Elastic response of polycrystalline and single-crystal YBa$_2$Cu$_3$O$_7$

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(Received 18 July 1988)

The elastic response (Young's modulus and internal friction) of the high-$T_c$ superconductor YBa$_2$Cu$_3$O$_7$ 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 A15 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,$^3$ and those associated with the relatively high transition temperatures of most $A15$ 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$_x$CuO$_4$, 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 ($\delta$) of both polycrystalline and single-crystal YBa$_2$Cu$_3$O$_7$, 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$_2$Cu$_3$O$_7$ 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 $1 \times 0.25 \times 0.1$ 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 $\lesssim 2$ K. dc magnetic susceptibility measurements using a superconducting quantum interference device (SQUID) magnetometer indicated typical diamagnetic onsets near 90 K with $\sim 10$ 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 $\omega_r$ were related to $Y$ by $\Delta Y/Y \approx 2\Delta \omega_r/\omega_r$, and $\delta$ was determined directly from the reciprocal of $Q$, where $Q$ is proportional to the resonance vibration amplitude.

Figure 1 shows $Y$ and $\delta$ for polycrystalline YBa$_2$Cu$_3$O$_7$ as a function of temperature.$^9$ The most striking feature is a sharp increase in $Y$ just below $T_c$ ($\Delta Y/Y = +4.5 \times 10^{-3}$); this is accompanied by a dramatic peak in $\delta$. The anomaly in $Y$ at a second-order phase transition can

![FIG. 1. Young's modulus ($Y$) and internal friction ($\delta$) in polycrystalline YBa$_2$Cu$_3$O$_7$. The dashed line is an extrapolation of the high-temperature $Y$ behavior.](image-url)
be related to the stress dependence of $T_c$ using thermodynamic considerations:

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

(1)

where $\sigma_i$ is the $i$th component of the stress and $C_p$ is the specific heat. With $\Delta C_p = 4.95$ J/K (Ref. 10) and assuming $\partial T_c/\partial \sigma_i = \partial T_c/\partial P = 0.07$ K/kbar (Ref. 11) and $Y = 1 \times 10^{12}$ dyn/cm$^2$, $\Delta Y/Y$ at $T_c$ is predicted to be of order $-3 \times 10^{-5}$. 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.\textsuperscript{12,13}

Recent elasticity studies\textsuperscript{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 nonintrusive features introduced by grain boundaries.

Figures 2(a) and 2(b) show, respectively, $Y$ and $\delta$ as functions of temperature for single-crystal $YBa_2Cu_3O_7$.\textsuperscript{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. $\delta$ 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 $\delta$ [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\textsuperscript{16} and can be attributed to the freezing out of phonon modes as $T \to 0$. 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 $\Delta Y/Y = -9 \times 10^{-5}$.\textsuperscript{17}
below $T_c$, observed in polycrystalline samples is not due to
intergranular effects, but is intrinsic to YBa$_2$Cu$_3$O$_7$.

It has been suggested\textsuperscript{14} that the dramatic elastic anoma-
ly near $T_c$ in YBa$_2$Cu$_3$O$_7$ is associated with a structural
phase transition, as evidenced by high-resolution x-ray
scattering experiments\textsuperscript{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\textsuperscript{16} relating $\omega$, $Y$, and $G$ is
\begin{equation}
\omega^2 = Yt^3s\left\{1 + Kt^2Y/LG - 2G/L^2M\right\}^{-1},
\end{equation}
where $t$ is the sample thickness (order $0.1\,\text{mm}$), $s$ is the
sample width (order $0.25\,\text{mm}$), $L$ is the sample length (order
$1\,\text{mm}$), $M$ is the loading mass, $G$ is the shear modulus,
and $K \approx 1$. From Eq. (2), $\omega$, is significantly influenced by
$G$ only in the limit $G \ll Y/100$. $G$ is bounded by the arith-
metic and geometric means of $c_{44}$ and $c_{55}$ and for
YBa$_2$Cu$_3$O$_7$ 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 straightfor-
ward because of the substantial twinning in the $a$-$b$
plane. If we assume that the $a$ and $b$ axes are randomly distrib-
uted in the $a$-$b$ plane, then in the Reuss limit
\begin{equation}
Y_R = \frac{8(c_{11} - c_{12}) [c_{33}(c_{11} + c_{12}) - 2c_{13}]}{(6c_{11} - c_{12})c_{33} - 4c_{13}^2 + \Delta/c_{66}},
\end{equation}
where
\begin{equation}
\Delta = (c_{11} - c_{12})[c_{33}(c_{11} + c_{12}) - 2c_{13}^2],
\end{equation}
where for convenience we have assumed $c_{11} \cong c_{22}$ and
$c_{13} \cong c_{23}$. In the Voigt limit,
\begin{equation}
Y_V = \frac{2(c_{11} - c_{12} + 2c_{66})[c_{33}(c_{11} + c_{12}) - 2c_{13}]}{(3c_{11} + c_{12} + 2c_{66})c_{33} - 4c_{13}^2}.
\end{equation}
These expressions act as formal boundaries for $Y$, i.e.,
$Y_R \leq Y \leq Y_V$. In both limits, the orthorhombic shear
modulus $G = (c_{11} - c_{12})/2$ influences the effective $Y$. This
modulus is conjugate to the orthorhombic strain $2(b - a)/(b + a)$, which from the structural studies\textsuperscript{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 ortho-
rhombic shear. The source of our observed single-crystal
elastic anomalies near $160$, $200$–$240$, and $265\,\text{K}$ is not
clear. There are no confirmed corresponding anomalies in
the structural or magnetic properties of YBa$_2$Cu$_3$O$_7$ in
these temperature ranges. Interestingly, numerous reports
have appeared of resistive fluctuations in Y-Ba$_2$Cu-
O between $220$ and $240\,\text{K}$.

In conclusion, the single-crystal Young's modulus of
YBa$_2$Cu$_3$O$_7$ 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. Integragin coupling in polycrystal-
line 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$_2$Cu$_3$O$_7$ near $T_c$, $160$, and
$200$–$260\,\text{K}$.

This research was supported in part by National Science
Foundation Grant No. DMR-840-0041 and by the
Director, Office of Research, Office of Basic Energy Science,
Materials Science Division of the U.S. Depart-
ment of Energy Sciences under Contract No. DE-AC03-
76F00098. S. Hoen acknowledges support from Fannie
and John Hertz Foundation, and A. Zettl received support
from the Alfred P. Sloan Foundation.

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