

## Ultrasonic evidence for a structural phase transition at 220 K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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Ultrasonic study of the superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  reveals the existence of a shear instability centered at  $\sim 220$  K. This instability is manifested by a large step in both the longitudinal and transverse velocities. This step is also accompanied by a peak in the attenuation. The analysis of the results suggests that the instability corresponds to a structural order-disorder transition.

Ever since the discovery of high- $T_c$   $A15$  "metallic" superconductors, the central question has been the possible mechanism responsible for the high transition temperatures. The advent of high- $T_c$  oxides such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has rendered this question even more interesting. In order to find a possible answer, it is useful to seek out the particular features that may be common to several of these high- $T_c$  superconductors; one such prominent feature is the existence of structural instabilities. In  $A15$  systems, e.g.,  $\text{V}_3\text{Si}$  (Ref. 1) and  $\text{Nb}_3\text{Sn}$  (Ref. 2), structural phase transitions have been observed to take place above, but relatively close to, the transition temperature ( $T_c + 4$  K and  $T_c + 22$  K, respectively). The superconducting oxides, on the other hand, are derived from the perovskite structure which is known to exhibit instabilities related to the existence of soft phonon modes.<sup>3</sup> These modes are characterized by a frequency that is decreasing with decreasing temperature and they can lead to elastic anomalies and structural phase transitions. For that reason, we have undertaken an ultrasonic study of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . The resistance and elastic properties of two characteristically different samples were measured and compared.

The polycrystalline samples were prepared by thorough mixing of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuCO}_3$  powders, milling with  $\text{Al}_2\text{O}_3$  balls and calcining for several hours at  $900^\circ\text{C}$  in air. The powders were twice reground and recalined to ensure homogeneity. One pellet (sample 1) was then pressed and sintered at  $930^\circ\text{C}$  in oxygen for four hours. The furnace was cooled down to  $550^\circ\text{C}$  and stabilized at that temperature for six more hours to allow for equilibration of the oxygen content, and finally cooled to room temperature. The other pellet (sample 2) was directly cooled, in the furnace, from  $930^\circ\text{C}$  down to room temperature, without equilibration at  $550^\circ\text{C}$ . The two samples were examined under the optical microscope to determine their grain size, and their oxygen content was measured using an iodine titration technique. The characteristics of the two samples are summarized in Table I.

For the four-probe resistance measurements, silver electrodes were painted at the two extremities of the samples and two sets of platinum leads were attached to the sample. These measurements were taken using a Keithley micro-ohmmeter with a current of 100 mA. For the ul-

trasonic measurements, a lithium niobate 10 MHz transducer was epoxied onto the sample. Four echoes were used simultaneously to determine the sound velocity and the attenuation. The measurements were taken with a fully automated superheterodyne ultrasonic system described elsewhere.<sup>4</sup> This system performs absolute attenuation but relative velocity measurements. The relative velocities are then scaled by a single manual measurement of the absolute velocity taken at room temperature. Both resistance and ultrasonic measurements were made simultaneously with the temperature drifting at a rate of approximately 0.1 K/m.

The resistance as a function of temperature is plotted in Fig. 2, for the two samples. Both resistance curves exhibit a clear linear dependence on temperature with  $dR/dT$  equal to 7.3 and  $4.7 \mu\Omega/\text{K}$  for samples 1 and 2, respectively. We note that the room-temperature resistance of sample 1 and its transition temperature are both higher than those of sample 2. This is contrary to the relationship usually obtained for samples that differ primarily in their oxygen content for which a high room-temperature resistance is normally accompanied by a low transition temperature. We note, however, that repeated measurements of the resistance of sample 2 as a function of temperature resulted in varying  $T_c$ 's between 78 K (see Fig. 1) and 91 K. Such an observation has been reported previously<sup>5</sup> and tentatively attributed to a structural phase transition or ordering occurring close to 239 K. Therefore, it appears that the principal difference between the two samples is not their oxygen content.

