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Frequency-dependent ultrasonic attenuation of $YBa_2Cu_3O_7$

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At temperatures near T_c, experimental measurements of temperature-dependent ultrasonic attenuation at three frequencies exhibit maxima, and velocity measurements display softening of the lattice. These attenuation maxima result from a relaxation process which occurs around the superconducting transition, and the softening of velocity around T_c may evidence a structural instability of $YBa_2Cu_3O_7$ at these temperatures.

Recently, ultrasonic velocity measurements[1] on high-temperature superconductors of $YBa_2Cu_3O_7$ have been reported at frequencies in the megahertz range (≤ 10 MHz). It was observed that there occurred a slope change on the velocity versus temperature curve at a temperature near T_c. In addition, temperature-dependent ultrasonic attenuation[2] of single-phase $YBa_2Cu_3O_7$ at 15 MHz has also been measured and shows an anomalous maximum located at a temperature close to T_c (90 K). Several explanations were proposed for the source of this anomaly.[2] The maximum can be the result of a Debye-relaxation process, where the temperature-dependent relaxation time may be associated with a two-energy-level system, which may be due to defect tunneling, plasmons, or excitons, or may be caused by structural phase transitions. It may also be associated with the superconducting transition in a way similar to what happens for the ultrasonic attenuation behavior of some of the heavy fermion superconductors, such as URu_2Si_2 and UPt_3.[3] While the mechanism of superconductivity for producing the high-temperature superconductors is not quite understood, it is important to determine if these variations of the acoustic properties that occur around T_c are a direct consequence of the onset of superconductivity, because they may provide useful information for discriminating between different theoretical models. Frequency-dependent attenuation measurements are a useful probe to identify whether an anomalous sound energy loss is caused by an absorption of photons associated with a phase transition or results from a relaxation process, which in turn could identify the possible mechanisms that produce the dissipation.

Based on current preparation methods for powder samples, it is believed that ultrasonic measurements, which can be employed to obtain the mechanical and superconducting properties of the high-T_c samples without involving Rayleigh scattering, would be at sound frequencies below 30 MHz. For our sample, pulsed 10-MHz signals which are good for attenuation as well as velocity measurements can be obtained in the temperature range from room temperature to liquid-helium temperatures. However, at higher frequencies which are obtained from overtones of the same transducer with a 10-MHz fundamental frequency, clean and measurable signals are only obtainable at temperatures below 150 K.

The samples were prepared from carbonate and oxide powders by calcining and sintering at high temperatures. The starting purities were as follows: $BaCO_3$, 99.999%; Y_2O_3, 99.999%; and CuO, 99.999%. The proper ratios of starting powders were mixed thoroughly in a mechanical mixer-grinder and pressed into 0.5-in.-diam pellet with a force of ~5 tons. The samples were then heated in air to ~950 °C over a period of several hours and left at that temperature for ~24 h. The resulting pellet was crushed and ground in alcohol in the grinder-mixer to reduce the particle size and produce a more homogeneous sample. The powder was repelletized and given a second air treatment identical to the first. After further grinding and pelletizing, the samples were given a final treatment in flowing oxygen (~0.2 ℓ/min through a 1-in.-diam quartz tube) with a dessicant in line to trap out water vapor. The heating schedule was as follows: Heat to 950 °C in a few hours; stay at 950 °C for 24 h, cool to 650 °C in a few hours, remain at 650 °C for 16 h to allow the completion of the tetragonal-to-orthorhombic transition; cool to 400 °C in a few hours; remain at 400 °C for 8 h to allow maximal oxygen take-up; and finally cool to room temperature in a few hours. The resulting samples were black, tough, with a mass density about 75% of that of a single crystal, and produced strong levitation of a magnet at 77 K.

