Ultrasonic study on Bi-based high-T_c superconductors with preferred orientations

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Ultrasonic experimental studies on Bi-based ceramic superconductors are reported. The specimens used in our experiments were hot pressed after sintering in air; therefore, a preferred orientation of the granules was obtained. The frequencies of ultrasound were about 10 MHz, both for longitudinal and for transverse waves. It has been found that anomalies in the attenuation coefficient and sound velocity occur near 220 K, in the range between 10 and 50 K above T_c, and at T_c, respectively. The investigation shows that the pretransition in the range between 10 and 50 K above T_c leads to a tendency of softness and instability in crystal lattice, and the superconducting transition is present on the background of a rapid decrease in attenuation with the decrease in temperature. It is believed that a strong superconducting fluctuation exists above T_c. The deformation-potential model for acoustic-phonon–electron interaction, which is the basis of BCS theory, may be unsuitable for the high-T_c superconductors. A model of superconductivity due to optical-phonon–electron coupling is suggested.

INTRODUCTION

Ultrasonic studies on high-T_c superconductors are limited primarily to ceramic specimens because large enough single crystals could not be obtained up to now. Ultrasound is attenuated greatly when propagating in porous ceramic samples; so it is difficult to obtain samples in which two or more pulse echoes can display pulse-echo patterns. It is necessary to prepare compact samples with preferred granule orientations in order to study the mechanism of high-T_c superconductivity, which is highly anisotropic.

Many ultrasonic investigations on Y-Ba-Cu-O and La-Sr-Cu-O specimens (sintered in air only) have been reported.[1-6] Most of the results show that no anomalies in attenuation and velocity, which are definitely related to superconducting transitions, were found, especially the phenomenon of rapid decrease attenuation with the decrease of temperature below T_c, which, in conventional superconductors, implies the existence of an energy gap in the quasiparticle excitation spectrum, and did not appear. For conventional superconductors, the ultrasonic attenuation coefficient due to electron-phonon coupling in superconducting states is expressed as[7]

$$\alpha_s(T)=\alpha_n\frac{2}{\exp[\Delta(T)/k_BT]+1}\ , \tag{1}$$

where α_n is the attenuation in normal state; $\Delta(T)$ is the energy gap and k_B is the Boltzmann constant. According to Pippard's theory,[8]

$$\alpha_n=\frac{4(m^*E_1)^2v}{5\pi\rho v_\theta^2\hbar^2}(qL_e)\quad(qL_e<1)\ . \tag{2}$$

In Y-Ba-Cu-O samples, Mase *et al.*[9] have estimated that $\alpha_n\sim 7\times 10^{-7}$ dB/cm for longitudinal waves of 10 MHz by using Eq. (2). This value is much lower than the resolution of the apparatus (e.g., 0.005 dB/cm for Matec 6600 system), so anomalies in attenuation due to superconducting transitions could not be observed even if they do exist. This seems to have been verified in Y-Ba-Cu-O.

We have prepared Bi-based specimens, hot pressed after sintering in air. Ultrasonic experimental investigations have been performed on the specmins. The ultrasound propagated along the direction of pressure, i.e., along the c axis of most granules. We found that a tendency of softness and instability in crystal lattice begins to occur in the range between 10 and 50 K above T_c; anomalies in attenuation are present at transition temperatures of all superconducting phases, which cannot be interpreted by the coupling between acoustic phonons and electrons.

FIG. 1. SEM photograph for a sample sintered in air only. Granules are thin plates in shape.

FIG. 2. SEM photograph for a sample hot pressed after sintering in air. The direction of pressure lies in horizon in this figure. The orientations of most granules (c axis) align the direction of pressure.

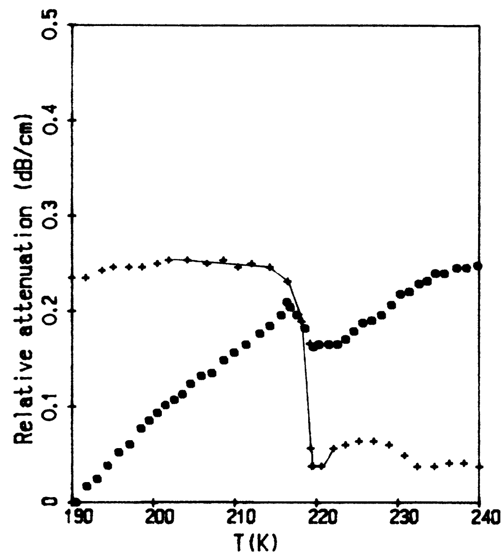

FIG. 3. Attenuation vs temperature for samples 3 (+) and 5 (⊙). Phase-transition-like anomalies for both of them are seen around 217 K. $f=10$ MHz; longitudinal wave.