Turning to the elastic properties, a pronounced difference between the two samples is apparent in Figs. 2 and 3. In Fig. 2, the sound velocity in sample 1 exhibits a significant step at  $\sim 220$  K for both shear and compressional waves. Sample 2, by contrast, only shows traces of

TABLE I. Characteristics of the two samples used in this study.

Sample	Treatment	Grain size	Oxygen content
1	$\text{O}_2$ annealed	25 $\mu\text{m}$	$\text{O}_{6.85}$
2	Furnace cooled	5 $\mu\text{m}$	$\text{O}_{6.75}$

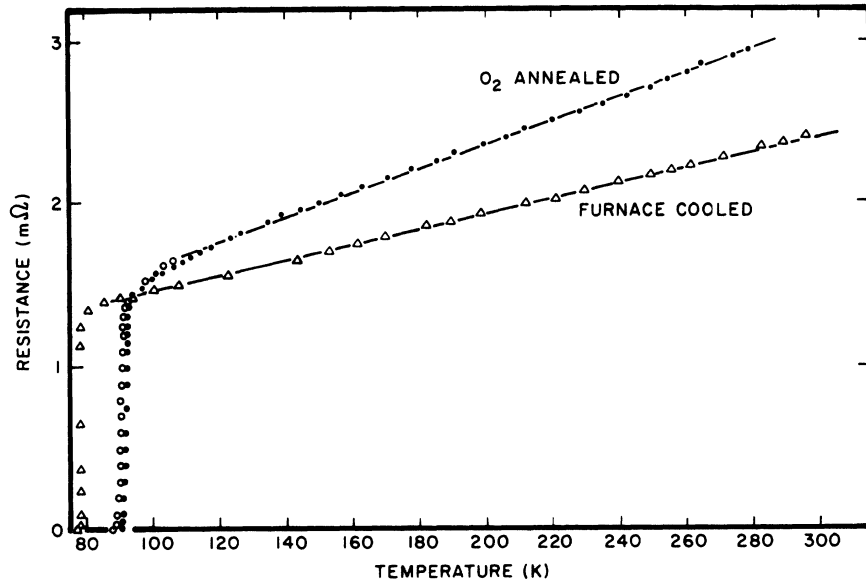


FIG. 1. Resistance as function of temperature; ●, cooling and ○, warming sequence.

a step at the same temperature. Regarding our present objective, the discrepancy in the compressional sound velocities of the two samples is not important, because the velocity measurements are relative, with temperature as the variable parameter. In Fig. 3 one can see that the step in sound velocity is also accompanied by a peak in the attenuation between 200 and 240 K, which is clearly larger for shear than it is for compressional waves. As we show below, this is primarily the result of a shear instability

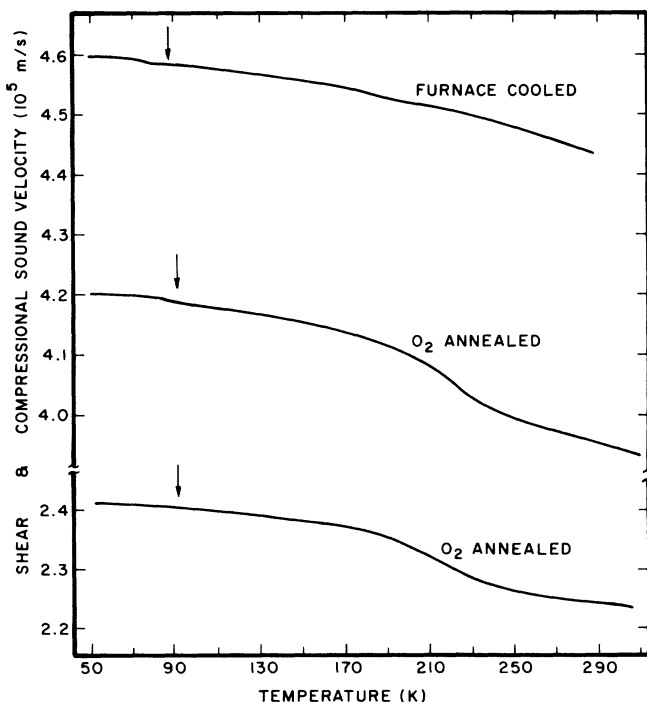


FIG. 2. Shear and compressional sound velocities. Arrows indicate the superconducting transition temperature.

