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# Bulk-modulus anomalies at the superconducting transition of single-phase $YBa_2Cu_3O_7$

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We report sound-velocity measurements on polycrystalline single-phase $YBa_2Cu_3O_7$ with a $T_c$ of 90 K. The sound velocity is found to increase as the temperature is reduced from room temperature in contrast to the decrease observed in $La_{1.85}Sr_{0.15}CuO_4$. At $T_c$ there is no discontinuity in the sound velocity within experimental resolution, as expected from thermodynamic arguments and the small value of $dT_c/dP$. As the temperature is lowered below $T_c$ the sound velocity increases at a greater rate. A similar increase below $T_c$ is observed in $La_{1.85}Sr_{0.15}CuO_4$. The magnitude of the sound-velocity increase below $T_c$ is much larger than observed in conventional superconductors.

The unprecedented interest in the high-$T_c$ superconductors has been fueled in part by the hope that they represent a class of materials in which a new pairing mechanism produces superconductivity. It is therefore important to measure a wide variety of properties of the superconducting state and identify any unconventional behavior in comparison with ordinary superconducting behavior. In this paper we report on sound-velocity measurements of single-phase $YBa_2Cu_3O_7$ through its superconducting transition. We find that the sound velocity increases monotonically on cooling from room temperature down to well below $T_c$. The behavior above $T_c$ is qualitatively different from that seen in $La_{1.85}Sr_{0.15}CuO_4$, which initially softens on cooling down to $\sim 100$ K, an effect which can perhaps be related to the structural transition known to exist in this temperature region. On the other hand, below $T_c$ we find that there is a pronounced hardening ($\sim 1000$ ppm) of the sound velocity, in agreement with previous measurements on $La_{1.85}Sr_{0.15}CuO_4$.[1,2] In ordinary superconductors there is typically a softening of the sound velocity at $T_c$, usually at the 10-ppm level. Therefore the changes seen at the superconducting transition in these materials have a different sign and are roughly 100 times larger than the effects normally seen. The standard thermodynamic expressions which relate the changes in sound velocity to thermodynamic variables of the transition seem incapable of explaining the magnitude of the effect we have seen.

Our experiments were performed on large single-phase, polycrystalline samples of $YBa_2Cu_3O_7$ prepared as described in Ref. 3. Lithium niobate transducers were epoxied on to the samples and ac susceptibility coils were also attached allowing us to correlate features in the sound velocity with the superconducting transition. The transducers were 10-MHz fundamental, longitudinal-mode, overtone polished crystals. However, because of the granular nature of our samples and the large Rayleigh scattering we were not able to perform useful measurements at frequencies in excess of 15 MHz. The changes in sound velocity were measured using the standard homodyne technique. The thermal expansion of this material has also been measured and the changes seen are small in comparison to the changes seen in the sound velocity, which indicates that what we are measuring are real changes in sound velocity and not changes in the length of the sample.

Shown in Fig. 1(b) are the changes in sound velocity from 150 to 50 K, which includes the superconducting transition. In Fig. 1 is also shown the ac susceptibility as measured simultaneously. In $YBa_2Cu_3O_7$ as the temperature is lowered from room temperature the sound velocity increases as it does for conventional solids. This is in con-