PREPARATION OF SAMPLES

Chemically pure powders of $CaCO_3$, $SrCO_3$, CuO, Bi_2O_3 (and PbO) were thoroughly mixed and sintered at 845 °C in air for several days to synthesize a ceramic sample with 2 or 3 superconductiong phases. The sample was ground, pressed into cylinders under pressures of about 30 bar, then hot pressed under pressures of about 10 kbar at 500 °C for 3 h, and finally, compact specimens of $\phi 12\times 3$ mm^2 were obtained with densities of about 6 g/cm^3.

Figures 1 and 2 are the scanning electron microscopy (SEM) photographs of samples before and after being hot pressed, respectively. Figure 1 shows that granules are thin plates in shape after sintering in air. Figure 2 shows that orientations of most granules (c axis, perpendicular to the plates) begin to be parallel to the direction of pressure after being hot pressed. The ultrasound propagated along this direction.

EXPERIMENTAL RESULTS

The apparatus used in our experiments is the Matec 6600 system. Quartz transducers with fundamental frequencies of about 10 MHz were bonded to the carefully polished surfaces of the specimens with Nonaq grease. A calibrated Rh-Fe resistor was used to measure temperature.

Ultrasonic attenuation and velocity measurements were carried out on five samples between 4.2 and 280 K. The samples are named as sample numbers 1, 2, 3, 4, and 5, respectively, and are well characterized by R-T, ac susceptibility and dc susceptibility measurements. Their nominal compositions and some parameters are listed in Table I, where T_{c1}, T_{c2}, and T_{c3} are superconducting transition temperatures of different phases; T_{p1} and T_{p2} are positions where phase-transition-like anomalies take place. Our results show some interesting features and are described as follows.

TABLE I. Nominal compositions and transition temperatures of samples used for ultrasonic study in this paper.

Sample	Composition	T_{c1} (K)	T_{c2} (K)	T_{c3} (K)	T_{p1} (K)	T_{p2} (K)
1	Bi-Sr-Ca-Cu_2O_x	?	86	106	?	130
2	(Bi,Pb)Sr-Ca-$Cu_{1.6}O_x$	?	86		?	136
3	As above	9.7	86		?	136
4	As above	8.9	86		32	140
5	$Bi_2Sr_2CaCu_2O_x$	10.8	70	86	?	110

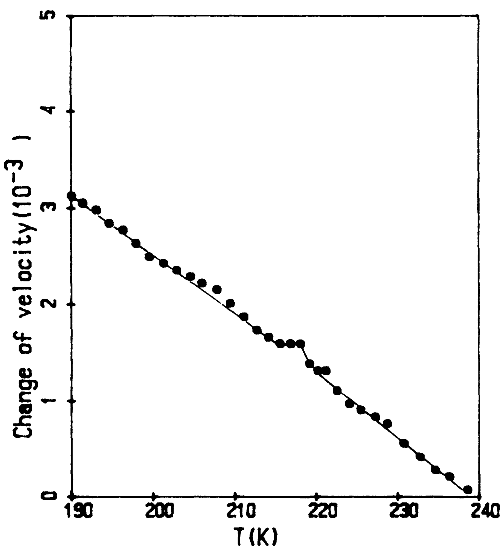

FIG. 4. Temperature dependence of velocity for sample 3. An anomaly around 217 K takes place and the slope of the curve below 217 K becomes smaller than that of above 217 K. $f=10$ MHz; longitudinal wave.

