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Anomalous ultrasound propagation in high-T_c superconductors: $La_{1.8}Sr_{0.2}CuO_{4-y}$ and $YBa_2Cu_3O_{7-\delta}$

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Attenuation and velocity of longitudinal ultrasound in both known classes of the high-T_c copper-oxide superconductors are found to be highly anomalous compared to conventional superconductors. Attenuation shows a pronounced peak below T_c followed by an approximately power-law decrease at low T. The velocity shows a discontinuity in its temperature derivative at T_c followed by a large increase. The results are inconsistent with dominant contributions from the carriers alone. Anomalies are also observed at higher temperatures suggesting the existence of other phase transitions.

Propagation of ultrasound is among the standard probes of superconductivity. An exponential decrease in the attenuation below T_c signifies the opening of an energy gap. A step discontinuity in the velocity marks the mean-field specific-heat jump at T_c. Below T_c, the velocity has little temperature dependence. In the high-T_c superconductors $YBa_2Cu_3O_{7-\delta}$ and $La_{1.8}Sr_{0.2}CuO_{4-y}$, we found the sound propagation characteristics to be highly anomalous. Sound attenuation in the Y-Ba system increases below T_c and shows a pronounced peak. A similar but much weaker anomaly is seen in the La-Sr system as well. The sound velocity at T_c shows a marked discontinuity in its temperature derivative. Furthermore, the sound velocity increases very rapidly below T_c. Anomalies are seen at higher temperatures that suggest the existence of other phase transitions. A striking velocity softening is found in the La-Sr system that is distinctly different from what is commonly associated with structural phase transitions.

Samples were prepared in the usual way, sintered into a pellet at (900–1000) °C and annealed in oxygen or air at lower T for several days. Thermogravimetric analysis yielded values of the oxygen deficiencies δ and y to be 0.04 and 0.05, respectively. X-ray scattering studies were performed to ensure that the samples were single phased. The surfaces were subjected to repeated grinding and polishing. X-cut overtone-polished quartz transducers were bonded with Armstrong C-1 epoxy. Sound velocity (transit time) was measured using the McSkimin interferometry where a coherent reference pulse passing through a phase shifter and an attenuator is combined with the main pulse. Relative changes in velocity were measured to about 50 ppm level from the phase shift necessary to obtain a "null" condition. Attenuation measurements were made by fitting the echo train to an exponential and absolute values could be determined to a few percent. Because of Rayleigh scattering from grain boundaries, measurements at frequencies greater than 25 MHz could not be performed.

Figures 1(a) and 1(b) show the temperature dependence of the sound velocity in the Y-Ba and La-Sr sys-