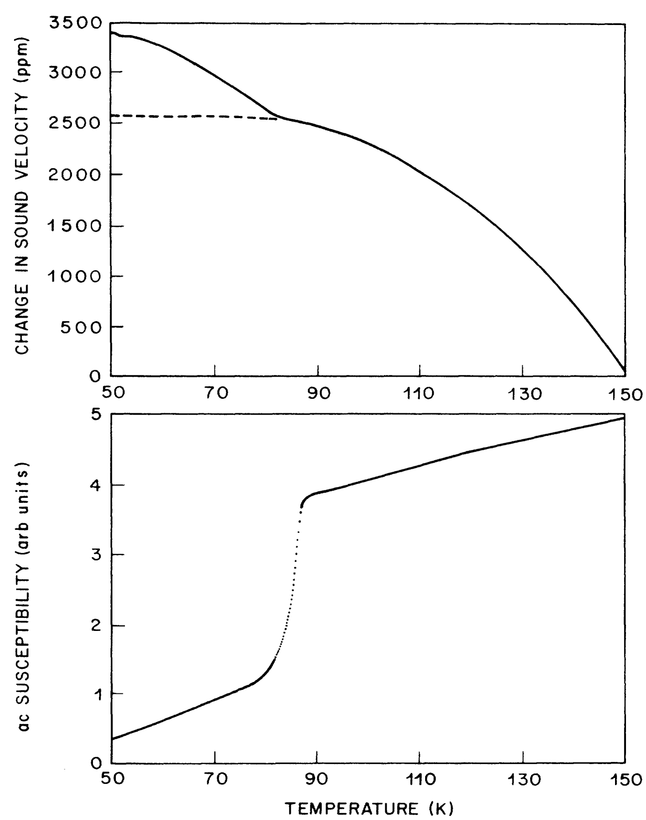


FIG. 1. The changes in sound velocity (upper) and ac susceptibility (lower) are shown for $YBa_2Cu_3O_7$.

trast to the anomalous behavior seen in $La_{1.85}Sr_{0.15}CuO_4$ in which the sound velocity softened upon cooling. Recent measurements on single-crystal $La_2CuO_4$ suggest that this anomalous softening is associated with the addition of Sr. Pure $La_2CuO_4$ shows the conventional behavior. However, as shown in Fig. 1 at the superconducting transition and as indicated by the ac susceptibility, the main result of this paper can be seen. There is a pronounced *hardening* of the sound velocity of $\sim 1000$ ppm that starts at the superconducting transition.

In Fig. 2 is a closer look at the region around the superconducting transition. Within the resolution of our experiment there does not appear to be a discontinuous drop in the sound velocity at $T_c$—merely the sharp increase roughly 2° below the temperature where the ac susceptibility indicates the onset of superconductivity. The linear dependence near $T_c$ and the overall shape of the deviations suggest that the changes in sound velocity are going as the gap squared. It should be noted that sound-velocity measurements are a true *bulk* probe of superconductivity similar to the specific heat. The small shifts in apparent onsets between the most optimistic probes, resistivity, or ac susceptibility and the sound velocity are to be expected. Our data, however, do provide compelling evidence that superconductivity in this material is a bulk effect, at least for our samples.

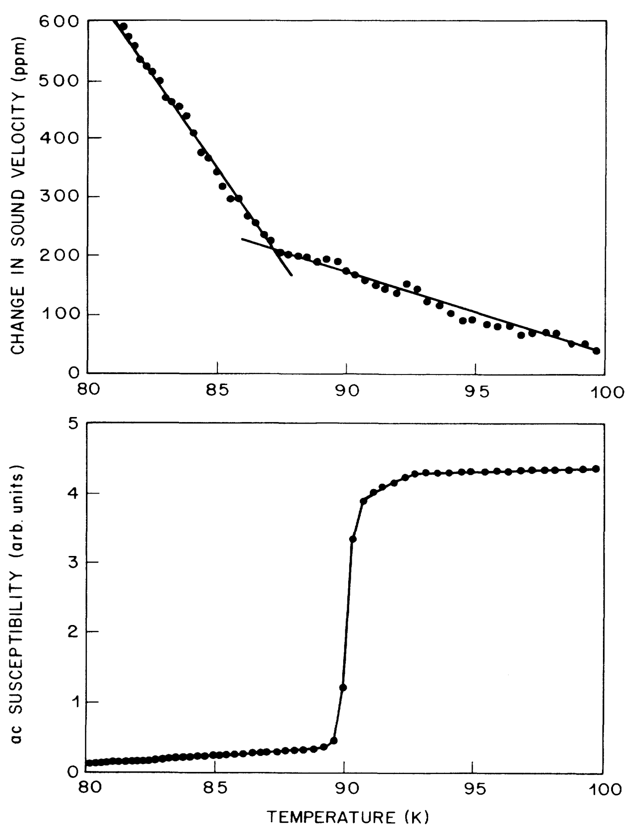


FIG. 2. The changes in sound velocity and ac susceptibility are shown on an expanded scale near $T_c$.

