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Ultrasonic study of structural instability of monocrystalline and polycrystalline Bi-Sr-Ca-Cu-O

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Two internal-friction (attenuation) peaks around 95 and 130 K in the polycrystal and single crystal of Bi-Sr-Ca-Cu-O are found to be related to the superconducting transition at 84 and 107 K, respectively. The jump of lattice parameter and shape-memory effect occurring at the peak temperatures reveal the characteristics of a martensitic transition. The velocity and attenuation versus temperature of ultrasonic longitudinal waves propagating along two directions in the *a-b* plane at 10° to the *a* and *b* axes and of [010] shear waves with [100] polarization were measured for the $Bi_2Sr_2CaCu_2O_8$ single crystals. The anisotropic elasticity in the *c* plane is manifested. Only the longitudinal waves in *a* direction and the shear waves show an obvious softening minimum of velocity around 250 K, which is associated with an attenuation peak due to a phaselike transition, but other longitudinal waves reveal a monotonic stiffening from room temperature down to T_c. The origin of the overall trend of elastic stiffening that appears in the measurements so far for high-T_c oxides is discussed.

I. INTRODUCTION

In order to understand the possible mechanism for the superconductivity in high-T_c oxides, many scientists have measured elasticity because it is very sensitive to structural instability. The results for $YBa_2Cu_3O_x$ indicate that a broad ultrasonic attenuation peak as well as an internal friction peak appears around 240 K,[1-4] and another peak occurs at about 120 K.[1,2,5,6] All the peaks exhibit the characteristics of a phase transition. X-ray-diffraction studies indicate that no structural symmetry change and only an abrupt jump of lattice parameters[1] is found to be associated with these peaks. We have referred to it as a phaselike transition (PLT) or martensite-like transition,[5] which has been further confirmed by specific-heat[7] and Debye-Waller factor measurements.[8,9] It is interesting to note that the PLT around 120 K always coexists with the 90-K superconducting phase[5,10] and a PLT around 75 K coexists with the 60 K phase in $YBa_2Cu_3O_{7-\delta}$.[11] It is worth investigating if there exists any PLT in Bi-Sr-Ca-Cu-O, another multiply perovskite oxide, and if any PLT coexists with the superconducting transition.

Although the correlation between the superconductivity and PLT in Y-Ba-Cu-O is very similar to that of *A*-15 alloys,[12] most elastic modulus measurements show stiffening with the temperature decreasing from room temperature down to T_c in $YBa_2Cu_3O_{7-\delta}$,[2-6,13-15] instead of softening as in the case of *A*-15 alloys[12] and even of La-Sr-Cu-O.[16] There occasionally exists a sign of softening near T_c in Y-Ba-Cu-O,[14,15,17] but no obvious softening has been observed around 240 K, although the ferroelastic stress-strain curve shows softening in Y-Ba-Cu-O.[18] Toulouse *et al.*[4] reported that a step instead of a softening cusp was found to appear on the sound velocity curve near 220 K in Y-Ba-Cu-O, and therefore suggested that the instability corresponds to a structural order-disorder transition. In addition, the thermal hysteresis between the heating and cooling curves was sometimes[14] but not always[13] observed in $YBa_2Cu_3O_{7-\delta}$. So far, most elasticity measurements have been made mainly on sintered bulk materials, and the results are significantly different; therefore, it is necessary to do some work with a single crystal in order to clarify the discrepancies. The following questions are important: (1) What is the origin of the overall trend of abnormal rapid stiffening between room temperature and T_c as mentioned by Sharma *et al.*?[19] (2) Is there any softening minimum or only a step or an inflection on the elastic modulus curve? (3) Does the thermal hysteresis of the phaselike transition exist?

