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Large "forbidden" change in elastic modulus at the superconducting transition of $Y_1Ba_2Cu_3O_{9-x}$

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The torsional modulus of $Y_1Ba_2Cu_3O_{9-x}$, measured by the composite oscillator method, shows a softening of $\simeq 1\%$ on cooling through the superconducting transition. The change is 3 to 4 orders of magnitude larger than that in an average modulus for a typical superconductor. For the high symmetry implied by our polycrystalline sample, furthermore, no change is allowed by symmetry for this mode at the superconducting (or any Landau-type) transition. The decrease in modulus is accompanied by an increase in damping.

The discovery of the new high-T_c superconductors by Bednorz and Müller,[1] and by Wu *et al.*,[2] has been followed by investigations to determine, among other things, whether the mechanism for this superconductivity is similar to that known to exist for conventional cases. We report here, with a possible bearing on this question, an unusually large change in an elastic modulus associated with the onset of superconductivity. We note that, according to the accepted theory, no change of any magnitude would be allowed by thermodynamics for the particular conditions of this experiment.

The samples were prepared in the now standard way[2] of reacting a compressed powder mixture of Y_2O_3, $BaCO_3$, and CuO first at 950 °C for 3 h, and then, following regrinding and recompaction, in a second firing again at 950 °C for about 12 h. The resulting samples are, according to powder x-ray data, largely single-phase[3] $Y_1Ba_2Cu_3O_{9-x}$. Two samples were used for the measurements, each having diameters of 0.63 cm and densities of about 4.7 gm/cm^3. The lengths were 0.3 and 0.8 cm. The superconducting transition, as detected by 2-kHz inductive measurements (real and imaginary parts), is shown in Fig. 1. The change in the imaginary part of the impedance (pure inductance) is consistent with flux exclusion over 95%–100% of the sample volume. This does not guarantee, however, a corresponding bulk superconductivity.

Measurements of the torsional modulus were made using the composite oscillator technique. The samples were bonded with vacuum grease or, in one case, with double-sided Scotch tape to a 100-kHz quartz torsional mode crystal. The diameter of the quartz crystal was 0.56 cm. The frequency was generated by a synthesizer and swept from 40 to 300 kHz. The current through the driving circuit was recorded and resonance could be detected by the occurrence of the expected "dispersionlike" behavior of the current (see Fig. 2). The maximum and minimum currents occur at frequencies f_r and f_a and correspond to damped resonance and antiresonance. For oscillating systems[4] with Q^{-1} (damping) large compared to the crystal bandwidth as determined by the quartz electromechanical coupling factor (and as occurred here), the undamped resonance frequency of the oscillator, f_{ur} is given to order $1/Q^2$ by the mean frequency $(f_a+f_r)/2$, and the damping by $Q^{-1}=(f_a-f_r)/f_{ur}$. Temperatures were measured with a thermocouple in contact with the sample.

The composite oscillator resonances were observed clearly from 80 to about 140 K. Above 180 K, the resonances were strongly damped due to the high losses in the softened vacuum grease bond. Figure 3 shows the temperature dependence of the first overtone resonance frequency from 80 to 140 K. The transition to the superconducting state is clearly marked by a reduction ~0.4% in f_{ur} occurring over a temperature range close to, but perhaps slightly below, that observed in the inductively measured transition. The torsional modulus of the sample can be

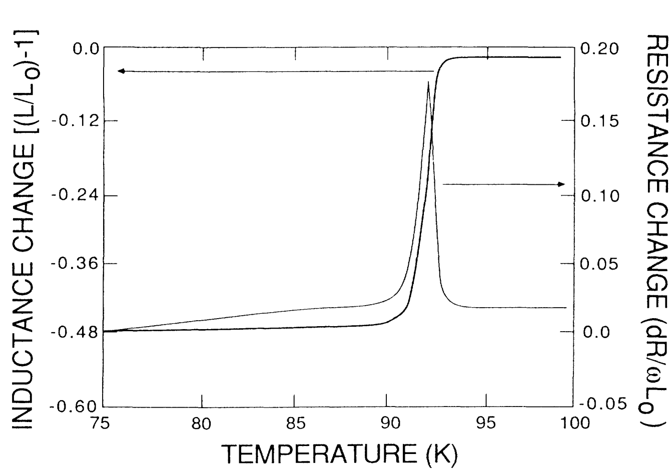

FIG. 1. Normalized imaginary and real parts of the impedance of the coil containing the sample vs temperature showing the superconductivity transition. L_0 is the empty coil inductance, dR is the reflected resistance of the sample filled coil minus that of the empty coil, and ω is the angular frequency.

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obtained[5] from the f_{ur} which are given by the roots of the equation

$$v_q\rho_q \tan\left(\frac{2\pi f_{ur}}{f_q}\right) + v_b\rho_b \tan\left(\frac{2\pi f_{ur}}{f_b}\right) + v_s\rho_s \tan\left(\frac{2\pi f_{ur}}{f_s}\right) - \frac{v_q\rho_q v_s\rho_s}{v_b\rho_b} \tan\left(\frac{2\pi f_{ur}}{f_q}\right) \tan\left(\frac{2\pi f_{ur}}{f_b}\right) \tan\left(\frac{2\pi f_{ur}}{f_s}\right) = 0 \; .$$

Here v_i, ρ_i, and f_i represent the torsional wave velocity, the density, and resonant frequencies $[=v_1/2(\text{length})]$ of the isolated ith component (quartz, bond, and sample). In the thin bond approximation ($f_b \rightarrow \infty$) we can solve this equation from known quantities and obtain $v_s = 1.7 \times 10^5$ cm/sec for the torsional or shear wave velocity of $Y_1Ba_2Cu_3O_{9-x}$. This value is low compared to a typical value for a ceramic solid, but probably results from the high porosity [ρ(measured)/ρ(theoretical) $= \sim 0.7$ of the sintered sample]. The solution of Eq. (1) also gives $\partial \ln f_{ur}/\partial \ln V_s \sim 0.5$ for the case at hand. Thus, for the sample the change in torsional sound velocity at T_c is $\sim 0.8\%$, and, from $c = \rho V^2$, a change in modulus c of $\sim 1.6\%$.