A 10-MHz $LiNbO_3$ longitudinal wave transducer was epoxy bonded on the surface of a pellet of a $YBa_2Cu_3O_7$ sample with a 1.23-cm diameter and 4.35 mm in thickness. By using the pulse-echo technique, a clean three-echo pattern was obtained at 10 MHz over the whole temperature range. Therefore, both the temperature dependence of attenuation and propagation time of the sound wave in the sample (using the echo overlapping method) could be measured. For the 27-MHz and 32-MHz signals, because their attenuation was much larger (approximately proportional to the square of frequency), only a single echo would be tuned for each frequency. In order to monitor occurrence of the superconducting transition, electrical resistance as a function of temperature of the sample was also measured simultaneously.

Figure 1 displays the temperature dependence of the ultrasonic attenuation coefficient at three frequencies, 10, 27, and 32 MHz, and of the electrical resistance, of the $YBa_2Cu_3O_7$ sample. Several features can be observed.

(1) There is an attenuation anomaly at a temperature near T_c for each frequency. This same behavior has been reported when ultrasonic attenuation was measured at 15 MHz by using a quartz transducer on a different sample.[2]

(2) The attenuation maximum has approximately a quadratic frequency dependence (see the inset in Fig. 1).

(3) The temperature at which the maximum occurs increases as the frequency of the sound wave increases.

Among these features, the temperature shift of the attenuation anomaly with frequency may be the most significant one. It illustrates the occurrence of a relaxation process, for which the attenuation can be qualitatively described by $\omega^2\tau/(1+\omega^2\tau^2)$, where ω is the angular frequency of the sound wave and τ is the temperature-dependent relaxation time. A possible source which induces the relaxation process can then be figured out by examining how the relaxation time varies with temperature.

To find the relaxation time τ, experimental data of the attenuation at any temperature were normalized to the maximum attenuation at the respective frequency, and then the following equation was used:

$$\alpha(T)\alpha_{\max}=2\omega\tau(T)/[1+\omega^2\tau^2(T)]\ , \qquad (1)$$

where α is the attenuation and $\alpha_{\max}$ is the maximum of attenuation. In Fig. 2, the natural logarithm of $\tau(T)$ is plotted with respect to temperature. A straight-line fit of the high-temperature data yields $\tau \sim \exp(450/T)$ while the low-temperature data yields $\tau \sim \exp(50/T)$. Although these three curves do not fall on top of each other, especially at low temperatures (below 70 K), we believe that an appropriate background attenuation subtraction would improve the agreement among the three curves. However, a relaxation time expressed by the above forms can mean that there exist relaxation processes with activation energies of 38 meV (450 K) and 4.3 meV (50 K). The former value is roughly equal to the value of the Debye temperature obtained by specific-heat measurements on $YBa_2Cu_3O_7$. This amount of energy appears to be less than the electron pairing energy needed for producing a high superconducting transition temperature; however it may be sufficient when both phonon and nonphonon mechanisms are produced,[2,4] especially when the multigap or anisotropic energy-gap models are considered.[5]

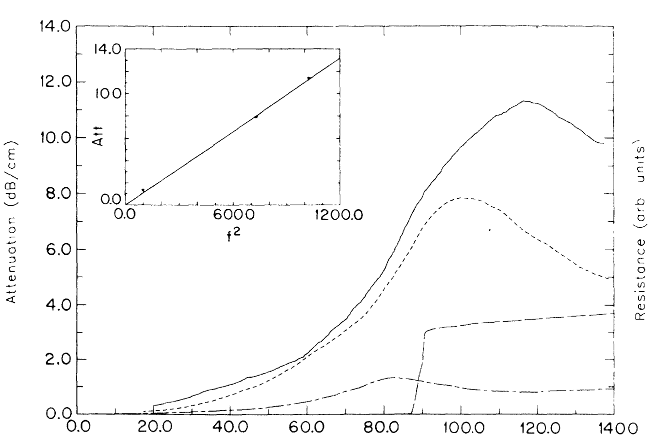

FIG. 1. Temperature-dependent ultrasonic attenuation and resistance curves of $YBa_2Cu_3O_7$ (curves from top to bottom belong to 32 MHz, 27 MHz, resistance, and 10 MHz, respectively). The inset shows the quadratic dependence of attenuation maximum on frequency.

