Elastic Anomalies and Phase Transitions in High-T_c Superconductors

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Ultrasound propagation in both known classes of high-T_c ceramic superconductors reveals the presence of an anomaly above T_c, at $T_s \simeq 95$ K in $La_{1.8}Sr_{0.2}CuO_{4-y}$ and $\simeq 120$ K in $YBa_2Cu_3O_{7-\delta}$, suggesting that the state between T_s and T_c is the "normal" state preceding superconductivity. The anomalous elastic behavior at and below T_c is dominated by the shear modulus and not by the bulk modulus, implying an unusually strong coupling of the order parameter to shear distortions. Implications of these results for superconductivity are discussed.

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The search for the mechanism responsible for superconductivity in the high-T_c materials[1] has led to a search for conventional and unconventional behavior in every physical property. Elastic properties[2] were among the first to display unconventional behavior. Longitudinal ultrasound velocity displayed an unprecedented hardening below T_c.[3,4] Reconciliation of the behavior below T_c in terms of a bulk-modulus anomaly due to the condensation of carriers has proved difficult.[4,5] A large background anharmonicity makes it difficult to separate the effects of superconductivity from the normal-state behavior. We have reported earlier[5] that while a large background anharmonicity can account for some of the observed hardening in $YBa_2Cu_3O_{7-\delta}$ [hereafter referred to as (1-2-3)], the hardening below T_c in $La_{2-x}Sr_xCuO_{4-y}$ [hereafter referred to as (2-1-4)] remains much too large. In this paper we report results of ultrasound propagation, both longitudinal and transverse, in ceramic samples of (2-1-4) with $x=0.2$, $y=0.5$. The results demonstrate that it is the shear modulus and not the bulk modulus that is primarily responsible for the highly anomalous hardening in (2-1-4). Using the shear modulus as a probe we have found evidence for a hitherto unknown phase transition in the (2-1-4) as well as the (1-2-3) systems ($\delta = 0.04$) at a temperature T_s above T_c. The state between T_s and T_c may represent the "normal" state from which the bulk superconducting transition occurs, or T_s may signify the onset of granular superconductivity, as discussed below.

For a polycrystalline ceramic sample, a standard isotropic-elastic-medium approximation[6] applies. An isotropic medium possesses two independent elastic moduli, the bulk modulus B and the shear modulus G, related to the standard Lamé constants. In this approximation the longitudinal and transverse sound velocities are given by

$$\rho v_l^2 = B + \tfrac{4}{3} G, \tag{1a}$$

$$\rho v_s^2 = G. \tag{1b}$$

For a polycrystalline anisotropic material, G represents an average value. We emphasize that the longitudinal sound velocity does not yield the bulk modulus alone. By measuring both v_l and v_s in the same sample one can separate the effects of B and G. The thermodynamics of second-order phase transitions yields[7] the following anomalies in the bulk and shear moduli and the strain at the transition temperature:

$$\frac{\Delta B}{B} = -\frac{\Delta C_p}{T_c} B \left(\frac{\partial T_c}{\partial P}\right)^2, \tag{2a}$$

$$\frac{\Delta G}{G} = T\Delta S G \left(\frac{1}{T_c}\frac{\partial^2 T_c}{\partial \sigma_s^2}\right), \tag{2b}$$

$$\Delta\epsilon_a = T\Delta S \left(\frac{1}{T_c}\frac{\partial T_c}{\partial \sigma_a}\right), \tag{2c}$$

where ΔS is the entropy change, σ_s is the shear stress, ϵ_a is the generalized strain, and σ_a is the conjugate stress. For a mean-field transition, a discontinuity occurs at T in the bulk modulus itself (or any modulus involving a volume-nonpreserving distortion) and in the temperature derivatives of G and ϵ_a (i.e., G and ϵ_a are expected to show kinks at T_c since ΔS is continuous at T_c).[8]

