Elastic response of polycrystalline and single-crystal $YBa_2Cu_3O_7$

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The elastic response (Young's modulus and internal friction) of the high-T_c superconductor $YBa_2Cu_3O_7$ has been measured in single-crystal and polycrystalline specimens. For the first time, we resolve the small expected lattice softening associated with the superconducting phase transition. The anomalous lattice stiffening below T_c in polycrystalline samples is present also in single crystals.

The unusually high superconducting transition temperatures associated with the metallic oxides La-Ba-Cu-O,[1] Y-Ba-Cu-O,[2] and related structures[3] suggest a new superconductivity mechanism. The observed zero or very small isotope shifts[4] give evidence for electron pairing mediated at least in part by nonphonon excitations. This is in contrast to conventional superconductors with relatively high T_c's, such as the *A*15 compounds, where a maximized T_c is thought to reflect only a very strong electron-phonon interaction.

A particularly useful probe of phonon structure and electron-phonon coupling in a solid is the determination of the bulk elastic properties of the material. For example, soft phonon modes associated with electron-phonon-driven Peierls transitions in charge-density-wave systems,[5] and those associated with the relatively high transition temperatures of most *A*15 compound superconductors,[6] are readily accessible by ultrasound propagation or vibrating-reed measurements. Indeed, the first study[7] of elastic properties of a high-T_c superconductor, performed on $La_{2-x}Sr_xCuO_4$, demonstrated a dramatic lattice-mode softening well above T_c, for $x \approx 0.15$ which maximizes T_c in this system.

In this Rapid Communication, we report on measurements of Young's modulus (Y) and internal friction (δ) of both polycrystalline and single-crystal $YBa_2Cu_3O_7$, employing a modified vibrating-reed technique. Our measurements allow intergranular effects in polycrystalline samples to be distinguished from intrinsic crystal elastic properties. Single-crystal elastic measurements in the *a*-*b* plane also yield information on the orthorhombic shear. In single-crystal studies, we find a small anomaly in the Young's modulus near T_c which we identify as resulting from the thermodynamics of the superconducting phase transition. In polycrystalline specimens, a large anomalous lattice stiffening is observed in the vicinity of T_c, in accord with other studies. Surprisingly, this anomaly persists in single-crystal measurements, suggesting it to be an intrinsic material property.

Polycrystalline samples of $YBa_2Cu_3O_7$ were prepared by standard methods. Needle-shaped specimens suitable for vibrating-reed measurements were cut from sintered pellets using a diamond saw. Single crystals were prepared from an off-stoichiometry eutectic melt. Following synthesis, crystals with typical dimensions $1\times0.25\times0.1$ mm^3 (the smallest dimension is the *c* axis) were further annealed in an oxygen environment at 750 °C. Resistivity measurements showed T_c's near 91 K for both polycrystalline and single-crystal samples, with transition widths ≤ 2 K. dc magnetic susceptibility measurements using a superconducting quantum interference device (SQUID) magnetometer indicated typical diamagnetic onsets near 90 K with ~10 K transition widths.

For elasticity measurements, samples were rigidly clamped at one end and a load mass was attached to the free end. Flexural vibrations were induced in the sample and detected with a capacitive technique.[8] Single crystals were mounted with the *c* axis parallel to the direction of oscillation. Changes in response frequency ω_r were related to Y by $\Delta Y/Y = 2\Delta\omega_r/\omega_r$, and δ was determined directly from the reciprocal of Q, where Q is proportional to the resonance vibration amplitude.

Figure 1 shows Y and δ for polycrystalline $YBa_2Cu_3O_7$ as a function of temperature.[9] The most striking feature is a sharp increase in Y just below T_c ($\Delta Y/Y = +4.5\times10^{-3}$); this is accompanied by a dramatic peak in δ. The anomaly in Y at a second-order phase transition can

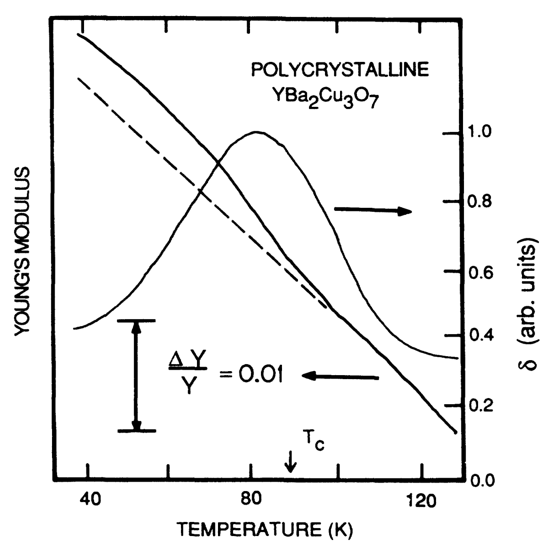

FIG. 1. Young's modulus (Y) and internal friction (δ) in polycrystalline $YBa_2Cu_3O_7$. The dashed line is an extrapolation of the high-temperature Y behavior.

