 oxygen removal with x returning to 6.5, and those in Fig. 4 the further removal of oxygen leading to the nonsuperconducting $x = 6$ phase.

It seems natural to associate the sharp features in these measurements with regions of well-defined oxygen ordering, regions sufficiently large to define sharp transition temperatures. For oxygen concentrations between $x = 6.5$ and 7, however, it is also evident that the actual distribution is not simply a function of oxygen content. Insertion appears associated with a progressive growth of regions with the 90-K ordered structure, whereas removal seems more or less random, with the development of 60-K ordered regions only as $x \rightarrow 6.5$. It does not appear possible to create homogeneous phases with true intermediate T_c values.

The "fine structure" at both 60 and 90 K points to long-range structural differences beyond those attributable to oxygen ordering. The most obvious evidences for this are the reproducible, but crystal-dependent 90-K features that reappear after cycles of oxygen removal and insertion. These would seem to be rooted either in cationic or copper oxide plane structural variations.

The facility of oxygen insertion and removal also appears remarkably fast. If we assume the entire bulk of the crystal is sensed by microwaves, oxygen diffusion coefficients of order 10^{-10} to 10^{-11} cm^2/s are required for diffusion parallel to the c axis, or values 10^3 times greater for diffusion in the ab planes. The former are of a magni-

tude consistent with values derived from thin-film resistivity changes by Grader *et al.*, while the latter are unconscionably large.[12]

A more rigorous interpretation of microwave loss hinges on an understanding of what it is these measurements are showing us and, in particular, what regions of the crystal are involved. Resistivity measurements of the normal state for similar crystals give values of 10^{-4} Ω cm.[13] The corresponding microwave skin depth is 5 μm and, in light of the 25-μm crystal thickness, the microwave field will be reduced to 20% of its surface value at the center of the crystal. The contribution of a superconducting region at the sample's center to the measured signal will thus be 3% of that for an equivalent surface layer. This penetration is sufficient to sense any superconducting region embedded in normal material, and regions of highest T_c should always be detected. Less evident is the degree to which we expect to find regions of lower T_c buried within high-T_c layers. Microwave superconducting currents are nominally confined to the London penetration distance of the superficial phase, i.e., ≥ 0.1 μm. A crystal that had been partially annealed to show principally the 90-K phase, but with a discernible 60-K component, was crushed and lightly ground. It did not show any significant change in the relative responses at 60 and 90 K, but this result is inconclusive as fractures along the *ab* planes are probably minor.

A more specific modeling of the microwave dissipation mechanism is required to explain how shallow surface currents may detect underlying superconducting regions, and we favor a model suggested by Gittleman and Rosenblum (GR) for dissipation in type-II superconductors.[14] They proposed that surface currents exert a force, the Lorentz force, on vortex lines and that the resulting displacements are impeded by a viscous force. Taking the y direction as that of the microwave current and the z direction normal to the surface, the vortex displacement in the x direction is given by

$$m\ddot{x}=(\Phi_0/c)J_{\rm mw}-\eta\dot{x}-kx-K(\delta^2x/\delta z^2)\ , \tag{1}$$

with m the vortex mass (hereafter assumed negligible), $J_{\rm mw}$ the microwave surface current density, η the viscosity, k an elastic pinning force constant, and K an elastic coefficient for vortex stiffness. Only the viscous term is dissipative and the net rate of energy dissipation per unit length vortex is $\omega^2\eta\langle xx^*\rangle$. GR considered only constant pinning and viscous coefficients, and a simple ac perturbation calculation then yields

$$x=(\Phi_0/c)J_{\rm mw}/(k+i\omega\eta)\ . \tag{2}$$

Supposing the viscosity to be the major temperature-dependent parameter, at least in the vicinity of T_c, the GR model predicts loss should increase with viscosity, reach a maximum when $\omega\eta/k=1$, and then drop off as the viscosity increases further and the relaxation frequency k/η exceeds the microwave frequency. We adopt this as a heuristic explanation for the shapes of the plots in Figs. 1–4. The Bardeen-Stephen analysis gives a viscosity proportional to H_{c2}/ρ, ρ being the normal-state resistivity, and the sharp drop in differential loss in pure 90-K material immediately below T_c is a consequence of a rapidly increasing H_{c2} and viscosity.[15]

When vortex-vortex interactions are insufficient to influence individual vortex displacements, dissipation will be directly proportional to the vortex density or the applied static field. The differential loss is then a measure of dissipation per vortex and its relative constancy at low fields is accounted for. At fields of order 5 kG, vortex separations are <0.1 μm and there is a discernible decrease in differential loss ($\sim 50\%$) that can be rationalized by a reduction in $\langle x^2\rangle$ displacements due to packing. Angular measurements of loss lend some additional support to the vortex dissipation model. For similar crystals we have found the $|\cos\theta|$ dependence expected for a loss proportional to vortex density.

Vortex stiffness provides a mechanism by which surface currents can detect superconductivity at distances beyond their direct penetration distance. If we consider only the viscous and stiffness terms in Eq. (1) for an arbitrarily thick crystal,

$$x(z)=x(0)\exp[-(i\omega\eta/K)^{1/2}z]\ , \tag{3}$$

giving a characteristic penetration distance of $(K/\omega\eta)^{1/2}$. We expect both K and η to be temperature dependent but, lacking a reliable estimate for their ratio, content ourselves by simply arguing that vortex stiffness affords a mechanism whereby dissipation can be observed at distances farther into a crystal than the London distance. It may also be noted that vortex bending losses involve $\sqrt{i\omega}$ terms and lead to a nonexponential relaxation behavior similar to that for one-dimensional diffusion models. In contrast, the original GR model predicts a Lorentzian or Debye relaxation.

Finally, we take note of the resistivity measurements of Fiory *et al.* on $YBa_2Cu_3O_x$ crystals of a common provenance during temperature jumps between 650 and 680 °C.[13] They report a rapid change during the first minutes followed by a slower, diffusion-controlled change extending over more than 10 h attributed to oxygen diffusion parallel to the *ab* planes. Our microwave results, on the other hand, indicate that the major changes affecting superconductivity occur within minutes and that these crystals should be predominantly 60 K superconductors. [A separate experiment looking at the time dependence of 650 °C annealing of a crystal previously kept at 450 °C for two days showed all traces of superconductivity ($<0.5\%$) above 75 K vanishing within 15 min.] The long-term resistance changes at elevated temperatures do not correlate with the changes in superconductive response evidenced by microwave measurements and may indicate structural alterations beyond those directly pertinent to superconducting transitions.

CONCLUSIONS

Microwave differential loss measurements have been found to be an effective technique for observing superconductivity during the reversible oxygen annealing of

$YBa_2Cu_3O_x$ crystals. Optimal conditions have been established for producing either 60- or 90-K superconducting crystals. The brief annealing times required indicate rapid oxygen diffusion normal to the crystal planes. These measurements also show well-resolved, crystal-dependent features in superconducting response versus temperature plots, which have not heretofore been revealed by other techniques.

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