Saint-Paul *et al.*[20] have measured the sound velocity of the longitudinal mode generated in the basal *a-b* plane of the $YBa_2Cu_3O_{7-\delta}$ single crystal at 210 MHz; no anisotropic property was observed because the types of twinning that exist in the orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$ yield that the two crystallographic directions *a* and *b* are not separated. The softening (inflection) of the C_{44} shear mode at 108 K was observed for the $YBa_2Cu_3O_{7-\delta}$ single crystal.[21] Other elastic measurements of the $YBa_2Cu_3O_{7-\delta}$ single crystal using a vibrating reed method have shown a steplike change in Young's modulus (hysteretic) associated with an internal-friction peak near 200–240 K.[22,23] Xiang *et al.*[24] have measured two jump steps around 150 and 240 K on Young's modulus and shear moduli (out of plane) of the $Bi_2Sr_2CaCu_2O_8$ single crystal using a vibrating reed method, but they attributed these to the vacuum grease and silver paint. However, it has been recognized that the direct investigation of the elastic properties of the *a-b* plane in these high-T_c materials is more important. In this paper, ultrasonic velocity and attenuation in the *a-b* plane were measured with a single crystal of $Bi_2Sr_2Ca_1Cu_2O_8$, in which no twins were observed by transmission electron microscopy (TEM), so the elastic anisotropy in the *a-b* plane, if it exists, may be detected. We believe that the results for single crystal Ba-Sr-Ca-Cu-O would be helpful to solve the above-mentioned problems.

II. EXPERIMENTAL METHODS

The ultrasonic attenuation and sound velocity were measured by a pulse-echo method using a Matec 6600. Marx's three-components-oscillator (longitudinal vibration) method was used to measure the internal friction and variation of Young's modulus at frequencies in the 100 kHz range. X-ray diffraction data were recorded on a Rigaku diffractometer. A pseudo-Kössel line pattern was obtained by a divergent-beam x-ray-diffraction method. The resistance was measured by the four-probe technique. Stress-strain curves were made on a Mi-44 micromachine.

Single crystals of $Bi_2Sr_2CaCu_2O_8$ were grown by a flux method.[25] The polycrystalline samples of Bi-Sr-Ca-Cu-O were prepared by a standard powder metallurgical method.

III. RESULTS AND DISCUSSION

A. Polycrystalline samples of Bi-Sr-Ca-Cu-O

The specimens with the nominal composition 1:1:1:2 ($BiSrCaCu_2O_x$) are classified into two main types depending on the procedures. For the first one (sample No. 1), the sintered temperature is about 865 °C–880 °C, the resistance sharply drops near 107 K, and reaches zero below 90 K as shown in the inset of Fig. 1(a). For the second one (sample No. 2), the sintered temperature is about 810 °C; the resistance reaches zero at 84 K as shown in the inset of Fig. 2. It has been recognized that there exist two superconductive phases with $T_c = 84$ K and $T_c = 107$ K, respectively, in the Bi-Sr-Ca-Cu-O system, and often coexist in a specimen. Although the characteristic of resistance seems to indicate a single phase, the two superconductive phases still coexist in both sample No. 1 and sample No. 2. It should be said that the higher temperature phase ($T_c = 107$ K) predominates in sample No. 1 and so does the lower temperature phase ($T_c = 84$ K) in sample No. 2.

Figure 1(a) shows the internal friction Q^{-1} as well as the relative change of Young's modulus $\Delta E/E$ as a function of temperature for sample No. 1. Two internal-friction peaks P_1 (around 95 K) and P_2 (around 130 K) are associated with two corresponding small kinks on the Young's modulus curve. The peak height of P_2 is higher than that of P_1. Since the higher-T_c phase predominates in this sample, it can be considered that P_1 and P_2 are related to the superconducting transitions at about 84 and 107 K, respectively. The further evidence for this suggestion can be found in Fig. 2. Contrary to sample No. 1, the curve of Q^{-1} versus temperature for sample No. 2 shows that the height of P_1 is greater than that of P_2, which coincides with the fact that the lower T_c phase predominates in this sample. Figure 3 shows similar results for sample No. 3 measured by the ultrasonic pulse-echo method, for which a $PbZr_{1-x}Ti_xO_3$ transducer of 5 MHz with area of 3.0×5.0 mm^2 was used. X-ray-diffraction measurements on sample No. 1 reveal that the lattice parameter *c* has a step change at about 130 K, but