be related to the stress dependence of T_c using themodynamic considerations[9]

$$\partial T_c/\partial \sigma_i = [-(\Delta Y/Y)T_c/(Y\Delta C_p)]^{1/2}, \quad (1)$$

where σ_i is the ith component of the stress and C_P is the specific heat. With $\Delta C_P = 4.95$ J/K (Ref. 10) and assuming $\partial T_c/\partial \sigma_i \approx \partial T_c/\partial P \approx 0.07$ K/kbar (Ref. 11) and $Y \approx 1\times 10^{12}$ dyn/cm^2, $\Delta Y/Y$ at T_c is predicted to be of order -3×10^{-5}. This predicted value is of opposite sign and orders of magnitude smaller that our measured Y change in the polycrystalline specimen. Similar unusually large anomalies at T_c have been reported for polycrystalline $YBa_2Cu_3O_7$ by ultrasonic and torsional measurements.[12,13]

Recent elasticity studies[14] of (polycrystalline) high-T_c superconductors have indicated that the polycrystalline Young's modulus may be strongly influenced by the single-crystal shear modulus, which demonstrates the importance of measuring the elastic properties of single-crystal specimens. Single-crystal measurements also isolate nonintrinsic features introduced by grain boundaries.

Figures 2(a) and 2(b) show, respectively, Y and δ as functions of temperature for single-crystal $YBa_2Cu_3O_7$.[15] Between 295 and 4.2 K, Y monotonically increases with a total change of 11%. However, substantial changes in slope in Y are apparent near T_c and at other temperatures. δ shows a dramatic peak near T_c. Before discussing these large anomalies, we examine the detailed behavior of Y near T_c. Figure 3 shows on a high-resolution scale Y as a function of T near 80 K. The data have been adjusted by subtracting a constant slope (that measured at 70 K) from experimental points. This adjustment allows discontinuities in Y to be more easily distinguished. Near 80 K, which corresponds roughly to the magnetic transition midpoint for this particular crystal, there is a discontinuity in the Young's modulus $\Delta Y/Y = -9\times 10^{-5}$ which is of the expected sign and order of magnitude from the thermodynamics of the superconducting phase transition (see above). From Eq. (1), our measured $\Delta Y/Y$ yields $\partial T_c/\partial \sigma_i = 0.13$ K/kbar. This is the predicted a-b plane stress dependence of T_c in single-crystal $YBa_2Cu_3O_7$, and the first such prediction for a high-T_c superconductor.

The data of Figs. 2(a) and 2(b) show additional unusual and unexpected features. Changes in the slope of Y are observed near 200–240 K (hysteretic) and 100 K, and there is a gradual rolloff in Y near 40–60 K. Figure 2(b) shows that many of the features in Y have associated structures in δ [the feature near 200 K in Fig. 2(b) is particularly interesting since it is largely suppressed upon sample warming]. Interestingly, a sharp peak at 160 K and additional structure near 260 K are visible in the internal friction, yet no associated anomalies are evident in the Young's modulus. The reduced temperature dependence of the Young's modulus which occurs below 60 K and the associated reduction of the internal friction has been seen in other materials[16] and can be attributed to the freezing out of phonon modes as $T \rightarrow 0$. A rather surprising finding is that near 100 K, the measured single-crystal data are similar to that for the polycrystalline samples (Fig. 1). This suggests that the anomalous stiffening