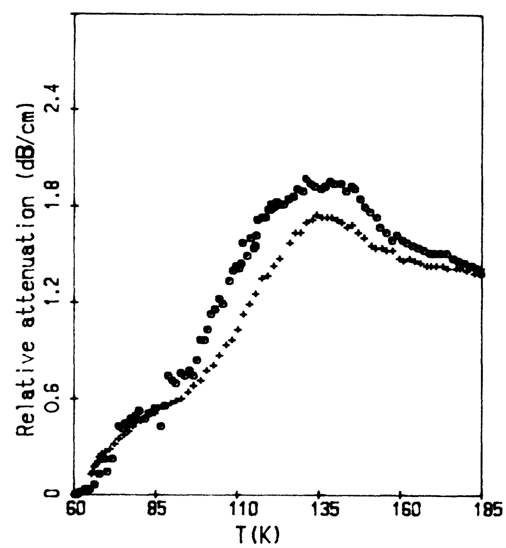

FIG. 6. Attenuation vs temperature for sample 2 in two warming up runs [(⊙) first run; (+) second run]. Stress reduction, anomalies near 81 and 136 K are seen clearly. $f=10$ MHz; longitudinal wave.

(a) Figure 3 shows the results of attenuation versus temperature for samples 3 and 5. Clearly, phase-transition-like anomalies centered at 217 K take place. Figure 4 shows the temperature dependence of longitudinal velocity for sample 3. An anomaly is centered at 217 K and the slope of the curve becomes smaller below 217 K than that of above 217 K. Figure 5 displays the measurement results of longitudinal attenuation and velocity and transverse attenuation for sample 5; anomalies centered at 217 K are common for the three curves. There is a change of slope for the velocity curve below and above 317 K. The attenuations decrease more rapidly below 217 K than above 217 K as temperature decreases. Results of other samples are similar to those of samples 3 and 5. Further study is undergoing to determine what kind of phase transition takes place around 217 K.

(b) Figures 6 and 7 show experimental results of longitudinal attenuation versus temperature between 60 and

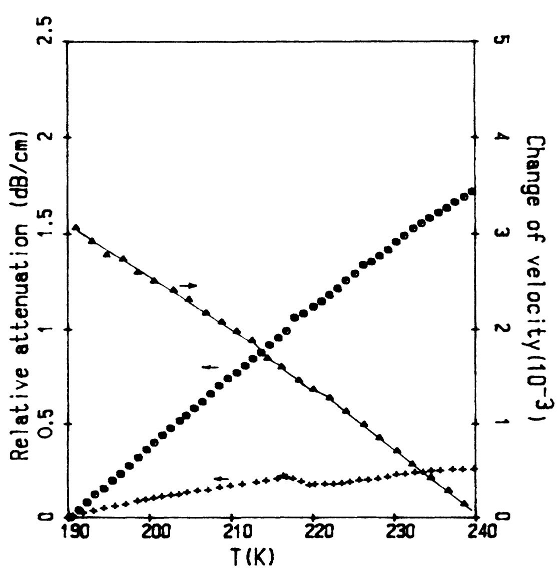

FIG. 5. Attenuation and velocity vs temperature for sample 5. A phase-transition-like anomaly appears around 217 K. Longitudinal (▲, +) and transverse waves (⊙); $f=10$ MHz.

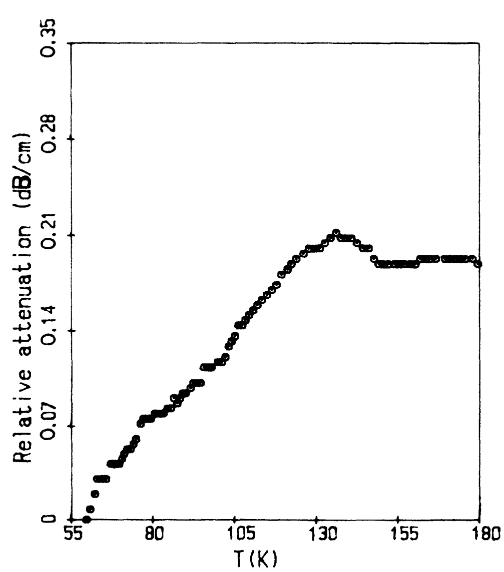

FIG. 7. Attenuation vs temperature for sample 3. Anomalies around 80 and 136 K are almost the same as those of sample 2. $f=10$ MHz; longitudinal wave.

