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Ultrasonic velocity anomalies in superconducting sinter-forged $YBa_2Cu_3O_{7-\delta}$

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The velocity of ultrasound was measured on sinter-forged polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples with a superconducting transition temperature of 91 K. The forging process results in crystallites which are preferentially aligned with their c axis aligned parallel to the forging axis as confirmed from optical and x-ray measurements. Sound-velocity measurements show that the material is elastically anisotropic. The temperature dependence of the sound velocity shows distinct anomalies. For propagation parallel to the forging axis, both longitudinal and shear waves displayed a thermal hysteresis between 65 and 260 K; however the longitudinal sound velocity with $\hat{\mathbf{q}}$ in the basal plane showed a much smaller thermal hysteresis. No effect of a magnetic field was observed on sweeping the magnetic field to 7.2 T at temperatures of 4 and 86 K.

Ultrasonic velocity measurements in isotropic polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples have been performed by several groups,[1-3] as a possible probe to explore the mechanisms of high-T_c superconductivity. In contrast to this work, our studies have been performed on sinter-forged samples. As will be discussed shortly, the sinter-forged material, developed at Northwestern University,[4] is highly textured and, hence, both structurally and elastically anisotropic.

The sinter-forging process consisted of the following steps. The material was calcined at 900 °C for 22 h, followed by a 950 °C "soak" in air for an additional five days. The powder was then removed from the furnace and reground in a mortar and pestle; this heat and grind process was repeated five separate times to hasten the reaction. Next the powder was pressed into a 2–3-g pellet in a 12-mm-diam double action die at 76 MPa with no binder added. The sinter-forging process itself was carried out in a resistance furnace. One of the above pellet samples was placed between two 25-mm-diam alumina rams; however, the pellet was separated from the rams by two sheets of 25-μm-thick platinum foil. Forging was carried out at 960 °C for 1 h under a constant force of 60-kg load in an atmosphere of flowing oxygen.

Since sinter forging provides no lateral restraint other than the friction between the platinum and the sample, a nonuniform densification resulted with higher density in the middle of the sample. However, the density of the whole pellet was 97% of the theoretical value. Physical measurements on the sample (x-ray diffraction and polarization microscopy) revealed strong morphological and crystallographic texturing. The grain size was 15 μm. A platelike grain shape, with an average thickness of 11 μm, an average diameter of 37 μm, and the c axis normal to the plate face, is characteristic of this material and is indicative of anisotropic surface energies. This texturing resulted in a significant anisotropy in the resistivity and magnetization.[5]

The Schulz reflection technique[6] was used to quantify the degree of preferred orientation. Shown in Fig. 1 is the normalized integrated intensity, I/I_0, of the (005) reflection versus the angle of the tilt α from the forging axis. The data can be fit to the equation

$$\frac{I}{I_0}=\exp\left[-\frac{\tan^2\alpha}{2(\Delta\alpha)^2}\right], \tag{1}$$

with $\Delta\alpha=0.29$. The c-axis distribution of the crystallites

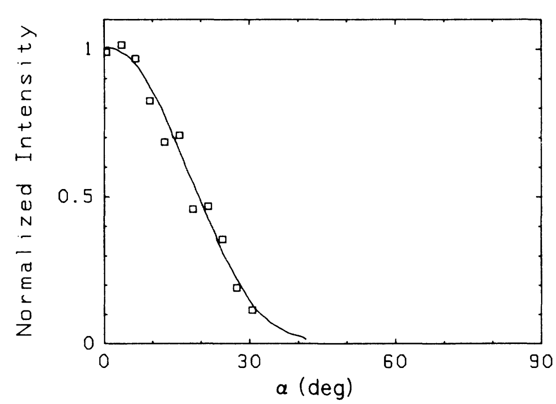

FIG. 1. Normalized x-ray intensity of the (005) reflection vs the tilted angle α from the forging axis.

exhibited rotational symmetry about the forging axis, i.e., a fiberlike texture as opposed to a sheetlike texture. In addition, the degree of preferred orientation varied within the sinter-forged specimens, being higher in the middle relative to regions near the surface. Generally, the variation in preferred orientation is a result of the aforementioned friction, leading to nonuniform flow patterns within sinter-forged specimens.