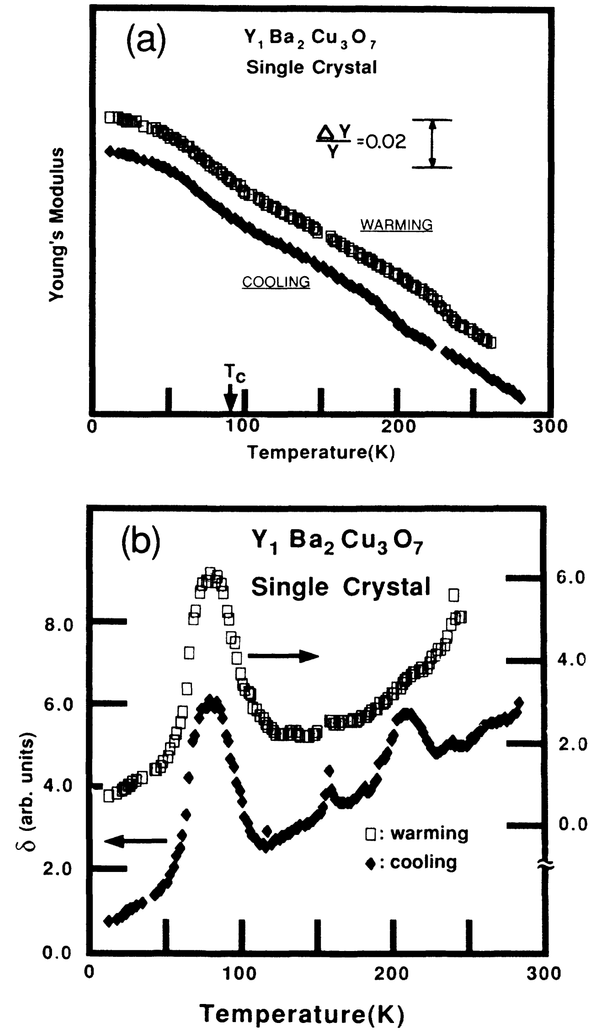

FIG. 2. (a) Young's modulus vs T in single-crystal $YBa_2Cu_3O_7$. The cooling and warming curves have been vertically displaced for clarity. (b) Internal friction vs T for single-crystal $YBa_2Cu_3O_7$.

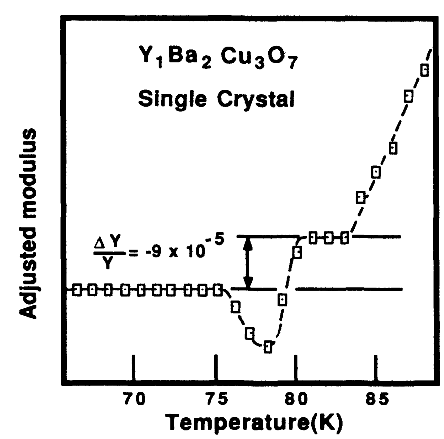

FIG. 3. Adjusted (see text) Young's modulus in single-crystal $YBa_2Cu_3O_7$ near T_c. The data indicate a discontinuity $\Delta Y/Y = -9\times 10^{-5}$.

below T_c observed in polycrystalline samples is not due to integranular effects, but is intrinsic to $YBa_2Cu_3O_7$.

It has been suggested[13] that the dramatic elastic anomaly near T_c in $YBa_2Cu_3O_7$ is associated with a structural phase transition, as evidenced by high-resolution x-ray scattering experiments[17] which show an anomaly in the orthorhombic splitting. In the geometry employed for our single-crystal vibrating-reed measurements, the measured Y is that associated with uniaxial loading along the a-b plane (Cu-O planes); the corresponding shear modulus is that between these planes. The general (first-order-corrected) expression[18] relating ω_r and Y is

$$\omega_r^2 = Yt^3s[(1+Kt^2Y/L^2G)4L^3M]^{-1}, \quad (2)$$

where t is the sample thickness (order 0.1 mm), s is the sample width (order 0.25 mm), L is the sample length (order 1 mm), M is the loading mass, G is the shear modulus, and $K\sim 1$. From Eq. (2), ω_r is significantly influenced by G only in the limit $G\leq Y/100$. G is bounded by the arithmetic and geometric means of c_{44} and c_{55} and for $YBa_2Cu_3O_7$ it is unlikely that the above limit is satisfied.