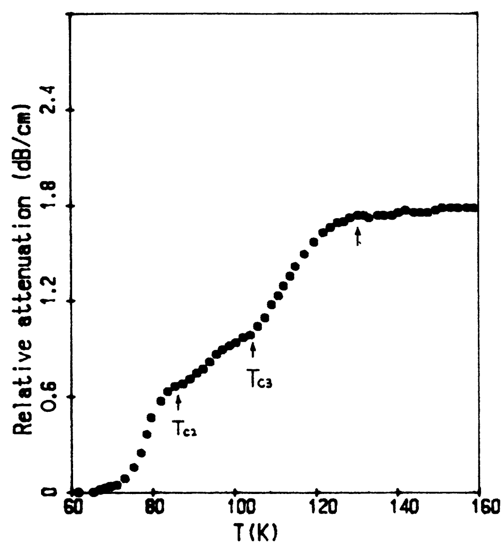

FIG. 8. Temperature dependence of attenuation for sample 1. Anomalies occur around 85, 106, and 130 K, respectively. $f=10$ MHz; longitudinal wave.

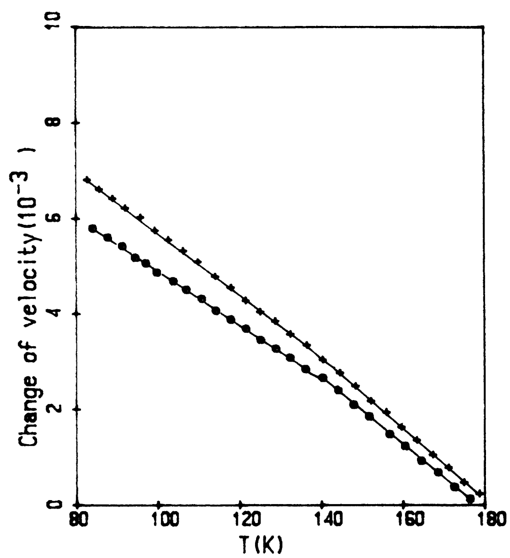

FIG. 10. Temperature dependence of velocities of both longitudinal, (⊙) and transverse (+) waves for sample 4. The slopes of both curves change at 140 K.

180 K for samples 2 and 3, respectively. Peaks at 136 K are the characteristic of another phase transition above T_c. The two samples are Pb doped. Figures 8 and 9 are the results of attenuation against temperature for samples 1 and 5, respectively; the anomalies at 130 and 110 K are rapid decrease after a plateau as temperature decreases. The two samples are Pb free. Figures 10 and 11 are the experimental results of velocity against temperature both for longitudinal and for transverse waves for samples 4, and 5, respectively. Apparently, there are changes of slope in the curves of sample 4 at 140 K and in the curves of sample 5 at 110 K, indicating a tendency of softness and instability in crystal lattice.

(c) Figures 12–15 and Fig. 8 show the attenuation behaviors near T_c of samples 2, 3, 5, and 1, respectively. A peak-like anomaly at T_c and rapid decrease below T_c with the decrease of temperature are the common features for all the samples.

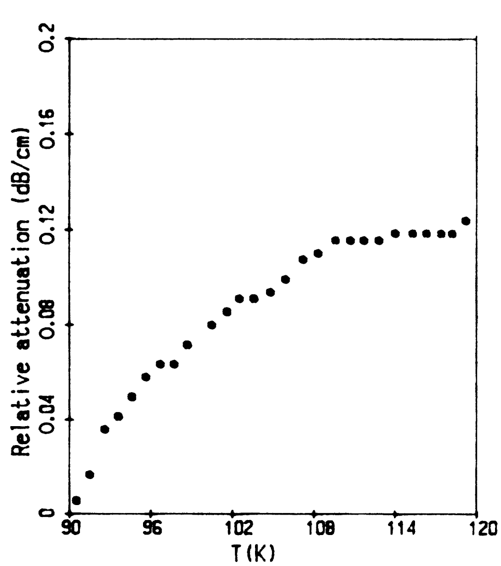

FIG. 9. Temperature dependence of attenuation for sample 5. An anomaly takes place at 110 K. $f=10$ MHz; longitudinal wave.