The standard thermodynamic analysis[4] of the changes in sound velocity at the superconducting transition suggest that there are two contributions. The first is a *drop* which occurs at $T_c$ and is given by the following specific-heat jump:

$$\frac{V_S^2 - V_n^2}{V_n^2} = -\frac{\Delta C}{T_c} B \left( \frac{\partial T_c}{\partial P} \right)^2 . \tag{1}$$

This may be rewritten as

$$\frac{\Delta B}{B} = \frac{-B}{4\pi} \left[ \left( \frac{\partial H_c}{\partial P} \right)^2 + H_c \frac{\partial^2 H_c}{\partial P^2} \right] .$$

In $La_{1.85}Sr_{0.15}CuO_4$ this drop is seen at $T_c$ and its magnitude agrees well with Eq. (1) using the independently determined values of $\partial T_c/\partial P$.[5] For $YBa_2Cu_3O_7$ as shown in Fig. 2, there is no measurable drop in the sound velocity at $T_c$. This is not surprising since the measured value of $\partial T_c/\partial P = 0.07$ K/kbar (Ref. 6) and Eq. (1) would predict a change of $\sim 1$ ppm, which is outside our resolution. Equation (1) therefore seems to be valid for both $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$.

One may extend the calculation in Eq. (1) away from $T_c$ by using a BCS model to compute the changes in the properties of the conduction electrons due to the superconductivity in combination with the Bohm-Stever expression for the conduction electron contribution to the sound velocity. Assuming that $\partial\Delta/\partial P = 1.76(\partial T_c/\partial P)$ and also that the other contributions to the lattice stiffness do not change with temperature, one finds for the change in sound velocity at $T=0$,

$$\frac{V_S^2 - V_n^2}{V_n^2} = \frac{(1.76)^2 \gamma}{B} \left[ \tfrac{1}{9} T_c^2 + \tfrac{4}{3} T_c B \frac{\partial T_c}{\partial P} - \left( B \frac{\partial T_c}{\partial P} \right)^2 \right] . \tag{2}$$

Substituting the known values for $T_c$, $dT_c/dP$, and $\gamma$, and using a reasonable estimate for $B = \rho_m v^2$ (where $\rho_m$ is the mass density and $V \sim 5 \times 10^5$ cm/sec) into Eq. (2) yields a velocity change of at most 10 ppm, which is a factor of $\sim 100$ smaller than we see. We conclude that this significant increase of the sound velocity below $T_c$ which varies like the gap squared and is seen in *both* $(La,Sr)_2CuO_4$ and $YBa_2Cu_3O_7$ is a generic feature of these materials and, unlike the specific-heat-related jump at $T_c$, cannot be explained within a simple BCS model. The only assumption which goes into deriving Eq. (2) is that the background lattice does not change its behavior near $T_c$. Thus, the present observations suggest the presence of an electronically driven structural anomaly in the vicinity of $T_c$, indicating the need for detailed, temperature-dependent crystallographic data.

To see why Eq. (2) fails, it is of interest to calculate the free electronic contribution to the bulk modulus for these materials. Using a carrier density of $3 \times 10^{21}/cm^{-3}$ we obtain $B = 2.4 \times 10^9$ dyn/cm$^2$ or about 0.1% of the total bulk modulus of $\sim 2 \times 10^{12}$ dyn/cm$^2$ for $YBa_2Cu_3O_7$. Therefore this very large increase in the sound velocity below $T_c$ due to superconductivity is even more surprising given the small, electronic contribution to the bulk modulus. The change below $T_c$ is comparable to the entire electronic contribution to the bulk modulus. Clearly, present theories are incapable of explaining this result.

In conclusion, we have measured the sound velocity of the high-$T_c$ superconductor $YBa_2Cu_3O_7$ through its superconducting transition. As in $(La,Sr)_2CuO_4$ there is an anomalously strong hardening of the bulk modulus below $T_c$. This behavior cannot be explained by the standard thermodynamics of the BCS model which describes conventional superconductors. This suggests that the transition drives or is driven by a change in the mechanical properties of the system. Clearly, our present understanding cannot explain this result.

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[1]D. J. Bishop, P. L. Gammel, A. P. Ramirez, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. **35**, 8788 (1987).

[2]L. C. Bourne, A. Zettl, K. J. Chang, M. L. Cohen, A. Stacy, and W. K. Ham, Phys. Rev. B **35**, 8785 (1987).

[3]R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 1676 (1987).

[4]G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. IVA, p. 277.

[5]J. E. Schirber, E. L. Venturini, J. F. Kwak, D. S. Ginley, and B. Morosin (unpublished).

[6]J. E. Schirber, D. S. Ginley, E. L. Venturini, and B. Morosin, Phys. Rev. B **35**, 8709 (1987).