The change in modulus at the superconducting (or any Landau-type second-order) transition is related to thermodynamic quantities by[6]

$$\Delta c_l = \left(\frac{d \ln T_c}{d\varepsilon_l}\right)^2 T\Delta C \; , \quad (2)$$

$$\Delta c_s = \frac{d^2 T_c}{T_c d\varepsilon_s^2} T\Delta S \; , \quad (3)$$

where l and s correspond to longitudinal (volume changing) and high-symmetry shear (volume-conserving) moduli (c's) and strains (ε's), and ΔC and ΔS are the changes in specific heat and entropy at and just below T_c. This result is based only on the assumption of a phase transition where the change in free energy at T_c is of the general form $f(T-T_c)$ or $f(T/T_c)$. For typical superconductors $\Delta c_l/c_l \sim 10^{-6}$, which is about four orders of magnitude less than the behavior reported here.

There is no discontinuity in entropy at T_c for a superconductor, and thus Eq. (3) shows that there can be no discontinuity in magnitude for high-symmetry shear (or torsional) modes. Since a polycrystalline sample is usually describable by isotropic symmetry, the observed effect is, in addition to its large magnitude, one not allowed by standard thermodynamic theory of the superconducting phase transition. No explanation of this effect, with supporting evidence, is known to us. It is possible that the superconducting transition is accompanied by additional phenomena for which the thermodynamic assumption leading to Eqs. (2) and (3) does not apply.

Figure 3 shows a small negative temperature coefficient $d \ln v_s/dT \sim -10^{-4}\ \text{K}^{-1}$, above 100 K. This value is typical for solids in this temperature range.

Finally, Fig. 3 also shows the Q obtained from the width of the dispersionlike behavior of the frequency response at resonance. [The amplitude of the dispersionlike current behavior in the vicinity of resonance is also found to be proportional to Q, as expected (see, for example, Fig. 2).] Note that , although the data show substantial scatter, the transition to superconductivity is accompanied by an increase in loss, Q^{-1}. Acoustic losses normally decrease with the onset to superconductivity due to the disappearance of electron-lattice scattering, which causes "Joule-type" losses in the normal state. This effect, however, would be unobservable at the low frequency of our experiment.

The modulus behavior of the first overtone for the 0.8-cm sample shown in Fig. 3 was also observed in the fundamental mode for both the 0.8- and 0.3-cm samples and with two types of sample/quartz bonding agents. The loss

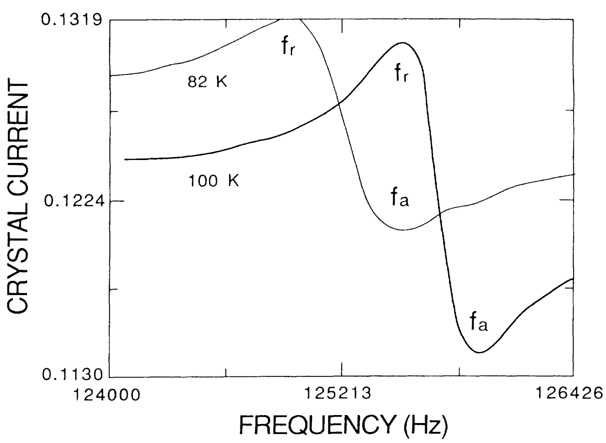

FIG. 2. Composite oscillator crystal current vs frequency in the vicinity of resonance at 82 and 100 K. The maximum and minimum current occur at resonance (f_r) and antiresonance (f_a), respectively.

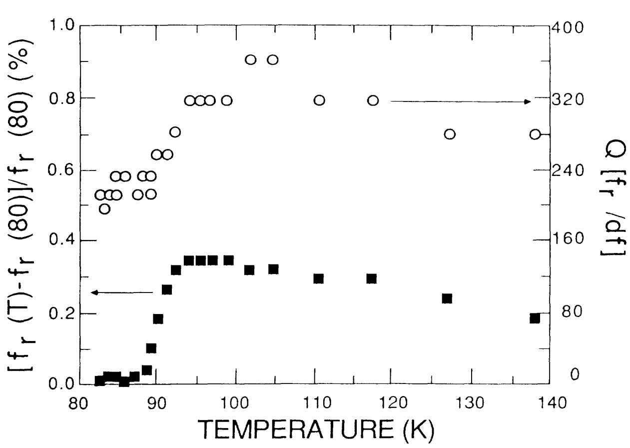

FIG. 3. Fractional change in oscillator resonance frequency (lower part) and Q (upper part) vs temperature. The fractional change in sound velocity for the torsional mode is approximately twice that shown on the left-hand side.

behavior, recorded only for the 0.8-cm sample, was not observed for the fundamental mode. The fundamental mode, however, had a substantially larger loss (due to the bond being positioned near the antinode of strain), which would likely have masked the effect at T_c.

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