manifested in sample 1 around 220 K. Conversely, the absence of a step in the sound velocity of sample 2 is also accompanied by the absence of the corresponding attenuation peak (figure not shown here). We now explain why the particular features observed in the sound velocity and in the ultrasonic attenuation correspond to a shear instability. In the absence of any special pressure treatment, a polycrystalline solid is, to a good approximation, isotropic. We can therefore write the velocities of compressional and shear curves as<sup>6</sup>

$$\rho v_c^2 = K + \frac{4}{3} G,$$

$$\rho v_s^2 = G,$$

where  $\rho$  is the density,  $K$  and  $G$  the bulk and shear moduli, respectively. These two expressions can be differentiated and then one divided by the other to give

$$\frac{\Delta K}{\Delta G} = \frac{v_c}{v_s} \frac{\Delta v_c}{\Delta v_s} - \frac{4}{3},$$

where  $\Delta v$  represents the magnitude of the step in velocity. Substitution of the experimentally determined values yields

$$\Delta K = +0.66 \Delta G.$$

Thus, we conclude that the features observed around 220 K result primarily from a shear instability.

Elastic instabilities in solids are usually manifested in the velocity of sound or equivalently in the elastic constants by either a downward cusp or by a step.<sup>7</sup> Cusps are usually observed near phase transitions where, due to the weakening of certain force constants, a particular phonon mode softens. Such is the case of displacive structural transitions. Steps, on the other hand, are observed near order-disorder transitions, corresponding to the cooperative reorientation of specific structural units. A particularly interesting example is given by  $\text{NH}_4\text{Cl}$  where the compressional velocity exhibits a downward cusp while

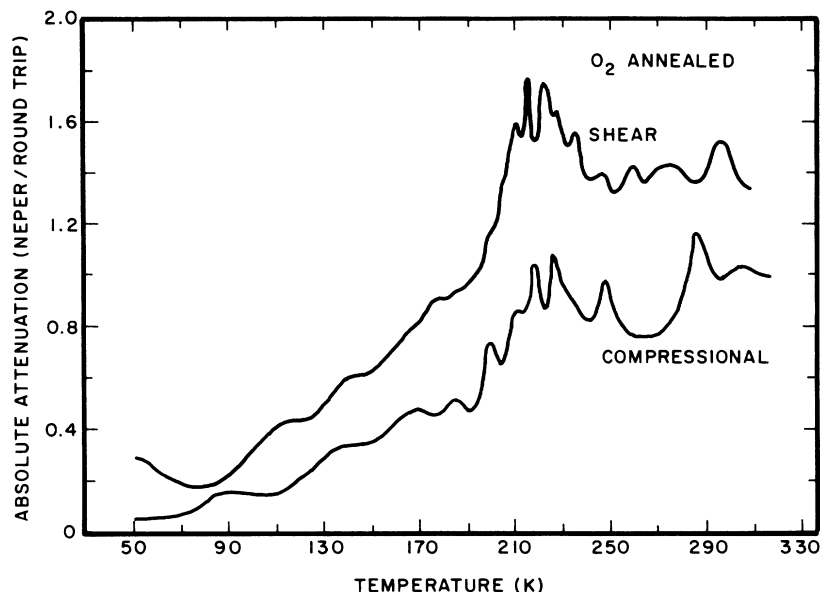


FIG. 3. Absolute ultrasonic attenuation of compressional and shear waves.

the shear velocity exhibits a step. Garland and Renard<sup>8</sup> successfully described the transition in terms of a compressible Ising model, in which the shear velocity step arises from an ordering or pure Ising contribution. In the present case, the experimental evidence therefore suggests an order-disorder transformation. A second remark can also be made to interpret the present results; namely that, in contrast with bulk modulus anomalies, a shear anomaly is only consistent with a change in structural symmetry.