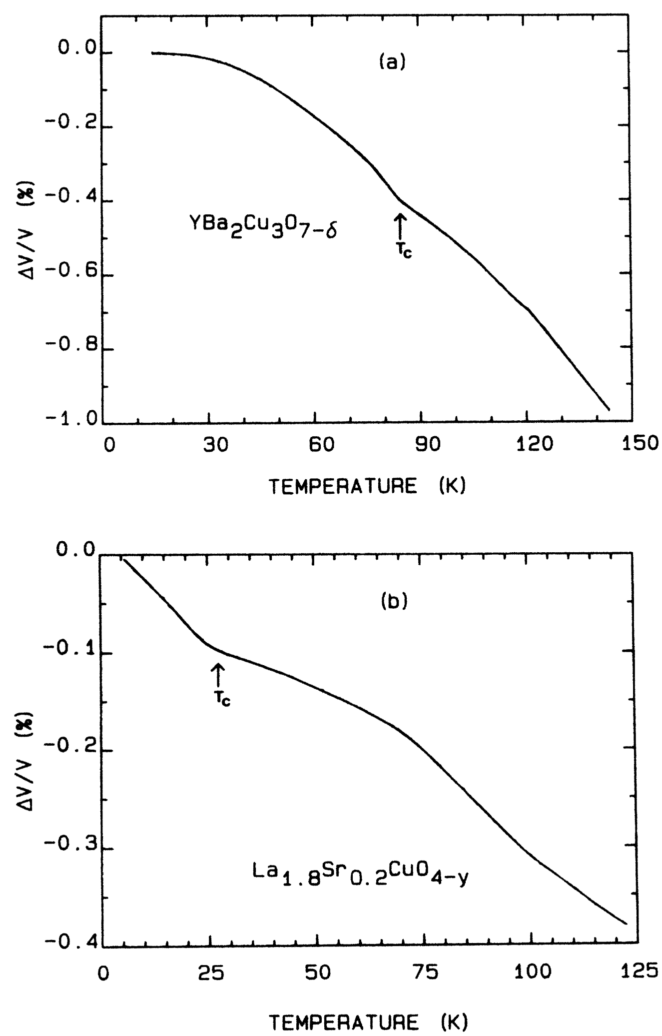

FIG. 1. Temperature dependence of the sound velocity in (a) $YBa_2Cu_3O_{7-\delta}$ and (b) $La_{1.8}Sr_{0.2}CuO_{4-y}$. Note the kink at T_c, i.e., a discontinuity in dv/dT, followed by a rapid increase.

tems, respectively. The velocities at 4 K are, respectively, 3.96×10^5 and 4.68×10^5 cm/sec. Qualitatively, the behavior is the same in both cases. The velocity increases with decreasing T and shows a pronounced kink at T_c followed by a rapid increase at lower temperatures. The behavior in the Y-Ba system is similar to that reported by Bishop *et al.*[1] although the changes are much larger in our sample. For the La-Sr sample we did not observe a step discontinuity at T_c as has been seen[2] on a $La_{1.85}Sr_{0.15}CuO_{4-y}$ sample. The results for the La-Sr sample are similar to the Young's modulus measurements.[3] A gigantic velocity hardening is observed in this system at higher temperatures; we shall return to this feature.

For an isotropic system, a good approximation for a polycrystalline material, the longitudinal sound velocity v_l is given by $\rho v_l^2 = B + \frac{4}{3} G$, where B and G are the average bulk and shear moduli, respectively. At this time we cannot separate the effects of the two quantities. In what follows we concentrate on the effects of the bulk modulus alone.

Using the generalized Clausius-Clapeyron relation for second-order transitions we obtain a step discontinuity in the bulk modulus of T_c given by

$$\frac{\Delta B}{B} = -\frac{\Delta C_p}{T_c} B \left(\frac{\partial T_c}{\partial P} \right)^2 . \quad (1)$$

Using the reported[4,5] values of ΔC_p and $(\partial T_c/\partial P)$ and assuming that B is nearly equal to ρv_l^2 we obtain a 15 and 300 ppm drop in the velocity at T_c for Y-Ba and La-Sr, respectively. While the former is below the resolution, the latter is not. But a smearing of T_c by a few degrees can account for the difference.

The temperature dependence of v_l below T_c is extremely anomalous. Compared to a typical change by a few ppm below T_c in conventional superconductors, v_l increases by 4000 and 1200 ppm in Y-Ba and La-Sr, respectively, between T_c and 4.2 K. In these superconductors, however, $T_c/\theta_{\mathrm{Debye}}$ is extremely large; so is the background anharmonicity in the vicinity of T_c. In the absence of a knowledge of the normal-state behavior, it is difficult to ascertain how much of the hardening below T_c is due to superconductivity. While some of it may indeed be due to the background in Y-Ba, this alone cannot account for the entire amount, particularly in La-Sr. We should also note that it is difficult to decide conclusively between (a) a precursor softening above T_c and a recovery below and (b) a hardening below T_c with no precursor above. Since the thermodynamic data are consistent with a mean-field behavior with no precursor effects above T_c, (b) is the likely scenario.