Samples made of this material show 80% ac shielding and 45% Meissner signals relative to an ideal superconductor. Magnetization measurements indicate that the lower critical field is about 700 G when the field is perpendicular to the forging axis and 1.3 kG when it is parallel, and that the critical currents parallel and perpendicular to the forging axis are 5.9×10^4 and 9.4×10^4 A/cm^2, respectively.[5]

The resistance of the samples used in this investigation was measured in zero field as they were cooled from room temperature to 4 K. The onset superconducting transition temperature, the 90%-10% width and the zero-resistance temperature were 92.8, 1.6, and 89.2 K, respectively.

X-cut or AC-cut piezoelectric transducers with fundamental frequencies of 12.0 and 14.5 MHz, respectively, were bonded to the samples with Epon 815 epoxy resin. Measurements were performed independently on two separate phase-coherent ultrasonic spectrometers and the results were identical within experimental error.

Both spectrometers measure the phase shift, $\Delta\phi$, of a received sound signal with frequency f_0 as the temperature or magnetic field is swept. The velocity change ΔV is related to the phase shift $\Delta\phi$ by

$$\frac{\Delta V}{V} = -\frac{\Delta\phi V}{2\pi f_0 d}\,, \tag{2}$$

where d is the distance traveled by the sound and V is the absolute sound velocity at some reference point (e.g., room temperature). The absolute velocity was determined using the expression

$$V_0 = 2\pi(d_2 - d_1)\frac{\Delta f}{\Delta(\phi_2 - \phi_1)}\,, \tag{3}$$

where subscripts 1 and 2 refer to two successive echoes; $\Delta(\phi_2-\phi_1)$ is the relative phase shift resulting from a shift of the oscillator frequency, Δf. From a linear fit of $\Delta(\phi_2-\phi_1)$ versus frequency plot for longitudinal waves propagating along the c axis, for a path distance of 3.28 mm we obtain a velocity of 3.76×10^5 cm/s. This result is consistent with the time-of-flight measurements.

The crystal structure of $YBa_2Cu_3O_{7-\delta}$ is orthorhombic and, hence, there are nine independent elastic constants. On general grounds we expect the sinter-forged material to display uniaxial symmetry. The elastic response would then involve five elastic constants. A model relationship between these two sets of elastic constants could be constructed by transforming the orthorhombic elastic constant matrix to a rotated reference frame, using the Euler matrix, and integrating over all Euler angles using the distribution function shown in Fig. 1 as a weight function. For the case of a cubic crystal this procedure has been discussed by Baral, Hilliard, Ketterson, and Miyano.[7] Since the results cannot be written down in general form (for our weight function), and since the elastic constants of the single-crystal material are unavailable for comparison, we will not perform the numerical calculations here.

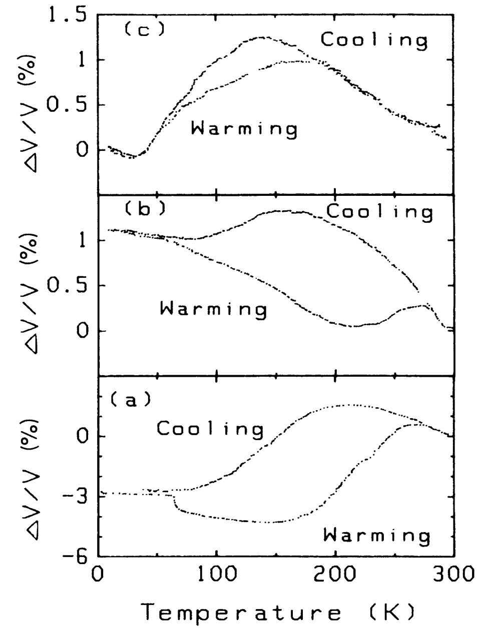

FIG. 2. (a) Temperature dependence of the longitudinal wave velocity with $\hat{\mathbf{q}}\parallel c$ in zero field at 12 MHz. (b) Shear wave velocity for $f=14.5$ MHz with $\hat{\mathbf{q}}\parallel c$ in zero field. (c) Longitudinal wave velocity with $\hat{\mathbf{q}}\parallel$(basal plane) in zero field at 12.0 MHz.

Table I lists the relation between the sound velocity and the uniaxial elastic constants, c_{ij}, for propagation directions $\hat{\mathbf{q}}$ and polarizations $\hat{\mathbf{e}}$ involving the c axis and basal plane directions. The table also summarizes our three independent absolute velocity measurements at room temperature. Note that for propagation along symmetry axis one can obtain only four of the five independent uniaxial elastic constants; a determination of the fifth elastic constant (c_{13}) would require propagation at an oblique axis, which was not studied in this work.

Temperature dependence of the velocity was also measured at zero field, shown in Figs. 2(a), 2(b), and 2(c).

TABLE I. Sound velocity for uniaxial symmetry and measured absolute velocity (m/s) at room temperature.

$\hat{\mathbf{e}}$ \ $\hat{\mathbf{q}}$	a	b	c
a	$\sqrt{c_{11}/\rho}$ 4.40×10^3	$\sqrt{(c_{11}-c_{12})/2\rho}$	$\sqrt{c_{44}/\rho}$ 2.66×10^3
b	$\sqrt{(c_{11}-c_{12})/2\rho}$	$\sqrt{c_{11}/\rho}$ 4.40×10^3	$\sqrt{c_{44}/\rho}$ 2.66×10^3
c	$\sqrt{c_{44}/\rho}$ 2.66×10^3	$\sqrt{c_{44}/\rho}$ 2.66×10^3	$\sqrt{c_{33}/\rho}$ 3.77×10^3

Figure 2(a) shows the temperature dependence of longitudinal waves for $\hat{\mathbf{q}} \parallel c$. The velocity initially increased on cooling until it reached a broad maximum around 230 K, after which it decreased until a temperature of 65 K, below which it flattened. The total velocity change was $\Delta V/V = 4.5\%$ from room temperature to 4 K. A surprising result was that on warming up from the lowest temperature the velocity started decreasing at 65 K. A distinct thermal hysteresis was observed between 65 and 270 K, as shown in Fig. 2(a).

All results are reproducible for a given thermal history. A run which focused on the hysteresis behavior was done as follows (Fig. 3): After warming up to 200 K, the sample was then cooled down to 4 K followed by a slow warm up to 145 K; a small thermal hysteresis was observed. We waited at 145 K for $\frac{1}{2}$ h and no further velocity change was observed. The sample was then cooled again to 4 K. The final warm-up from 4 K was unusual in that the velocity abruptly changed slope around 210 K so as to join the warming curve shown in Fig. 2(a).

Figure 2(b) shows the behavior of shear waves for $\hat{\mathbf{q}} \parallel c$. The velocity increased by 1.2% on cooling from room temperature to 160 K, followed by a small change of 0.25% between 160 and 4 K. During warming, thermal hysteresis was observed between 65 and 260 K. Sound propagation at both the first and third harmonic of the transducer was studied and only small differences in the behavior of the velocity was observed.

Figure 2(c) shows the temperature dependence of sound velocity for longitudinal waves in the basal plane. The sound velocity increased on cooling and reached a maximum around 150 K, after which it started dropping rapidly. Around 40 K, the velocity reached a minimum, which was approximately equal to the value at room temperature. We obtained $\Delta V/V = 1.5\%$ between 290 and 4 K. Note there is a smaller thermal hysteresis observed for longitudinal waves propagating in the basal plane. The temperature was swept at a rate of about 1 K/min for all

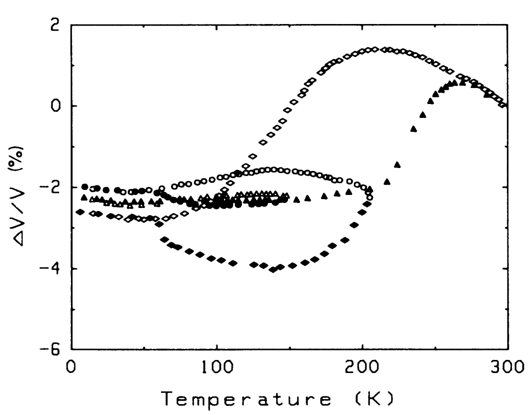

FIG. 3. Thermal hysteresis behavior of the longitudinal wave velocity with $\hat{\mathbf{q}} \parallel c$ in zero field at 12 MHz. The point designations and the order of the temperature steps are as follows: cooling down from room temperature to 4 K (◇); warming from 4 to 200 K (◆); cooling from 200 to 4 K (○); warming from 4 to 145 K (●); cooling from 145 to 4 K (△); and warming from 4 K to room temperature (▲).

of the above measurement configurations.