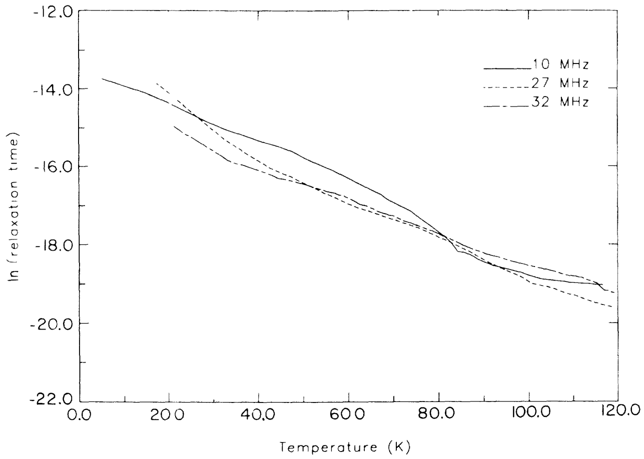

FIG. 2. Temperature-dependent relaxation time of $YBa_2Cu_3O_7$.

Temperature dependence of sound velocity in this $YBa_2Cu_3O_7$ sample at 10 MHz was calculated by using the room-temperature thickness of the sample divided by the propagation time measured with echo-overlapping method. Since the thermal expansion coefficient of $YBa_2Cu_3O_7$ is relatively small [the total change is within 20 ppm (Ref. 6) from room temperature to below 10 K] as compared with the measured variation of velocity, the thickness corrections were not taken into account in this treatment. In general, the sound velocity increases with decreasing temperature from 270 to 77 K. However, at temperatures close to T_c, the velocity decreases, deviating from its increasing trend, and exhibits a small dip on the velocity-versus-temperature curve. Also, the velocity increases faster in the superconducting state than it does in the normal state.

A recent report by Horn *et al.*[7] about the temperature variations of the lattice constants of $YBa_2Cu_3O_7$ indicated that an orthorhombic distortion occurs at temperatures between 60 and 140 K and showed that a maximum difference between b and a appeared around the superconducting transition. This distortion does not result in changes of the volume of the unit cell and the area of a unit basal plane. It may be possible that the softening of the sound velocity which occurs at T_c reflects this structural instability. It has been found[8] that softening due to the change of shear modulus at T_c is predominant over that of the bulk modulus. This further illustrates that the distortion is shear in nature. In fact, the results of temperature-dependent velocity measurements of $YBa_2Cu_3O_7$ in constant external magnetic fields up to 8 T (Ref. 9) showed that this softening shifted to lower temperatures with increasing field, which may be evidence that this softening around T_c is an intrinsic property of $YBa_2Cu_3O_7$ and is closely related to the superconducting transition.

It is possible that this distortion also enhances the energy loss of sound at temperatures around T_c. The difference between the temperature variation rates of the lattice constants a and b may produce anisotropic grain-boundary expansion or constriction with respect to the propagation direction of the sound wave. These grain-boundary motions together with their vibrations induced by the traveling sound waves result in a relaxation attenuation. Usually, for a relaxation process, the $\alpha_{\max}$ varies with ω. The quadratic dependence of $\alpha_{\max}$ on ω in our data may also be interpreted to be caused by this broad-temperature-range structural distortion. Some of the *A*15 structure superconductors have the similar frequency-dependent attenuation behavior resulting from their structural transformations at low temperatures.[10]

