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Hysteretic phase transition in $Y_1Ba_2Cu_3O_{7-x}$ superconductors

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We studied ultrasonic-wave velocities, both longitudinal and shear, in $Y_1Ba_2Cu_3O_{7-x}$, between 5 and 295 K, during both cooling and warming. Both waves, especially the longitudinal, show thermal hysteresis. The results suggest a hysteretic phase change that occurs between 160 and 70 K during cooling and between 170 and 260 K during warming. This phase-change hypothesis explains anomalies in several physical properties. The phase change agrees with thermodynamic-instability predictions. We confirmed the hysteresis in Ho-Ba-Cu-O, where it is smaller than in Y-Ba-Cu-O, and in Eu-Ba-Cu-O, where it is larger. In a companion perovskite, $BaTiO_3$, we observed zero hysteresis. At T_c, 91 K, sound velocities show no measurable change in either magnitude or slope. This continuity disputes the current popular view that, contrary to thermodynamics, elastic stiffness increases upon cooling through T_c into the superconducting state. We believe that stiffening results from the usual thermal effects after a phase transformation from a stiffer phase.

We need to know a superconductor's elastic constants (shear modulus, bulk modulus, and so on) because they relate closely to the Debye temperature, acoustic-phonon frequencies, and interatomic forces. Furthermore, elastic constants provide a sensitive probe of phase transitions, more sensitive than other related physical properties: thermal expansivity and specific heat. We need to understand a superconductor's phase transitions because its properties depend strongly on its crystal structure.

Several authors[1-8] reported low-temperature sound velocities or elastic constants of $Y_1Ba_2Cu_3O_{7-x}$. ($C=\rho v^2$ describes the relationship between sound velocity v, mass density ρ, and elastic stiffness C.) Many of these studies conclude that elastic stiffness increases upon cooling though the normal-superconducting transition temperature T_c. That the superconducting state stiffness exceeds the normal-state stiffness violates usual thermodynamic requirements for second-order and normal-superconducting phase transformations.[9,10]

Datta and co-workers[11,12] proposed a solution to the observation-thermodynamics dilemma on elastic stiffening below T_c. These authors suggested that reentrant softening occurs in the high-temperature phase above T_c. This softening ceases at T_c where the usual elastic stiffening during cooling resumes.

The present ultrasonic-velocity study provides another solution of the observation–thermodynamics elastic-stiffening dilemma. During both cooling and warming, we measured the longitudinal and shear sound-wave velocities in Y-Ba-Cu-O, Ho-Ba-Cu-O, and Eu-Ba-Cu-O. Results for all three superconductors show a hysteretic phase change. For brevity, we describe only the Y-Ba-Cu-O results. The Ho superconductor showed a smaller hysteresis; the Eu superconductor showed a larger hysteresis. Other Y-Ba-Cu-O specimens showed hysteresis, but with different transformation temperatures and curve shapes.

The studied Y-Ba-Cu-O material consisted of a 94% dense sintered pellet produced by usual powder ceramic methods. The oxygen atmosphere sintering schedule consisted approximately of 525 °C for 7 h, 900 °C for 5 h, 1000 °C for 3 h, cool to ambient temperature over 15 h. The specimen showed the following electrical properties: $J_c=353$ A/cm^2, $\rho(T_c)=258$ $\mu\Omega$ cm, $T_c=91.2$ K, RRR $=2.92$. The macroscopic mass density is 5.981 g/cm^3. By x-ray diffraction, we found orthorhombic unit-cell dimensions of $a=3.8270$, $b=3.8938$, $c=11.6668$ Å, and a unit-cell volume $abc=173.85$ Å^3. Using a molecular formula of $Y_1Ba_2Cu_3O_7$, this gives a theoretical mass density of 6.363 g/cm^3, thus, macroscopic mass density 94% of theoretical. Elsewhere, we report this specimen's elastic constants.[13]

Using a 3.4-mm-thick, 11.0-mm-diam pellet, we measured ultrasonic (near 5 MHz) longitudinal and shear sound-wave velocities using methods described elsewhere.[14,15] Transducers consisted of 1-cm-diam quartz disks, x cut and ac cut. From these velocities and mass density, we calculated elastic constants using standard formulas.[16] We neglected to correct for thermal expansion; from another study,[17] we estimate this introduces less than a 0.2% error in elastic stiffness at 4 K, and that no significant volume change occurs near T_c. From repeated measurements (removing and replacing transducer), we found a sound-velocity uncertainty of a few parts in 1000. Figure 1 shows a pulse-echo pattern.

Figure 2 shows our principal measurement results: shear modulus, bulk modulus, and Poisson ratio between 4 and 295, for both cooling and heating.

All the elastic constants show hysteresis. Especially, hysteresis emerges in the dilatation modes, the bulk modulus being the paradigm. Shear-mode-related elastic constants such as shear modulus, Young modulus, torsional modulus, and bending modulus show (or would show) smaller hysteresis. For the bulk modulus, the line diagram in Fig. 2 shows our interpretation of the temperature behavior. Upon cooling to 160 K, a transition begins (perhaps in two steps) from A phase to B phase. This transition continues to 70 K, below which we see the normal temperature dependence of the B phase to 5 K.