The magnitude of the change of the bulk modulus due to the condensation of carriers is given by

$$\Delta B_e \approx n \frac{\Delta^2(T)}{E_f} . \quad (2)$$

While the increase below T_c is indeed linear with $(T_c - T)$, i.e., consistent with a mean-field Δ^2 dependence, the magnitude is at least two orders of magnitude larger than the most favorable estimates of the parameters. Therefore, the hardening cannot be due to the carrier condensation alone. Whether this implies a cocondensation of other excitations that couple to the phonons remains to be seen.

We note that the enhancement of the temperature dependence of v_l below T_c is significantly larger in La-Sr which also has a much larger isotope effect.[6] It is also important to recognize that the shear modulus is expected to have a discontinuity in its temperature derivative at T_c on thermodynamic grounds;[7] a similar effect is seen in v_l in these experiments. It is, therefore, crucial to measure the shear modulus in order to separate the coupling of the superconducting order parameter to volume preserving (shear) distortions and volume nonpreserving (compressive) distortions.

In order to understand these results we have also measured the sound attenuation. Because of the low value of the conductivity, the low measurement frequency and the relatively high values of T_c, one does not expect to see a significant contribution to the sound attenuation from the conduction electrons. Figure 2(a) shows the temperature dependence of the attenuation for the Y-Ba system. First, we concentrate on the range below T_c. Surprisingly, the sound attenuation increases rapidly below T_c, reaches a pronounced peak around 65 K and then decreases slowly

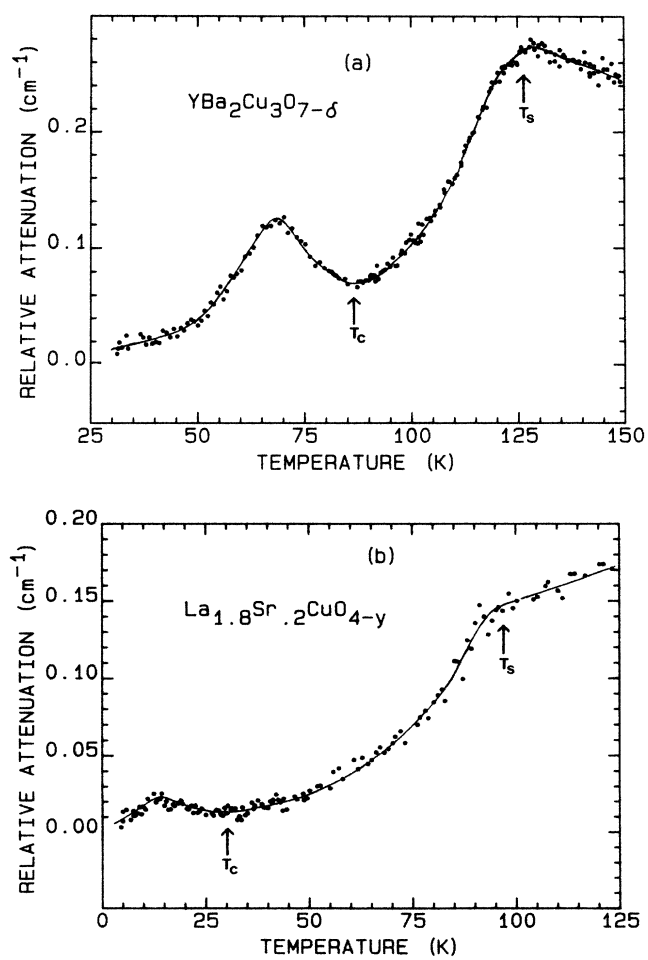

FIG. 2. Temperature dependence in attenuation in (a) $YBa_2Cu_3O_{7-\delta}$ at 5 MHz and (b) $La_{1.8}Sr_{0.2}CuO_{4-y}$ at 15 MHz. Residual attenuation at 4.2 K has been subtracted.

with decreasing T. Figure 2(b) shows the results for the La-Sr system. The effect below T_c is very small, essentially no change is observed below T_c until 15 K where a small and barely resolvable peak occurs. Moreover, at lower T the decrease in α is consistent with an approximate power-law T^β ($\beta \sim 3$–4) form. The exact value of β is sensitive to the estimate of the background; the power-law form should be taken as a qualitative distinction from the exponential form.