Experimental techniques and sample-preparation methods are described elsewhere.[5] Figure 1(a) shows the temperature dependence of v_l and v_s in the sample of (2-1-4) mentioned above. Obviously, both v_l and v_s show pronounced hardening below T_c. The fractional changes in B and G are obtained from v_l and v_s with the relations

$$\frac{\Delta B}{B} \approx \frac{v_l^2(2\Delta v_l/v_l) - \frac{4}{3} v_s^2(2\Delta v_s/v_s)}{v_l^2 - \frac{4}{3} v_s^2}, \tag{3a}$$

$$\frac{\Delta G}{G} \approx \frac{2\Delta v_s}{v_s}. \tag{3b}$$

The variation of G is obvious from the variation of v_s

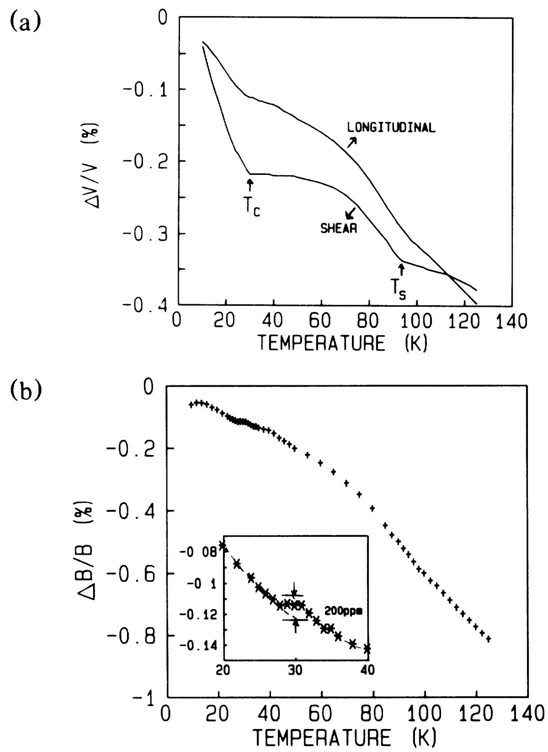

FIG. 1. (a) Temperature dependence of the longitudinal and transverse ultrasound velocities in the $La_{1.8}Sr_{0.2}CuO_{4-y}$ system. Two phase transitions at T_c and T_s are marked with arrows. (b) Temperature dependence of the bulk modulus evaluated from data in (a). Inset: The region around the nominal T_c marked by the resistive transition. The dashed line demonstrates the discontinuity reflecting the specific-heat jump. See text for discussion.

in Fig. 1(a). Figure 1(b) shows the variation of B. The remarkable feature of Fig. 1(b) is that much of the anomaly below T_c disappears. The inset shows the region around T_c; a smeared jump discontinuity at T_c is clearly visible as shown by the dashed line. This jump is of precisely the right magnitude from Eq. (2a), and no large enhancement in the background T dependence is seen in the superconducting state above the normal-state behavior. Thus, the hardening below T_c is dominated by the shear modulus, suggesting a large coupling between the superconducting order parameter and shear distortion. We are not aware of any theoretical model that anticipates or predicts such an occurrence.

Figure 1(a) also shows a marked anomaly in G at $T_s \simeq 95$ K, suggesting the existence of yet another (second-order) phase transition. We have reported earlier[5] a sharp longitudinal-sound-attenuation anomaly at this temperature whose origin could not be ascertained. The anomaly in G suggests, on thermodynamic grounds, that there is a phase transition at T_s.

We have also reported earlier[5] a similar attenuation anomaly at $T_s \simeq 120$–130 K in the (1-2-3) material.

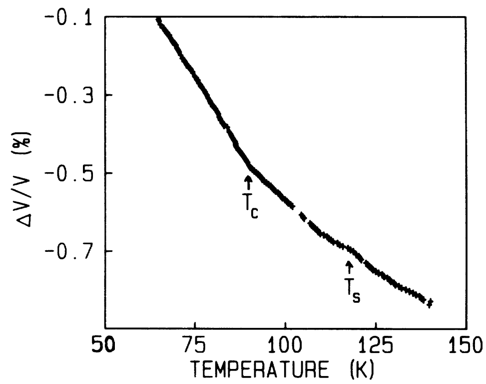

FIG. 2. Temperature dependence of the transverse ultrasound velocity in $YBa_2Cu_3O_{7-\delta}$. Two phase transitions at T_c and T_s are marked by arrows.

Therefore, we have used the shear modulus, a sensitive probe of phase transitions of this kind, to investigate the same system. The results are shown in Fig. 2. Two kinks, at T_c and T_s, are visible. The behavior of v_s near T_c is identical to that observed[4] for v_l but significantly larger. [In (1-2-3) the bulk modulus discontinuity is expected to be small, $\simeq 10$ ppm, because of the smallness of $\partial T_c/\partial P$ and is below the resolution of the measurements reported so far.] The other anomaly at $T_s \simeq 120$ K shows that a phase transition occurs here as well. The magnitudes of the anomalies at T_c and T_s in (1-2-3) are considerably smaller than those in (2-1-4).

Together, these results demonstrate that an intermediate phase transition precedes the superconducting transition in both known classes of superconductors. To the best of our knowledge, the existence of this phase transition has not been recognized before. This is a crucial result since it suggests that the state between T_s and T_c is the true "normal" state from which the bulk superconducting condensation occurs.

While the ultrasonic anomalies are sensitive probes of the existence of a phase transition, they are somewhat nonspecific as to its origin, much like the specific heat. We have therefore investigated other properties to find correlations. Earlier we reported[5] transport anomalies at T_s in both systems. In (1-2-3), dR/dT deviates at T_s from an essentially T-independent value above T_s. The precise location of T_s varies somewhat from sample to sample (typically between 120 and 135 K) and appears to depend on the oxygen stoichiometry. This effect is evident in essentially all the resistance data reported in literature and has been attributed to superconducting fluctuations.[9] Our results suggest that it may be caused by a second-order phase transition instead. The excess conductivity below T_s is found[10] to diverge logarithmically at T_c in contrast with the earlier reports of a power-law divergence.[9] Since this behavior persists in the single crystals[11] for conduction within the Cu-O planes, this phase transition may indeed be one affecting the planes.

High-resolution structural data[12] on (1-2-3) show a monotonic increase in the orthorhombic strain $\epsilon=2(b-a)/(b+a)$ with decreasing T. Around T_s, however, the strain deviates upwards from this background, i.e., a change in $d\epsilon/dT$ occurs around T_s. A further anomaly occurs at T_c. The unit-cell volume $(\hat{\mathbf{a}}\times\hat{\mathbf{b}}\times\hat{\mathbf{c}})$ and the planar area $(\hat{\mathbf{a}}\times\hat{\mathbf{b}})$ remain essentially featureless through this temperature range. We note that the relevant elastic constant[11] conjugate to the orthorhombic strain is the shear modulus $C_s=\frac{1}{2}(C_{11}\text{-}C_{12})$. Thus, it is likely that it is C_s that dominates the anomalies at T_s and T_c in the average shear modulus G measured in our experiments.

We are not aware of temperature-dependent structural data of comparable precision in the specific (2-1-4) system we have studied. But high-resolution neutron-diffraction data are available[13] for a closely related (2-1-4) system, namely $La_{1.85}Ba_{0.15}CuO_{4-y}$. For this system the reported longitudinal ultrasound propagation results[14] are essentially identical to what we have reported[5] in our specific sample. Inspection of the longitudinal sound-velocity data[14] in this system revealed an anomaly, although not discussed, around $T_s\simeq70$ K similar to what we observed around $T_s\simeq95$ K. Remarkably, the structural data show a monotonic increase in the orthorhombic strain with decreasing T until a departure downwards occurs in close proximity to T_s. The strain decreases between T_s and T_c until another kink in ϵ, i.e., a discontinuity in $d\epsilon/dT$, occurs at T_c in much the same way as in the (1-2-3) system. We note that the magnitudes of the anomalies are much larger in the (2-1-4) system in agreement with our observation of a much larger G anomaly. The transition at T_s is accompanied by features in magnetic properties as well. The magnetic susceptibility χ of (1-2-3) with the Curie term subtracted shows a pronounced downturn at T_s from a flat T dependence above.[10] The bare χ for (2-1-4) has an inflection point at T_s; but the Curie-term subtraction is much more difficult for this system. Moreover, ESR data[15] show the appearance of spin-wave-like excitations below T_s moving to lower g values with decreasing T. ESR data[16] on single-crystal (1-2-3) material shows a marked anisotropy in g values between the geometries with the field parallel and perpendicular to the planes. Below T_s, the former decreases sharply with decreasing T, the g values becoming nearly isotropic around T_c.

All these results imply that T_s is associated with some ordering transition affecting the $\hat{a}$-$\hat{b}$ planes in both materials. Since the structural data[12,13] in both systems show that an overall orthorhombic symmetry is preserved through T_s, the transition at T_s, undoubtedly subtle, occurs between two structures with orthorhombic symmetries. The primary order parameter for this particular transition remains unknown at this stage. A rotation of the Cu-O complex in the plane is a likely candidate. Since this is accompanied with features in transport and spin structure, it is likely to be driven by strong spin-phonon/carrier-phonon interactions. Possibilities of a spin-Peierls or a resonating-valence-bond-like transition[17] need to be investigated.

Now we return to the anomalies at T_c. An analysis of the orthorhombic strain in terms of the thermodynamic relation in Eq. (2c) yields a value of $\partial T_c/\partial\sigma\simeq4$ K/kbar for (2-1-4), about 10 times larger than $\partial T_c/\partial P$. For (1-2-3), this yields $\partial T_c/\partial\sigma\simeq-0.2$ K/kbar, again much larger than $\partial T_c/\partial P$, but curiously, of the opposite sign. Our results on shear-modulus anomaly, on the other hand, obtained from Eq. (2b), suggest that the second derivative, $\partial^2T_c/\partial\sigma^2$ [$\simeq0.2$ K/(kbar)^2 and $\simeq0.01$ K/(kbar)^2 in (2-1-4) and (1-2-3), respectively], is of the same sign in both systems but opposite to what is commonly observed in conventional superconductors.[8] These results illustrate the strong coupling of the order parameter to shear distortions, as mentioned earlier. Any successful mechanism of superconductivity has to address this extraordinary feature of this class of materials. Curiously, the elastic anomalies at T_c and T_s bear a striking resemblance to those in quasi-1D organic conductors at the charge-density-wave or spin-density-wave transition[18] that also opens a gap in the electronic energy spectrum. The hardening has been interpreted in terms of a reduction of the screening of lattice distortions due to the depletion of carrier density. Obviously, such a reduction of screening by carriers does not occur in superconductors. Therefore, the pronounced hardening of the shear mode below T_c may be due to the depletion of an excitation that cocondenses with the carriers and that also couples strongly to transverse-acoustic phonons. Spinons in the resonating-valence-bond model[17] or polarons (electronic or magnetic) are possible examples of such excitations. It should be noted that the condensation of carriers below T_c increases the thermal relaxation time τ as manifested in the thermal conductivity.[19] This mechanism can also harden the lattice in addition to yielding an attenuation peak that we have reported elsewhere.[5] In this picture, the damping and velocity change are given by

$$\alpha\approx\frac{D(\gamma)E_0(T)}{\rho v^3}\frac{\omega^2\tau}{1+(\omega\tau)^2},\tag{4a}$$

$$\frac{\Delta v}{v}\approx\frac{D(\gamma)E_0(T)}{\rho v^2}\frac{(\omega\tau)^2}{1+(\omega\tau)^2},\tag{4b}$$

where $D(\gamma)$ is a measure of the anharmonicity γ and $E_0(T)$ is the internal energy [i.e., $C_p(T)=dE_0(T)/dT$]. Whether it yields a quantitative explanation of the data is not known at this time. This would imply the presence of strong carrier-phonon interaction in the normal state. Whether it also implies phonon-mediated superconductivity is unclear. Specific theoretical calculations are needed for a more detailed interpretation of the results.

In summary, we have demonstrated that the striking ultrasound anomaly below T_c in (2-1-4) is dominated by the shear modulus and not by the bulk modulus. Analysis of shear-modulus data and structural data in both (2-1-4) and (1-2-3) implies that the order parameter has a much stronger coupling with shear distortions than with compressive distortions. What this implies for the symmetry of the order parameter remains to be seen. We have also found evidence for a phase transition at T_s, above T_c, in both classes of superconductors. Comparison with structural, magnetic, and electronic transport properties suggests that it is associated with ordering primarily in the $\hat{a}$-$\hat{b}$ planes. Whether this is restricted to the Cu-O planes alone in (1-2-3) without affecting the chains is not clear. Detailed structural measurements of the Cu—O bond lengths and occupancy of oxygen in various sites are needed. Furthermore, single-crystal data on shear modes with different polarizations would be valuable in further clarifying the nature of this transition.

The identification of the phase transition at T_s remains an outstanding problem. Interpretation of data such as reported here implicitly assumes a homogeneous sample. However, inherent inhomogeneities such as in oxygen stoichiometry in bulk grains versus in grain boundaries have not been ruled out even in the best samples. Therefore, we cannot eliminate possibilities that T_s may in fact be connected to superconductivity, e.g., an onset of granular superconductivity.[20] Indeed, evidence supporting such scenarios has already been reported.[21] Systematic investigations of such effects are necessary in order to establish at least the empirical phenomenology of this class of superconductors.

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