Sound velocity measurements were also performed in a magnetic field with $\mathbf{H} \parallel \hat{\mathbf{q}}$. Experiments were carried out to search for any magnetic field dependence of the velocity for shear waves propagating parallel to the c axis and longitudinal waves propagating both parallel and perpendicular to the c axis. For the shear waves, a temperature sweep was carried out at 7.2 T. This was followed by field sweeps at 4.2, 86, and 150 K. These temperatures were chosen since they correspond to states well below, just below, and well above, the superconducting transition temperature. No field dependence of the velocity was observed in any of these measurements. For longitudinal propagation, field sweeps to 9 T were performed at $T = 86$ K and for both propagation directions; we again observed no field dependence of the velocity.

The behavior of the sound velocity above T_c in isotropic $YBa_2Cu_3O_{7-\delta}$, as measured by other groups,[1] basically obeys the Varshni function[8]

$$c_{ij}(t) = c_{ij}(0) - S/[\exp(\Theta/t) - 1] , \qquad (4)$$

where $c_{ij}(t)$, S, and Θ are an elastic constant, a quantity related to the zero-point motion and the Einstein temperature, respectively.[9] These groups also observed a kink, or a "reentrant softening,"[10] in the velocity versus temperature curve at T_c. In our work the velocity of ultrasound was measured in sinter-forged $YBa_2Cu_3O_{7-\delta}$ as a function of orientation, temperature and magnetic field. The results show the following novel features relative to other measurements.

(a) The longitudinal wave velocity starts softening dramatically at temperature much higher than T_c as the sample is cooled. The velocity softening stops between 40 and 60 K. For shear waves along the c axis, the velocity softening is much smaller [Figs. 2(a) and 2(b)]. We may compare this behavior with the temperature dependence of the sound velocity observed in $A15$ superconductors. For V_3Si,[11] the behavior of the sound velocity is similar to the longitudinal velocity softening observed here as the sample is cooled. This similarity may suggest a growing lattice instability with decreasing temperature. Note the velocity stops softening when a "stable" superconducting phase sets in. We see no clear anomaly (change in slope) in our velocity measurements on these samples at T_c; and this was confirmed by measurements with both spectrometers. This is not due to limited sensitivity of our spectrometers, since we do see the anomaly reported earlier in Ref. 1, when we make measurements on isotropic sintered pressed powders of the same compound. The strong hysteresis seems to be masking this effect, which is the same in all directions. The physics of this is not clear, though similar results have been reported elsewhere.[2,12]

(b) A strong velocity hysteresis is observed in the temperature dependence. One of our hysteresis curves (Fig. 3) looks much like that reported before.[2] It is interesting that all three of the temperature-dependent velocities measured in this work have about the same onset temperature for the hysteresis of 65 K, and the velocity softening is arrested in the vicinity of that temperature. This hysteresis effect may suggest a gradual (strain arrested) first-order transition between 40 and 270 K. Thermal analysis has been performed by some groups[13] on the isotropic $YBa_2Cu_3O_{7-\delta}$ material in the above-mentioned temperature region. Specific-heat anomalies were observed near 250 K, 160 K, and T_c. These anomalies were argued to be first-order-like structural phase changes.

(c) In more traditional superconductors, it is common to use a magnetic field to suppress superconductivity. However, in our measurements we see no visible magnetic field effect on the sound velocity. No visible effect of a magnetic field on the sound attenuation is observed either.[14] We should point out that in this particular measurement of sound velocity in a magnetic field our velocity resolution was limited to 0.1%. Recent measurements[15] on superconducting $LaSrCuO_4$ shows a small increase of 100 ppm at 4 K for a field change of 6.5 T. This has been interpreted as an increase in rigidity due to a well-formed flux lattice. The effect of the field is much smaller at higher temperatures. Measurements on sintered pellets of $YBa_2Cu_3O_7$ showed a much smaller increase in a magnetic field.[15]

The most intriguing question is whether the observed softening and hysteresis effects are related to the occurrence of high-temperature superconductivity in this material.

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