Taken together, these results bear an intriguing resemblance to the heavy-fermion systems.[8] While we cannot rule out some yet unknown analogies with them, the exact mechanism is unlikely to be the same since in the high-T_c superconductors α is expected to have very small contributions from the carriers near T_c, as mentioned above.

We note that phonon-phonon interactions provide an alternative explanation of this behavior. The sound damping is given by the Mason-Bateman formula[9] (for $\omega\tau < 1$ regime)

$$\alpha \approx \frac{D(\gamma) C_p T}{\rho v^3} \omega^2 \tau \, , \tag{3}$$

where $D(\gamma)$ is a measure of the anharmonicity γ and τ is the thermal relaxation time. If τ is limited by the scattering of phonons by the carriers in the normal state, then the condensation of the carriers below T_c enhances τ and thereby increases α. At lower temperatures the effect of τ saturates and the decrease in α is dominated by $C_p(T)$. Since in this picture the thermal conductivity $K \sim \alpha/T$, the temperature dependence of K is a stringest test of this hypothesis. Indeed, recent thermal conductivity measurements[10] are in excellent agreement with this picture.

The other striking feature of the data in Fig. 2 is the existence of yet another anomaly, marked T_s ($\sim$130 K for Y-Ba and 100 K for La-Sr) below which the attenuation decreases rapidly. The velocity data in Fig. 1 also shows anomalies near T_s. Comparison with electronic transport properties of the same samples show interesting correlations. In Y-Ba, the resistance shows a departure downwards at T_s from T dependence at higher T. In the literature[11] this has been attributed to superconducting fluctuations. In La-Sr this is masked by what appears to be a metal-semiconductor-like transition. But in both cases, a peak in $|\partial \ln\rho / \partial (1/T)|$ occurs at T_s. Furthermore, the thermopower in La-Sr system has a peak at T_s followed by precursor decrease until T_c where it decreases to zero.[12] However, the anomaly in α is too sharp to be caused by fluctuations. Furthermore, T_s is roughly the same in the two systems while T_c's are different by a factor of 3. Another possibility is the freezing out of a phonon with large density of states such as the one in La-Sr at 10 meV. Thermal depopulation of this phonon upon cooling can reduce α if this is a strongly coupled mode.[13] In the Y-Ba system there is no such phonon of comparable energy scale;[14] the lowest-energy phonon peak occurs at 20 meV ($\sim$240 K). Moreover, the decrease in α is inconsistent with the behavior expected from such an effect. It is likely that T_s is the signature of a phase transition. Detailed studies are needed to establish if this is indeed the case. Correlations with magnetic properties are also being investigated. ESR measurements[15] on the La-Sr system showed evidence for spin-wave-like excitations below T_s. Studies of Y-Ba are underway to determine if such excitations exist there too.

The most striking anomaly is seen in the La-Sr system at higher temperatures. Figure 3(a) shows the softening of sound velocity in this system which has been reported earlier.[16] Sound velocity starts to soften from room temperature with decreasing T. A gigantic drop ($\sim$10%) occurs between 220 and 190 K. Below 160 K, the softening is interrupted and slow hardening begins [cf., Fig. 1(b)]. Associated with the rapid softening is a pronounced increase in the attenuation in the same temperature range. The attenuation decreases linearly with decreasing T between 190 and 100 K where the rapid drop occurs, as shown in Fig. 2(b). X-ray scattering shows that this anomaly is apparently not due to a tetragonal to orthorhombic transition. The most significant feature of this anomaly is that the velocity at lower T does not recover to a high value, unlike in typical structural transitions and remains low over an extraordinarily large temperature range. In fact, the velocity at liquid-He temperatures