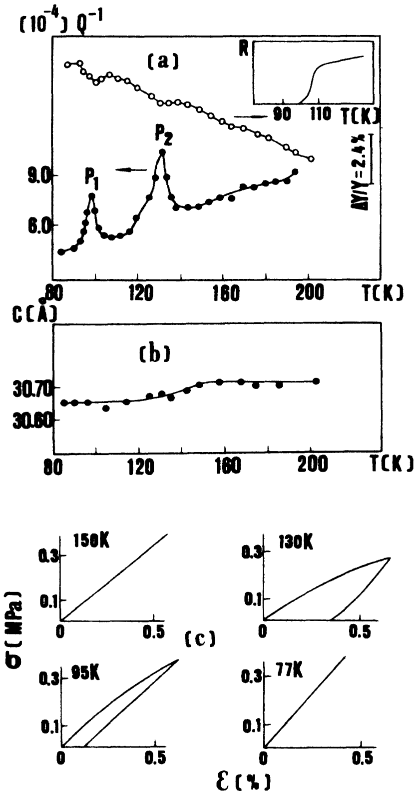

FIG. 1. Internal friction Q^{-1} and relative change of Young's modulus $\Delta E/E$ (a), lattice parameter *c* (b), and stress-strain curves (c) as a function of temperature for sample No. 1. The inset (a) is a curve of resistance *R* (arbitrary units) vs temperature.

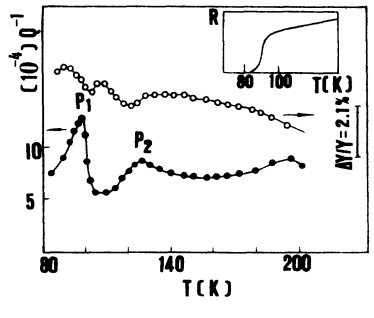

FIG. 2. Internal friction Q^{-1} and relative change of Young's modulus $\Delta E/E$ as a function of temperature for sample No. 2. The inset is a curve of resistance *R* (arbitrary units) vs temperature.

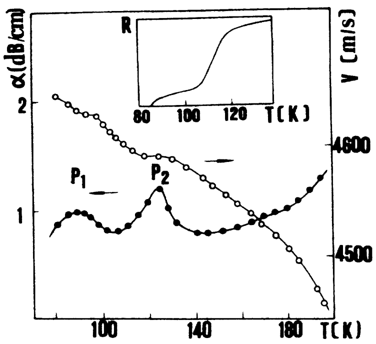

FIG. 3. The ultrasonic attenuation α and longitudinal wave velocity V (5 MHz) as a function of temperature for the $BiSrCaCu_2O_x$ polycrystalline.

the jump near 95 K is not clearly seen because of the limitation of measuring precision of the diffractometer [Fig. 1(b)]. The general features of other diffraction lines are similar to this line (00<u>10</u>). It is referred to as a phaselike transition of first order.[1,5] The stress-induced movement of phase interfaces is considered to be responsible for the internal-friction peaks.

The mobility of the phase interfaces in sample No. 1 has been further confirmed by a tensile test from room temperature to liquid nitrogen temperature. As shown in Fig. 1(c), an obvious ferroelastic loop appears near 130 K, and a smaller one around 95 K; both correspond to the Q^{-1} peak temperatures. The origin of ferroelasticity comes from the stress-induced displacement of interfaces between two phases with slightly different lattice parameters, which cannot recover after the release of applied stress because of the smaller elastic recovery force. The feature implies the appearance of elastic softening or lattice instability near these temperatures.[5,18]

The results for Bi-Sr-Ca-Cu-O demonstrate that the phaselike transition at T_m denoted by the Q^{-1} peak temperature precedes the superconducting transition at T_c, just the same as that for $YBa_2Cu_3O_{7-\delta}$ (Refs. 10 and 11) and Tl-Ba-Ca-Cu-O.[27] In summary, there always exists a phaselike transition at T_m about 10–30 K above T_c for these three kinds of oxides as shown in the Table I.

This correlation between T_c and T_m is similar to that for high-T_c A-15 alloys.[12] It is speculated that the soft phonon might have direct or indirect contributions to the superconductivity of high-T_c oxides. At least, the coexistence of structural instability and superconductivity suggests a relationship between them, such as an electronic state varied by oxygen doping might influence both transitions simultaneously.

TABLE I. Phaselike transition temperature and critical temperature for three oxides. An asterisk denotes an unknown value.

Material	T_c	T_m
$YBa_2Cu_3O_x$	90 K	120 K
	60 K	75 K
Bi-Sr-Ca-Cu-O	107 K	130 K
	84 K	95 K
Tl-Ba-Ca-Cu-O	115 K	135 K
	*	90 K

B. Single crystal of $Bi_2Sr_2CaCu_2O_8$

The specimen of single crystal $Bi_2Sr_2CaCu_2O_8$ (T_c=84.5 K, obtained from resistance measurements) used for ultrasonic longitudinal waves measurements had dimensions of 8.0×7.0×1.7 mm^3, with the c plane nearly parallel to the plane of (8.0×7.0 mm^2). The x-ray pseudo-Kössel line pattern showed that the whole specimen was a fairly good single crystal. The $PbZr_{1-x}Ti_xO_3$ transducers of 7.5 MHz with size of 1.5×5.0 mm^2 were bonded with Nonaq stopcock grease to two planes perpendicular to each other and parallel to the c axis, as shown in Figs. 4 and 5. X-ray diffraction of the single crystal determined that the propagation direction of the longitudinal sound waves had about 10° angle deviation from the a or b axis. We refer to the two perpendicular directions as the A direction and the B direction. The specimen for ultrasonic shear wave measurements had dimensions of 7.0×6.0×2.0 mm^3, with the a-b plane parallel to the plane of 7.0×6.0 mm^2. A 5 MHz ac cut-quartz transducer with an area of 1.5×5.0 mm^2, was bonded to the a-c plane of a single crystal Bi-Sr-Ca-Cu-O

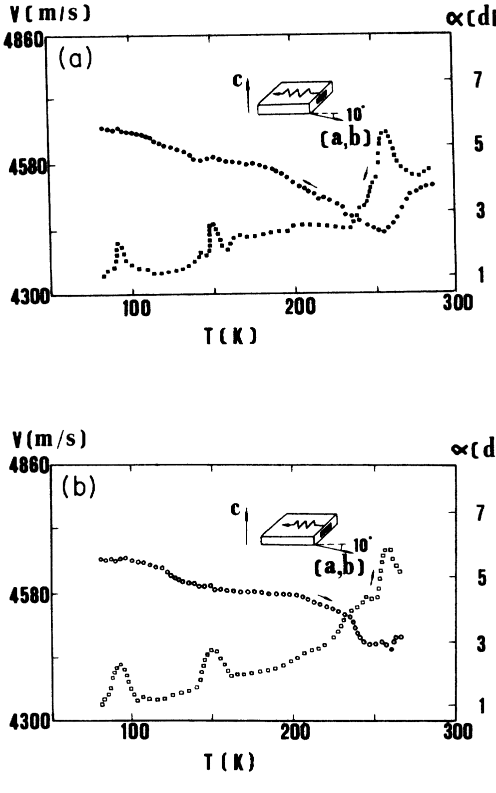

FIG. 4. Temperature dependence of velocity V and attenuation α with ultrasonic longitudinal wave (7.5 MHz) propagated along the A direction (see the text) measured on cooling (a) and on heating (b) for the $Bi_2Sr_2CaCu_2O_8$ single crystal.

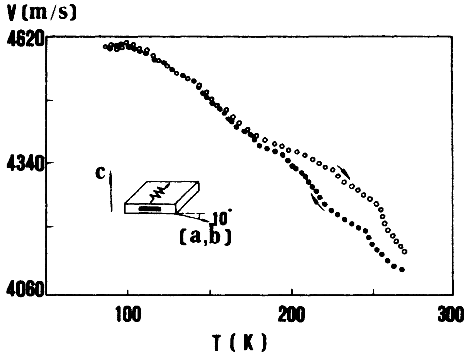

FIG. 5. Temperature dependence of velocity of ultrasonic longitudinal waves (7.5 MHz) propagated along the *B* direction (perpendicular to the *A* direction) measured on cooling (●) and heating (○) for the $Bi_2Sr_2CaCu_2O_8$ single crystal.

(Fig. 6), so that the shear strain (e_{21}) waves propagated along the *b* axis.

Because the dimensions of the transducer and the thickness of the specimen are rather narrow, Rayleigh or Lamb waves may occur. However, when we measured the sound velocity at room temperature, we obtained $V_L = 4540$ (m/s) (Figs. 4 and 5) for the longitudinal case, and $V_S = 2460$ (m/s) for the shear waves (Fig. 6). These values are reasonable. It is known that the velocity of Rayleigh waves V_R is less than V_S and much less than V_L. Because no small pulse echo is seen between the main echoes with a fairly good exponential fit, it may be considered that the influence of Rayleigh waves on velocity measurements is negligible, although the interference effects may make some problems for the attenuation measurements.

Figures 4(a) and 4(b) show the velocity and attenuation of the longitudinal sound waves propagating along the *A* direction as a function of temperature at different conditions: (a) cooling and (b) heating. The heating or cooling rate was about 0.5 K/min. A broad attenuation peak appears around 250 K, and a corresponding sound velocity curve reveals a pronounced softening minimum in the same temperature range as the peak, instead of a step or an inflection as measured for ceramic samples. This shows a characteristic of a displacive phase transition, even though we must include the possibility of an order-disorder reconstruction. X-ray-diffraction measurements on the Bi-Sr-Ca-Cu-O powder sample reveal that the lattice parameter *c* has a step change at about 150 and 250 K (Fig. 7). When the longitudinal sound wave propagates in the *B* direction perpendicular to the first one, as shown in Fig. 5, the sound velocity increases monotonically with decreasing of temperature, just like the results measured in ceramic Bi-Sr-Ca-Cu-O (Figs. 1–3), Tl-Ba-Ca-Cu-O (Ref. 27), and $YBa_2Cu_3O_{7-\delta}$ samples. It can be recognized that the soft component of the elastic constants makes a much smaller contribution to the longitudinal modulus in the *B* direction than in the *A* direction. We have not identified the *a* and *b* axes in the single crystal because the lattice parameters *a* (5.40 Å) and *b* (5.42 Å) are nearly the same. However, the elastic anisotropy in the *a*-*b* plane is quite noticeable for these two directions. This is consistent with the fact that the incommensurate modulation appears along the *b* axis only.[26] Figure 6 shows the velocity and attenuation as a function of temperature for the shear waves propagated along [010] and polarized along [100] in a single crystal of Bi-Sr-Ca-Cu-O. The velocity minimum and attenuation peak were also obtained around 250 K. The softening of the shear mode is in accordance with the mobility of the phase interfaces. The exact soft mode is planned to be studied.

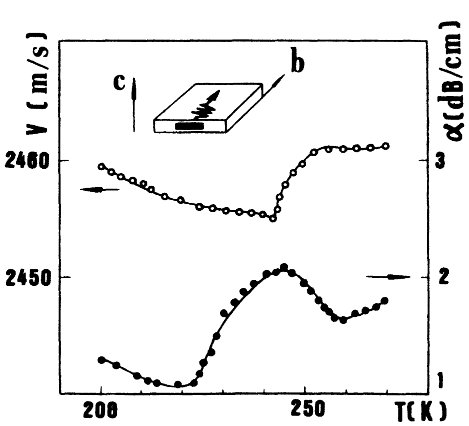

FIG. 6. Temperature dependence of velocity *V* and attenuation *α* with ultrasonic shear waves of 5 MHz propagated along [010] and polarized [100] measured on cooling for the $Bi_2Sr_2CaCu_2O_8$ single crystal.

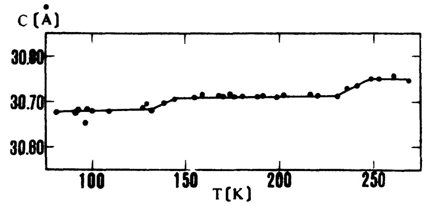

FIG. 7. Lattice parameter *c* as a function of temperature for the $Bi_2Sr_2CaCu_2O_8$ powder sample.

There are two smaller attenuation peaks at 95 and 150 K (Fig. 4) and two corresponding shallow minima of sound velocity can be observed as well. The 95 K peak has been confirmed to be closely related to the 84-K superconducting phase from the studies of ceramic samples (Figs. 1-3).

From Figs. 4 and 5 it can be seen that thermal hysteresis exists between heating and cooling curves, showing a feature of a first-order phase transition. The hysteresis around 250 K is found to be more pronounced than the others.

It has been noted that the overall trend of stiffening of the elastic modulus for ceramics $YBa_2Cu_3O_{7-\delta}$ and Bi-Sr-Ca-Cu-O is faster than in the normal case, especially above 200 K. This may be attributed to a faster decrease of the lattice parameter than expected from normal thermal expansion.[28] Because of the abnormal large stiffening background, the softening is not easy to observe in ceramic polycrystal materials, but can be observed with suitable modes in a single crystal (Figs. 4 and 6).

[1] Y. N. Wang, H. M. Shen, J. S. Zhu, Z. R. Xu, M. Gu, Z. M. Niu, and Z. F. Zhang, J. Phys. C **20**, L665 (1987).

[2] G. Cannelli, R. Cantelli, F. Cordero, G. Costa, M. Ferretti, and G. L. Olsece, Europhys. Lett. **15**, 271 (1988).

[3] Y. S. He, B. W. Zhang, S. H. Lin, J. Xiang, Y. M. Lou, and H. M. Chen, J. Phys. F **17**, L243 (1987).

[4] J. Toulouse, X. M. Wang, and D. J. L. Hong, Phys. Rev. B **38**, 7077 (1988).

[5] Y. N. Wang (unpublished).

[6] S. Battacharya, M. J. Higgins, D. C. Johnston, A. J. Jacobson, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. B **37**, 5901 (1988).

[7] T. Laegreid, K. Fossheim, E. Sandvold, and S. Julsrud, Nature **330**, 637 (1987).

[8] R. Z. Ma, S. K. Xia, G. H. Cao, Z. W. Li, and Y. R. Fong, Solid State Commun. **70**, 141 (1989).

[9] U. Murek, K. Keulerz, and J. Rohler, Physica C **153–155**, 270 (1988).

[10] X. H. Cheng, L. H. Sun, Y. N. Wang, H. M. Shen, and Z. Yu, J. Phys. C **21**, 4603 (1988).

[11] X. H. Chen, Y. N. Wang, and H. M. Shen, Phys. Status Solidi **113**, K85 (1989).

[12] L. R. Testardi, in *Physical Acoustics: Principles and Methods,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. 10, p. 193.

[13] S. Ewert *et al.*, Solid State Commun. **64**, 1153 (1987).

[14] D. P. Almond, E. Lambson, G. A. Saunders, and H. Wang, J. Phys. F **17**, L221 (1987).

[15] H. Ledbetter, J. Metals **40**, 24 (1988).

[16] L. C. Bourne and A. Zettl, Phys. Rev. B **35**, 8785 (1987).

[17] S. Battacharya, M. J. Higgins, D. C. Johnston, A. J. Jacobson, J. P. Stokes, D. P. Goshorn, and J. T. Lewandowski, Phys. Rev. Lett. **60**, 1181 (1988).

[18] H. M. Shen, Y. N. Wang, Z. F. Zhang, S. Y. Zhang, and L. H. Sun, J. Phys. C **20**, L889 (1987).

[19] R. P. Sharma, L. E. Rehn, P. M. Baldo, and J. Z. Jiu, Phys. Rev. B **38**, 9287 (1988).

[20] M. Saint-Paul *et al.*, Solid State Commun. **66**, 641 (1988).

[21] M. Saint-Paul *et al.*, Solid State Commun. **69**, 1161 (1989).

[22] S. Hoen *et al.*, Phys. Rev. B **38**, 11 949 (1988).

[23] X. D. Shi *et al.*, Phys. Rev. B **39**, 827 (1989).

[24] X.-D. Xiang *et al.*, Solid State Commun. **69**, 833 (1989).

[25] