Thermal diffusivity of superconducting $YBa_2Cu_3O_{7-x}$

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Thermal diffusivity results for superconducting $YBa_2Cu_3O_{7-x}$ systems are reported. Two laser excitation techniques were used: photoacoustic phase-lag and the flash method. We observed an anomalous jump in the thermal diffusivity at the critical temperature and related it to the electronic specific heat anomaly. This correlation yielded a characteristic phonon frequency of 320 cm^{-1} in the range of an active Raman mode already observed in a single crystal of the same compound. This result reinforces the current electron-phonon coupling mechanism as responsible for superconductivity.

I. INTRODUCTION

The recent discovery of high-T_c superconductivity[1,2] triggered a variety of experimental studies in order to characterize these new compounds and to understand the causes of the superconducting state at such high temperatures. Much progress has been made in understanding this phenomenon, and Y-Ba-Cu-O with a $T_c \sim 90$ K has been one of the most studied systems. Heat capacity of superconducting La-Sr-Cu-O,[3,4] La-Ba-Cu-O,[5] and Y-Ba-Cu-O[6] systems has recently been reported. For the La-Ba-Cu-O compound system, the expected anomaly was not observed at the superconducting transition.

In this paper we report, for the first time, absolute value measurements of the thermal diffusivity of Y-Ba-Cu-O pellets prepared in our laboratories. This physical quantity, α, of the bulk material relates in a simple way the thermal conductivity K to the specific heat C_p through the relation $\alpha = K/\rho C_p$ where ρ is the mass density.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Single-phase $YBa_2Cu_3O_{7-x}$ compounds were prepared by thoroughly mixing Y_2O_3, $BaCO_3$, and CuO in a 1:4:6 mass ratio. The mixture was then ground and heated for 12 h at 950 °C under a constant flow of O_2 at atmospheric pressure. The mixture was then slowly cooled to room temperature at a ratio of 25 °C per hour. After this procedure, a standard powder metallurgical method followed, i.e., grinding, pressing, and sintering pellets of the compound at 950 °C under O_2 for 12 h and again slowly cooling to room temperature at a ratio of 25 °C per hour. Powder x-ray diffraction pattern (Fig. 1) taken by commercial x-ray equipment (from Rigaku) showed the presence of single-phase $YBa_2Cu_3O_{7-x}$ compound identified according to published data.[7] The amount of single-phase $YBa_2Cu_3O_{7-x}$ present in the samples was found to critically depend on the preparation conditions and thermal cycling. Due to that dependence, samples from different batches may show slight differences. In the present work we studied three samples, identified as B-7, B-8, and B-15, from different batches.

The superconducting behavior of the samples was checked by measuring their Meissner effect. To test this effect a very simple probe was designed and constructed consisting of three coils in a T-shape geometry, enclosed in magnetic shielding. A schematic drawing of this probe is given in Fig. 2. The vertical coil is the inductor producing an ac magnetic field. The flux lines of this field penetrate the identical coils A and B producing two signals that are analyzed and subtracted ($V_A - V_B$) by a lock-in amplifier. The sample, with a very thin thermocouple type T (from Omega) attached to its surface with silver paint (from GC Electronics), was placed inside coil A, as shown in Fig. 2. When the sample becomes a superconductor, the magnetic flux originally present is ejected from the sample, decreasing the signal induced in coil A. Consequently, the signal difference ($V_A - V_B$) deviates from zero (level reference of nonmagnetic state) when the sample is in a specific magnetic state. In the case ($V_A < V_B$), the sample is in a diamagnetic or superconducting state. The opposite state ($V_A > V_B$) is the paramagnetic one. The temperature dependence of that effect was taken during a slow warming up of the probe from liquid-nitrogen temperature. The obtained Meissner effect is

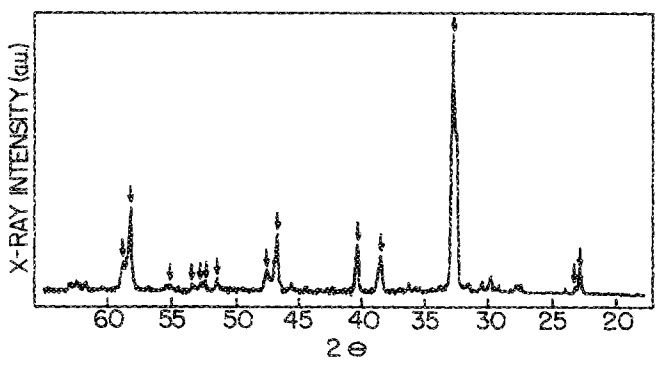

FIG. 1. X-ray diffraction pattern of the $YBa_2Cu_3O_{7-x}$ compound. The arrows indicate the superconducting phases already identified by other authors.

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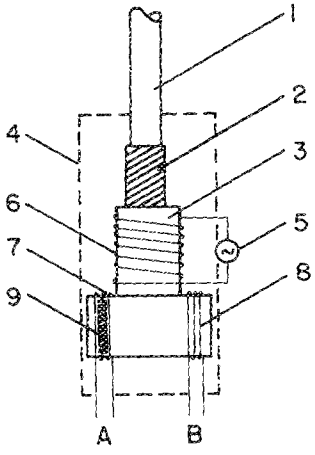

FIG. 2. Schematic diagram of the probe used for Meissner effect measurements. (1) Stainless-steel anchor tube; (2) rubber coupling; (3) nylon T-shape frame; (4) magnetic shielding; (5) ac frequency generator; (6) inducting coil; (7) and (8) sensor coils A and B; (9) sample.

shown in Fig. 3. One can see that the samples have a high transition temperature between 80 and 90 K, corresponding mostly to a single-phase transition with 3-K width.

III. APPLIED TECHNIQUES

After the characterization of the superconductivity of our samples we measured their thermal diffusivities. Two different techniques were used: phase-lag photoacoustic technique and the flash method. In the photoacoustic method we measured the phase-lag of the signals generated at the front and back surface of the sample, as described in Ref. 8. The thermal diffusivity α is related to the phase-lag θ by the expression:

$$\tan\theta = \tanh[(\pi f d^2/\alpha)^{0.5}]\tan[(\pi f d^2/\alpha)^{0.5}],$$

where d is the sample thickness and f the modulation frequency. The homemade measuring system consists of a liquid-nitrogen Dewar, a photoacoustic cell in the configuration of a Helmholtz resonator with helium as the filling gas. A 10-mW chopped argon laser modulated at 14.5 Hz was used for excitation. The temperature stability was within 0.1 K and the sample thickness was 340 μm (B-15). The performance and capability of this system was verified by measuring the absolute value of the thermal diffusivity of a silicon sample in a wide low-temperature range. The detailed description and thermal characteristics of this system will be described elsewhere.[9] Tests for temperature variation due to laser excitation were made at room temperature and deviations smaller than 0.2 K were observed by a thermocouple placed 3 mm apart from the illuminated spot. The phase-lag method results are frequency independent and agree well with those from other photoacoustic techniques.[10] The data are reproducible within 0.5%, although we can have larger systematic errors ($\sim$5%) from other sources, namely the frequency and thickness measurements.

The second method used for measuring the thermal diffusivity was the flash method.[11] This method consists of measuring the time necessary for the back surface to attain half the value of the maximum temperature of the transient after a single shot of a Nd-YLF laser[12] on the front surface of the pellet. The time duration is known as $t_{1/2}$. The temperature transient was measured by attaching a thermocouple (type E from Omega, thickness 0.003 in.) to the back surface with silver paint (which has a suitable thermal conductivity for that application). The response time of such a thermocouple is much shorter ($\sim$0.001 s) than the total time involved in the temperature transient. The experimental conditions were such that this total time involved in the transient was smaller than the time for the sample to reach its equilibrium temperature.

The flash method was largely used in the 1960s to measure the thermal diffusivity of metals and oxides.[11] By measuring the quantity $t_{1/2}$ as a function of the temperature, assuming the sample has a steady initial temperature distribution, one can calculate the absolute value of the thermal diffusivity, by the relation

$$\alpha = 0.139 d^2/t_{1/2},$$

where d is the sample thickness.

For that kind of measurement, the sample was fixed to a copper holder attached to the cold finger of a liquid helium cryostat from Janis, provided with a gas exchange chamber as a thermal switch. That cryostat has two concentric Dewars working with liquid nitrogen. For measurements below 77 K we pumped over the N_2 liquid bath from the internal Dewar allowing temperatures down to solid nitrogen.[13]

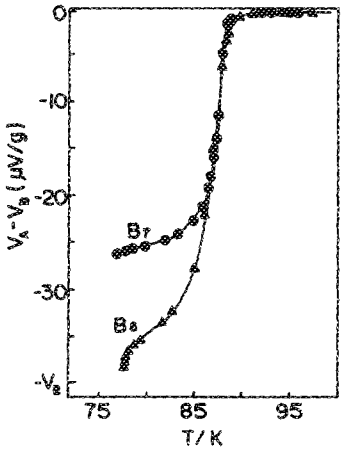

FIG. 3. Meissner effect measurements on samples B-7 and B-8. The $(V_A - V_B)$ signal was normalized to the pellets weight (in grams).

IV. RESULTS AND DISCUSSION

The results of such measurements from both techniques can be seen in Fig. 4. The anomalous behavior of the three curves is quite evident. A correlation of these curves (B-7, B-8) with the two curves (B-7, B-8, respectively) from Fig. 3 shows that there is a clear correspondence between the temperature where the deviation from the normal behavior of the thermal diffusivity starts and the temperature where the material becomes diamagnetic. One can observe that this onset temperature involving the heat transport phenomena is always equal or lower than the onset observed by the Meissner effect measurements. For sample B-7, this temperature value is 89 K and for sample B-8 this temperature is 90 K. Sample B-8 is almost entirely superconducting as is shown in Fig. 3, since $(V_A - V_B) \sim -V_B$ in the superconducting state, below 77 K.

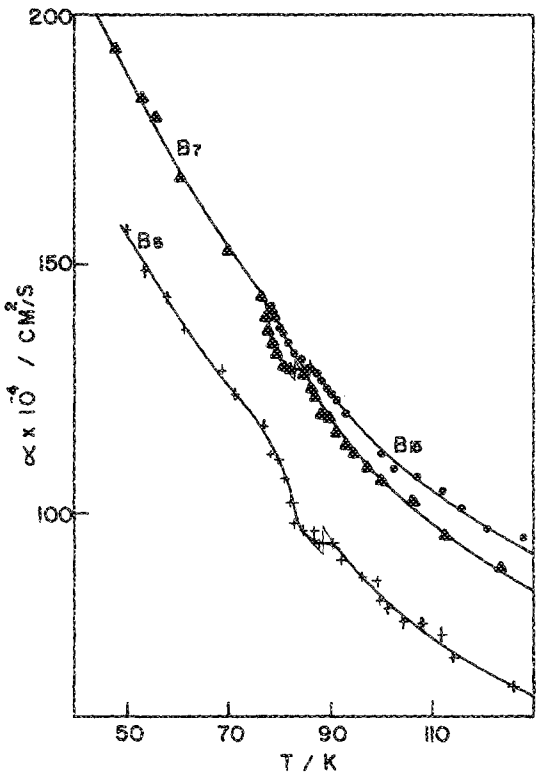

FIG. 4. Thermal diffusivity measurements obtained using two techniques: flash method (B-7 and B-8) and photoacoustic phase-lag (B-15). Sample thickness was 1.9 mm for B-7 and 1.3 mm for B-8.