The direct connection between Y measured in our experiments and the stiffness tensor c_{ij} is not straightforward because of the substantial twinning in the a-b plane. If we assume that the a and b axes are randomly distributed in the a-b plane, then in the Reuss limit

$$Y_R = \frac{8(c_{11}-c_{12})[c_{33}(c_{11}+c_{12})-2c_{13}^2]}{(6c_{11}-c_{12})c_{33}-4c_{13}^2+\Delta/c_{66}}, \quad (3)$$

where

$$\Delta = (c_{11}-c_{12})[c_{33}(c_{11}+c_{12})-2c_{13}^2],$$

where for convenience we have assumed $c_{11}\cong c_{22}$ and $c_{13}\cong c_{23}$. In the Voigt limit,

$$Y_V = \frac{2(c_{11}-c_{12}+2c_{66})[c_{33}(c_{11}+c_{12})-2c_{13}^2]}{(3c_{11}+c_{12}+2c_{66})c_{33}-4c_{13}^2}. \quad (4)$$

These expressions act as formal boundaries for Y, i.e., $Y_R\leq Y\leq Y_V$. In both limits, the orthorhombic shear modulus $C_s = (c_{11}-c_{12})/2$ influences the effective Y. This modulus is conjugate to the orthorhombic strain $2(b-a)/(b+a)$, which from the structural studies[17] shows anomalous behavior near T_c. This suggests that the anomalous elastic behavior below T_c in polycrystalline and single-crystal samples is at least in part due to orthorhombic shear. The source of our observed single-crystal elastic anomalies near 160, 200–240, and 265 K is not clear. There are no confirmed corresponding anomalies in the structural or magnetic properties of $YBa_2Cu_3O_7$ in these temperature ranges. Interestingly, numerous reports have appeared of resistive fluctuations in Y-Ba-Cu-O between 220 and 240 K.

In conclusion, the single-crystal Young's modulus of $YBa_2Cu_3O_7$ has been measured and compared to the polycrystalline result. The expected elastic anomaly at T_c has been resolved for the first time, and it is consistent with thermodynamic predictions. Integrain coupling in polycrystalline samples does not appear to be the sole source of the lattice stiffening below T_c. It would be interesting to measure directly the shear moduli of single-crystal high-T_c materials, in particular $YBa_2Cu_3O_7$ near T_c, 160, and 200–260 K.

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1987).

[2]M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987); L. C. Bourne *et al.*, Phys. Lett. A **120**, 494 (1987).

[3]C. Michel *et al.*, Z. Phys. B **68**, 421 (1987); H. Maeda *et al.*, Jpn. J. Appl. Phys. **27**, L209 (1988); Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 55 (1988).

[4]L. C. Bourne *et al.*, Phys. Rev. Lett. **58**, 2337 (1987); L. C. Bourne *et al.*, Phys. Rev. B **36**, 3990 (1987); B. Batlogg *et al.*, Phys. Rev. Lett. **58**, 2333 (1987); T. Faltens *et al.*, *ibid.* **59**, 915 (1987); B. Batlogg *et al.*, *ibid.* **59**, 912 (1987).

[5]M. Barmatz *et al.*, Phys. Rev. B **12**, 4367 (1975).

[6]L. R. Testardi, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. 10, p. 193.

[7]L. C. Bourne *et al.*, Phys. Rev. B **35**, 8785 (1987).

[8]See J. T. Tiedje *et al.*, J. Acoust. Soc. Am. **65**, 1171 (1979); R. C. Lacoe, Ph.D thesis, University of California, Los Anglees, 1983 (unpublished).

[9]L. R. Testardi, Phys. Rev. B **12**, 3849 (1975).

[10]L. B. Nevitt *et al.*, Phys. Rev. B **36**, 2398 (1987); S. E. Inderhees *et al.*, *ibid.* **36**, 2401 (1987).

[11]J. E. Schirber *et al.*, Phys. Rev. B **35**, 8709 (1987).

[12]M. A. Migliori *et al.*, Solid State Commun. **65**, 827 (1987); D. J. Bishop *et al.*, Phys. Rev. B **36**, 2408 (1987); C. Duran *et al.*, Solid State Commun. **65**, 957 (1988).

[13]S. Battacharya *et al.*, Phys. Rev. Lett. **60**, 1181 (1988).

[14]X. D. Xiang *et al.*, Solid State Commun. **65**, 1073 (1988).

[15]S. Hoen *et al.*, Bull. Am. Phys. Soc. **33**, 513 (1988). We note that an independent ultrasonic study of single-crystal $YBa_2Cu_3O_7$ was not able to resolve any anomaly in Y at T_c [M. Saint-Paul *et al.*, Solid State Commun. **66**, 641 (1988)].

[16]G. Grimvall, *Thermophysical Properties of Materials* (North-Holland, Amsterdam, 1986), p. 54.

[17]D. M. Horn *et al.*, Phys. Rev. Lett. **59**, 2772 (1987).

[18]E. Goens, Ann. Phys. (N.Y.) **11**, 649 (1931).