The two previous remarks suggest that the transition at 220 K may involve the reorientation of structural units already present at higher temperature, and that this reorientation should also lower the symmetry. Finally, this reorientation should only affect the central part of the unit cell and not the chains, since the resistance does not show any departure from linearity around 220 K. A possible model, satisfying the three above conditions, is that the transition would correspond to correlated flips of the buckled Cu-O-Cu links along either the *a* or *b* directions in the two planes straddling yttrium, from upward to downward positions. Such an ordering of the bonds could lower the symmetry from orthorhombic *Pmmm* to *Pmm2* by loss of a mirror plane through the yttrium.

As mentioned earlier with regard to the respective resistance curves of the two samples, the absence of a transition in the furnace cooled sample 2 is probably not attri-

butable to the slightly lower value of  $\delta$ . This absence is more likely due to a different configurational state of the oxygen vacancies in sample 2 as a result of the different high temperature treatment. Such a suggestion would be consistent with the recent study of DeFontaine, Wille, and Moss<sup>9</sup> which predicts various possible states of order of oxygen vacancies in the Cu-O basal planes. It is important to stress that the oxygen vacancy ordering taking place at high temperature is frozen at 220 K and the order-disorder transition proposed here would only involve small reorientations (e.g., Cu-O-Cu bonds).

Other experimental techniques also provide evidence of the presently discussed  $\sim 220$  K transition. We note in particular a Raman line at  $646 \text{ cm}^{-1}$  which vanishes at 235 K (Ref. 10), a step in the dielectric constant<sup>11</sup> and a small peak in the heat capacity.<sup>12</sup>

In conclusion, we have reported evidence, from ultrasonic measurements, for a transition centered at  $\sim 220$  K. This transition appears to be of the order-disorder type and giving rise to a significant shear instability. Its occurrence may depend upon the state of ordering of the oxygen vacancies.

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<sup>1</sup>L. R. Testardi and T. B. Bateman, *Phys. Rev.* **154**, 402 (1967).  
<sup>2</sup>L. Pintschovius, H. Takei, and N. Toyota, *Phys. Rev. Lett.* **54**, 1260 (1985).  
<sup>3</sup>J. F. Scott, *Rev. Mod. Phys.* **46**, 83 (1974).  
<sup>4</sup>J. Toulouse and C. Launay, *Rev. Sci. Instrum.* **59**, 492 (1988).  
<sup>5</sup>R. N. Bharghava, S. P. Herko, and W. N. Osborne, *Phys. Rev. Lett.* **59**, 1468 (1987); **60**, 1455(E) (1988).  
<sup>6</sup>H. F. Pollard, in *Sound Waves In Solids* (Pion Ltd., London, 1977).  
<sup>7</sup>C. W. Garland, in *Physical Acoustics*, edited by W. P. Mason

and R. N. Thurston (Academic, New York, 1970), Vol. 7, p. 51.  
<sup>8</sup>C. W. Garland and R. Renard, *J. Chem. Phys.* **44**, 1130 (1966).  
<sup>9</sup>D. De Fontaine, L. T. Wille, and S. C. Moss, *Phys. Rev. B* **36**, 5709 (1987).  
<sup>10</sup>M. Zhang *et al.*, *Solid State Commun.* **65**, 487 (1988).  
<sup>11</sup>L. R. Testardi *et al.*, *Phys. Rev. B* **37**, 2324 (1988).  
<sup>12</sup>S. E. Inderhees *et al.*, *Bull. Am. Phys. Soc.* **33**, 466-I6.9 (1988).