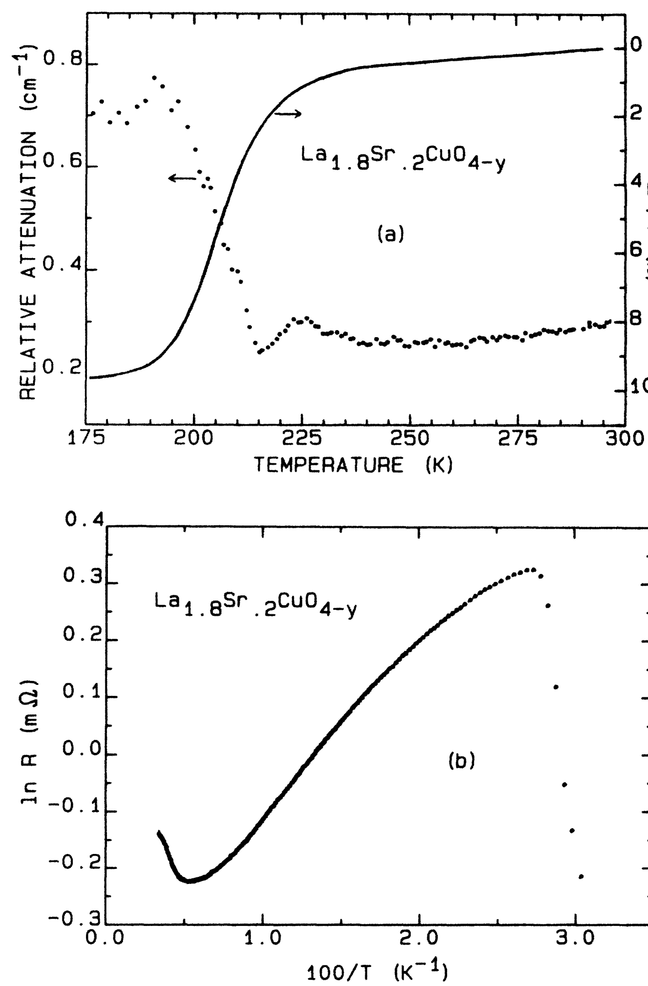

FIG. 3. (a) Temperature dependence of velocity and attenuation in oxygen deficient $La_{1.8}Sr_{0.2}CuO_{4-y}$. (b) The resistivity of the same sample. The resistance minimum occurs at 200 K, the midpoint of the ultrasonic anomaly.

is much smaller than the room-temperature value, while the attenuation is much larger. These results would indicate that the system remains near a mechanical instability over a large temperature range. At this time we have no explanations for this extremely anomalous behavior. Figure 3(b) shows the temperature dependence of the resistivity of the same sample. Clearly, a metal-semiconductor-like transition occurs at 200 K, the midpoint of the ultrasonic anomaly. The small apparent energy gap suggests disorder effects. This resistive anomaly was suppressed in our samples by reducing the oxygen deficiency by heating it at 600 psi O_2 at 500 °C. This suggests that the oxygen-defect-induced metal-semiconductor-like transition is accompanied with a strong mechanical instability.[17] The difference in the amount of velocity softening near 200 K between this sample and that of Ref. 2 may be related to the difference in oxygen deficiency. Ultrasonic studies with varying oxygen deficiency are in progress.

To conclude, the velocity and attenuation of ultrasound in the high-T_c superconductors are highly anomalous compared to conventional superconductors. The anomalies are not compatible with dominant contributions from electrons alone. Ultrasonic anomalies at a higher temperature (T_s) correlate with electronic transport anomalies which may signify the onset of some type of electronic or magnetic state probably accompanied by structural changes as well. As in the case with magnetism[18] in these systems, oxygen deficiencies appear to play an important role. The coupling of optical oxygen modes to acoustic modes and/or magnetoelastic effects may be relevant.

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