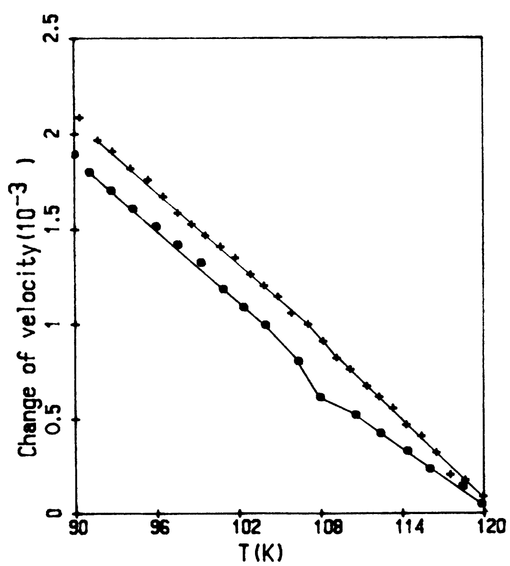

FIG. 11. Velocities of both longitudinal (⊙) and transverse (+) waves vs temperature for sample 5. Anomalies around 110 K indicate the pretransition in crystal lattice above T_c. $f=10$ MHz.

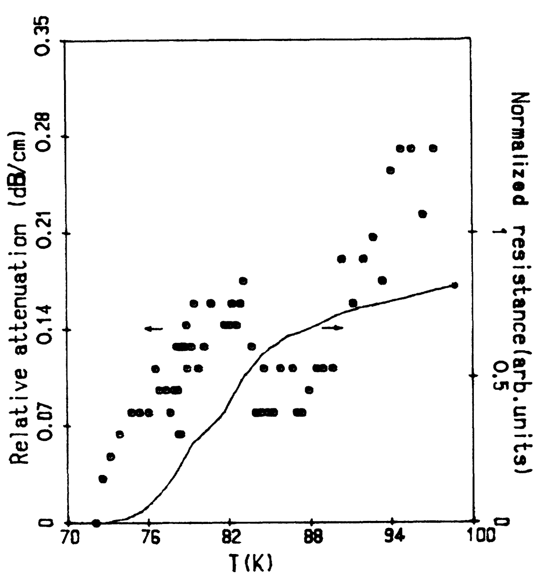

FIG. 12. Attenuation and normalized resistance vs temperature for sample 2. A weak peak near 82 K (T_{cmid}) shows the characteristic of superconducting transition. $f=10$ Mhz; longitudinal wave.

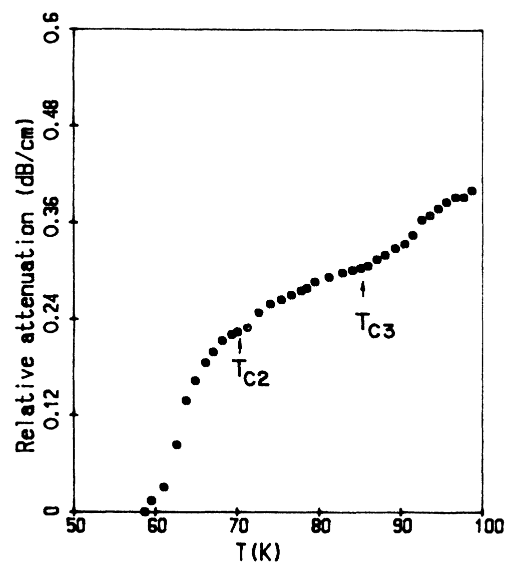

FIG. 14. Temperature dependence of attenuation for sample 5. Anomalies around 70 and 86 K are related to two superconducting transitions at these positions, respectively. $f=10$ MHz; longitudinal wave.

DISCUSSION

(1) Superconducting transitions are present on the background of softness and instability in crystal lattice, beginning in the range between 10 and 50 K above T_c. The rapid decrease in attenuation with the decrease of temperature on the background seems to imply the existence of strong superconducting fluctuation above T_c, and the nearer to T_c the temperature is, the stronger the fluctuation is . In the regions of fluctuation, the amount of energy absorbed by carriers and other elementary excitations is reduced.