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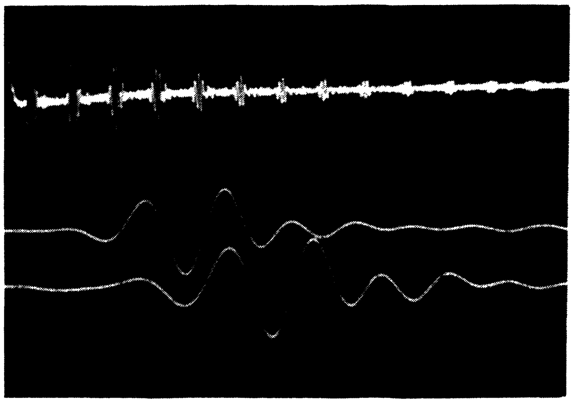

FIG. 1. Composite oscilloscope display of transverse-wave pulse-echo pattern at 4 K. Expanded first and second echoes are shown at bottom. Transit time was measured between the first minimum in these adjacent echoes. Carrier frequency equals 4 MHz.

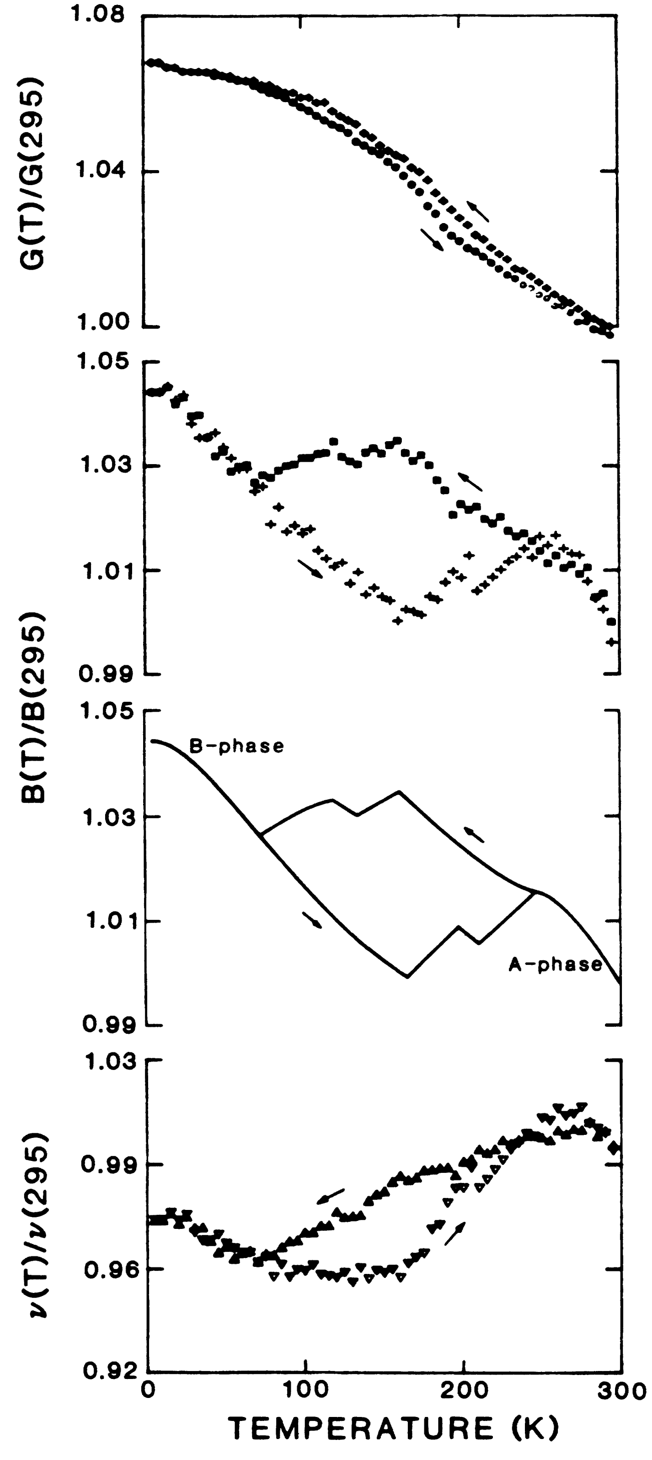

FIG. 2. For $Y_1Ba_2Cu_3O_{7-x}$, temperature variation of G=shear modulus, B=bulk modulus, and ν=Poisson ratio.

Warming follows the B phase to 170 K, where a transition begins (again, perhaps in two steps) to A phase, which reaches completion at 260 K. (Note that other Y-Ba-Cu-O specimens showed different transition temperatures.)

At the superconducting-transition temperature, 91 K, none of the elastic constants change measurably. This agrees with the high-precision ultrasonic velocity measurements by Laegreid, Fossheim, Vassenden, and Bough,[18] who found a $\Delta v/v$ decrease of only 5 parts in 10^5 during cooling through T_c.