However, the possibility that an attenuation anomaly results directly from the intrinsic properties of $YBa_2Cu_3O_7$ cannot be totally excluded. As has been mentioned, a relaxation process can also be attributed to a perturbed tunneling effect when the sound wave deforms the lattice potential. It was reported[11] that the activation energy for the migration of oxygen is inferred to have a mean value close to 1.3 eV. Therefore, if the activation energy of 38 meV which we obtained is associated with a tunneling mechanism, it may be related to the motion of the copper electrons in a multiwell potential set by the surrounding oxygens in the Cu-O plane. A similar effect is the acoustoelectric effect,[12] which arises from the simultaneous bunching of electrons and holes in semiconductors caused by the passing of sound waves. The return of these carriers to their instantaneous equilibrium state in a multiwell potential shows a relaxation time, which exponentially depends on the inverse of temperature and has a similar mathematical expression to

$$1/\tau(T)=1.3\times10^{7}/[\exp(50/T)-1] + 9.95\times10^{9}/[\exp(450/T)-1]\,, \qquad (2)$$

which gives a reasonable fit to the data in Fig. 2. The attenuation coefficient of this effect is proportional to the square of the frequency of the sound wave. The fact that the electric current carriers of $YBa_2Cu_3O_7$ are holelike in the *ab* plane and electronlike along the *c* axis (or *ac* plane) could provide an environment for this type of relaxation process to happen. Although the above effects could account for the magnitude of activation energy that we obtained, measurements on the metal-doped $YBa_2Cu_3O_7$ samples are necessary to select between these different mechanisms.

In order to examine how the attenuation background changes with temperature, the relaxation attenuation at the three frequencies can be calculated by using the right-hand side of Eq. (1) times ω^2, with τ as expressed in terms of $1/T$ in Eq. (2), and using the slope of the straight line (1.11×10^{-2} dBμsec^2/cm) shown in the inset of Fig. 1. If these resulting curves are subtracted from the experimental attenuation data with appropriate adjustment of the zero in attenuation, it is found that an attenuation peak survives in the vicinity of T_c for all three frequencies. Figure 3 shows the result of this subtraction for the data of 15 MHz. The magnitudes of these remaining peaks are between 10% and 20% of the heights of the original peaks, and their temperature positions are much closer to T_c and not frequency dependent. Determining whether the remaining peak is associated with the superconducting transition or is just due to experimental uncertainties (which is about 5% in our measurements) will require attenuation measurements of longitudinal and shear waves with magnetic fields applied on the sample.

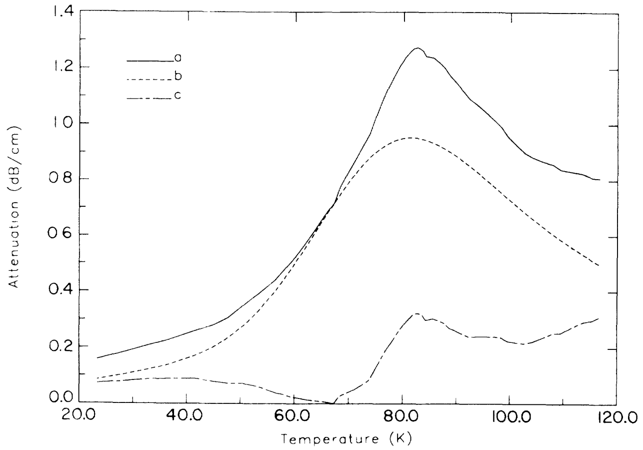

FIG. 3. An attenuation peak remains at temperature close to T_c (curve *c*) when the calculated relaxation attenuation (curve *b*) is subtracted from the experimental results (curve *a*). Experimental error is within 5% in our measurements.

In summary, temperature-dependent ultrasonic attenuation data of $YBa_2Cu_3O_7$ at various frequencies exhibits anomalies at temperatures close to T_c. These attenuation maxima are found to be the result of a relaxation mechanism added on top of an unusual attenuation background. It is proposed that the grain-boundary motions induced by the structural distortion and the propagation of the sound wave enhances the energy dissipation around T_c. Whether this structural distortion is the consequence of the onset of a superconducting state remains undetermined. It is also possible that either a tunneling effect or the acoustoelectric effect will contribute to sound energy dissipation. Furthermore, the temperature dependence of ultrasonic velocity shows a softening at T_c which may be an intrinsic property of high-temperature superconductors.

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