(2) By using Eq. (2), one can estimate the ultrasonic attenuation coefficients in specimens of $(Bi,Pb)_2Sr_2CaCu_2O_x$ in normal states about 5×10^{-7}

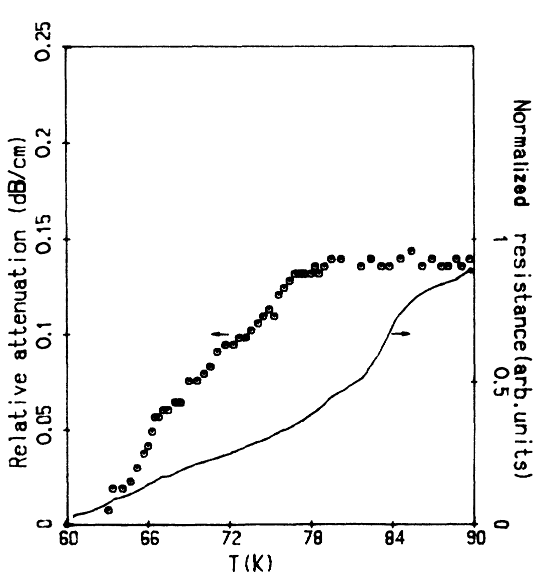

FIG. 13. Attenuation and normalized resistance vs temperature for sample 3. Rapid decrease after a short plateau is the anomaly in attenuation around T_c. $f=10$ MHz; longitudinal wave.

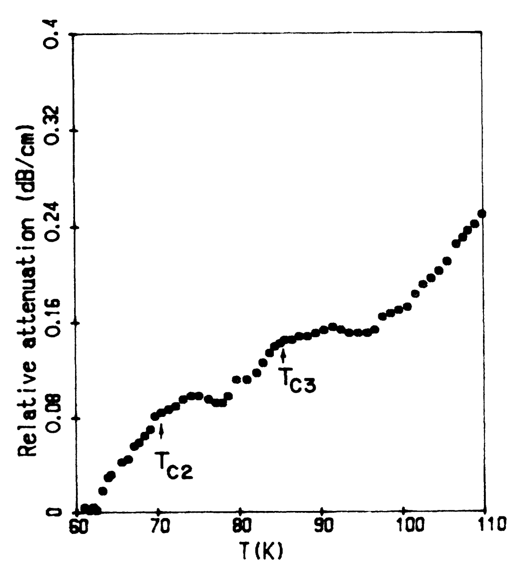

FIG. 15. Temperature dependence of attenuation for sample 5. Anomalies around 70 and 86 K are related to two superconducting transitions at these positions, respectively. $f=10$ MHz; transverse wave.

dB/cm, which is much lower than the resolution of our apparatus. Therefore, the anomalies in attenuation at T_c cannot be interpreted by the deformation-potential model for the coupling between acoustic phonons and electrons. The possibilities of strong couplings between acoustic phonons and optical phonons, and between optical phonons and electrons, are speculated. The anomalies in attenuation at T_c may be due to the enhancement of coupling between acoustic phonons and optical phonons, driven by superconducting transitions in which the optical-phonon–electron interaction would result.

(3) Below T_c, the attenuation data cannot be fitted by Eq. (1), which, further, proved the ineffectiveness of BCS theory for oxide perovskite superconductors.

(4) The presence of pretransition in the range between 10 and 50 K above T_c is an important feature for Bi-based specimens and it is also present in the superconductiong phase with lowest T_c. For instance (see Fig. 16), the measurement at low temperatures on sample 4 shows that anomalies in attenuation and velocity at about 32 K are similar to those present at 140 K in the same sample (see Fig. 10). Another anomaly in attenuation takes place, centered at 9 K, which is the lowest superconductiong transition temperature in sample 4 (see Table I). It is difficult for the 9 K phase to intergrow with the 85 K phase; therefore, they are separated in space. But the 85 K phase is easy to intergrow with the 110 K phase and their phase transitions in crystal lattice will correlate strongly, so the pretransition above T_c are usually the same in order to reduce the stress caused by sudden imbalance in lattice constants.

(5) Anomalies in attenuation and velocity in Y-Ba-Cu-O and La-Sr-Cu-O ceramic specimens in the range between 40 and 60 K above T_c have been observed by Bhattacharya *et al.*[5] Their results are very similar to ours. It seems that the pretransition above T_c is a common feature for all of the high-T_c superconductors.