The results from both techniques, magnetic and heat transport, are very consistent. In order to better see the changes in behavior of the heat transport in those samples, we constructed the curve in Fig. 5 by plotting the thermal diffusivity data of sample B-7 on a double-logarithmic scale. Using this very wide range of measurements, starting at room temperature, one can see that the curvature drastically changes after going through the critical temperature. In the superconducting state (below T_c) the behavior follows a straight line, at least for temperatures down to ~ 50 K. In both Figs. 4 and 5, quite a pronounced shoulder, that appears at the transition from normal to superconducting state, is observed. That shoulder, verified through the thermal diffusivity curves, around T_c, suggests that the samples do not have a unique superconducting phase, centered on a certain T_c, but, instead, have a phase distribution with distinct temperature transitions in agreement with theoretical calculations.[14] This fact probably smears out the jump in the thermal diffusivity transition, affecting the ΔC_p derived below. In spite of that, one can associate the electronic specific heat jump ΔC_p to the observed thermal diffusivity jump $\Delta\alpha$ by simple extrapolation of both behaviors, the normal and the superconducting one, as is indicated in Fig. 4. By considering that the thermal conductivity does not have a discontinuity in its behavior when passing through the critical temperature, one can conclude that $\Delta\alpha/\alpha \sim \Delta C_p/C_p$. With this relation we estimate that the electronic specific heat jump represents 5% of the total specific heat (electronic + lattice) value at T_c. Kitazawa *et al.*[6] have already measured such a specific heat jump which was 1.6% of the total specific heat. Making use of their value ($\Delta C_p = 2$ J/mol K) we estimated the jump in our case to be 6 J/mol K. With the value of ΔC_p one can estimate the electron-phonon coupling by evaluating the constant relation $\beta = \Delta C_p/\gamma T_c$, where γ is the electronic specific heat coefficient. The value of γ can be estimated using the expression for the electronic specific heat of a free-electron gas and assuming that only copper atoms ($3d$ state) contribute to the superconductivity. The density of states of the $YBa_2Cu_3O_{7-x}$ compound at the Fermi level has been estimated to be 2.6 states/eV Cu atom from the magnetic susceptibility of the normal state.[15] Matheiss and Hamann[16] reported 3 states/eV Cu atom for the Fermi density of states based on linear-augmented-plane-wave (LAPW) calculation. Assuming 3 states/eV Cu atom for the Fermi density of states to calculate the electronic specific heat coefficient, we obtained $\gamma = 21$ mJ/mol K^2. With this value we estimated β to be 3.3 which is larger than 1.43, the predicted value from Bardeen–Cooper–Schrieffer (BCS) theory. This value indicates that the $YBa_2Cu_3O_{7-x}$ compound exhibits strong coupling superconductivity.

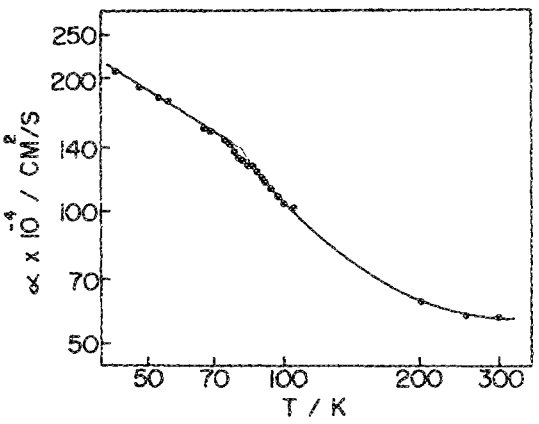

FIG. 5. Thermal diffusivity data of sample B-7 plotted on a double-logarithmic scale.

Kresin and Parkhomenko[17] have shown that one can utilize the Eliashberg equation to give the expression

$$\beta = 1.4\{1 + 1.8[\ln(w/T_c) + 0.5](\pi T_c/w)^2\},$$

where w is the characteristic frequency for the phonons involved in the superconductivity. Using our estimated value of β in the above equation we obtained the characteristic phonon frequency of 320 cm^{-1}. This value turns out to be in the frequency range of the active Raman mode, located at 338 cm^{-1}, recently observed in a single crystal of the same compound.[18]

The consistency of all the data presented (ΔC_p derived from thermal diffusivity, electronic specific heat coefficient, constant β, and the characteristic phonon frequency) reinforces the current model where the electron-phonon coupling is the main mechanism responsible for the high-temperature superconducting state in Y-Ba-Cu-O systems.

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