These new measurements show that the increased elastic stiffness below T_c does not result from condensation into the superconducting phase. It results from the usual temperature dependence of the elastic stiffness *after* transformation from the higher-temperature phase. For the bulk modulus, during cooling, this transformation involves an elastic softening.

Comparisons with other physical-property measurements are difficult because usually authors fail to report whether they measured during warming or cooling. Laegreid, Fossheim, Sandvold, and Julsrud[19] measured specific heat during warming and found anomalies near 90 and near 220 K; they interpreted the latter as arising from oxygen-atom ordering. Figure 2 shows that the B phase-to-A phase transition centers near 215 K. Thus, it may correspond to the Laegreid *et al.* specific-heat anomaly. In studying the Raman spectrum of Y-Ba-Cu-O, Zhang *et al.*[20] found a peak that appeared below 240 K. Kurtz *et al.*[21] measured the decay of this peak with increasing temperature in $GdBa_2Cu_3O_{7-x}$ and concluded that it corresponds to a "broad diffuse phase transition." For $Y_2Ba_{0.8}Cu_3O_{7-x}$, Jackson *et al.*[22] found thermal-hysteretic behavior in reflected microwave power; the cooling transition centered near 150 K and the warming transition near 235 K; the authors attributed the hysteresis to "another transformation." Our results correlate with those of Bhargava, Herko, and Osborne.[23] These authors found T_c enhancement caused by temperature cycling below 239 K. Warming above 239 K destroyed the enhancement. Tentatively, the authors interpreted their results as "a phase transition with a two-dimensional to one-dimensional structural change or ordering." Interpreted against Fig. 2, their results suggest that the B phase (perhaps properly conditioned) possesses a higher T_c than the A phase.

Thermodynamic arguments also support the idea of a low-temperature phase transformation. Invoking the Nernst principle, Khachaturyan and Morris[24] predicted a low-temperature instability of the *Pmmm* crystal structure. They present two possibilities: orthorhombic (O_{7-x}) to a mixture of orthorhombic (O_7) and tetragonal (O_6); and orthorhombic (O_{7-x}) to orthorhombic (ordered) and orthorhombic (disordered). A phase transformation finds some support in the monocrystal x-ray-diffraction studies by Zhu, Zabel, and Salamon,[25] who found two orthorhombic phases with different lattice parameters, especially the *a* axis. (But, a similar powder-diffraction study by Horn *et al.*[26] showed only one phase and no thermal hysteresis.)

The cause of the hysteresis remains unclear. Usually, hysteresis arises from two sources: a nonchemical free energy from the elastic strain or the interface; or a barrier to nucleation of a new phase. Also unclear is why the phase transition occurs over such a wide temperature range. This temperature range resembles the sluggish phase transitions that occur in ferroelectrics, which the Y-Ba-Cu-O superconductors resemble in many ways.[21] Even though large sound-velocity changes occur, the transition may be subtle and not reflected in some physical properties. For example, the well-known 110-K cubic-tetragonal phase transition in $SrTiO_3$ involves only a two-degree rotation of the oxygen octahedron. This transition produces a large sound-velocity change but no change in dielectric constant.[27]

Ultrasonic-velocity measurements by Almond, Lambson, Saunders, and Hong fail to show the closed hysteresis loops shown in Fig. 1. These authors refer to "hysteresis ... characteristic ... in crystalline ceramics" and to "internal pressures ... during structural phase transitions." To explore this possibility, we measured the 5-295 K sound velocities of a similar material: $BaTiO_3$; within measurement uncertainty (1 part in 1000), we failed to observe hysteresis, despite the three low-temperature phase transitions that occur in $BaTiO_3$.

In summary, our sound-velocity measurements show thermal hysteresis suggesting a phase transition in *R*-Ba-Cu-O superconductors. For Y-Ba-Cu-O, the transition centers near 115 K during cooling and near 215 K during warming. (Between the two phases, this suggests an equilibrium temperature near 165 K.) This phase transition should affect both physical and electronic properties.

Note added. Since completing this study, we discovered two related studies. First, Ewert *et al.*[28] measured low-temperature longitudinal and transverse sound velocities in Y-Ba-Cu-O. They found hysteresis, which they attributed to coarse granularity, an interpretation different from ours. Second, Kurtz *et al.*[29] gave strong arguments for a ferroelectric state.

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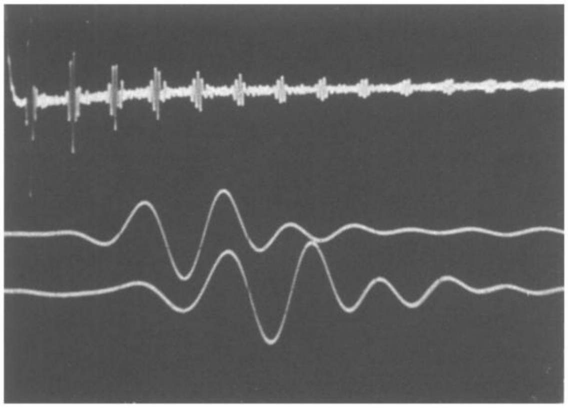

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