(6) Xu *et al.*[3] and Bhattacharya *et al.*[5] have observed that a peak appears at about 10 K below T_c in Y-Ba-Cu-O samples for a longitudinal wave of 10 MHz. Sun *et al.*[4] verified that this peak is due to a relaxation process, because the peak position could be removed to above T_c by increasing the frequency of ultrasound and the height of the peak becomes larger at the same time. This relaxation peak seems to have no relationship with superconductivity and may be caused by phonon-phonon coupling in grain boundaries. Such a peak did not appear in our samples. We believe that, in hot-pressed specimens, anharmonic effect in grain boundaries is reduced greatly and total attenuation is lowered, too.

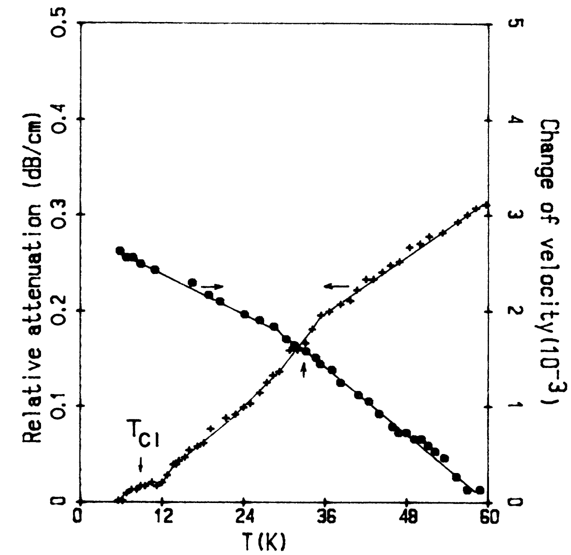

FIG. 16. Temperature dependence of velocity and attenuation for sample 4. Anomalies near 9 and 32 K are indicated by vertical arrows. $f = 10$ MHz; longitudinal wave.

In summary, ultrasonic attenuation and velocity data have been obtained on Bi-based, hot-pressed specimens having a *c*-axis alignment of the crystallites along the direction of pressure. Phase-transition-like anomalies in attenuation and velocity were found near 220 K. There is another phase transition in the range between 10 and 50 K above T_c, at which a tendency of softness and instability in crystal lattice begins to occur. The superconducting transitions are present on the background of rapid decrease in attenuation with the decrease of temperature, which seems to indicate the existence of strong superconducting fluctuation above T_c. Anomalies around T_c may be evidence that the coupling between optical phonons and electrons is responsible for high-T_c superconductivity.

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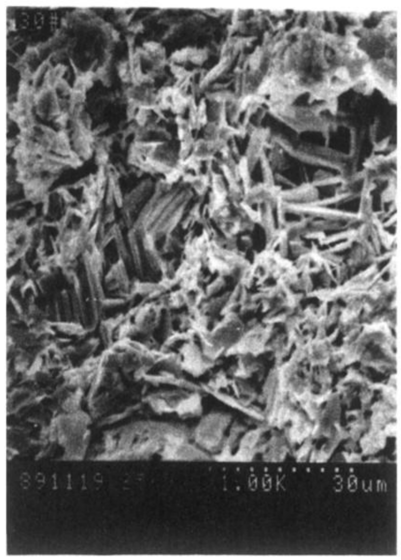

FIG. 1. SEM photograph for a sample sintered in air only. Granules are thin plates in shape.

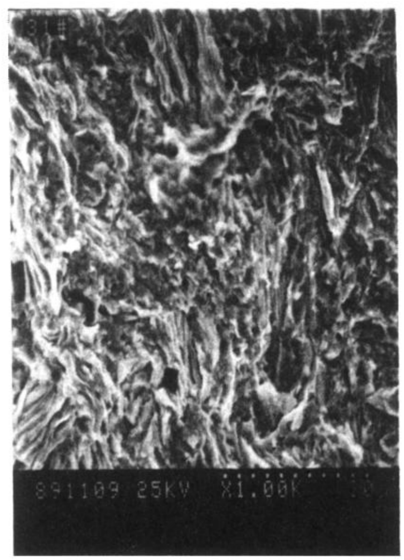

FIG. 2. SEM photograph for a sample hot pressed after sintering in air. The direction of pressure lies in horizon in this figure. The orientations of most granules (*c* axis) align the direction of pressure.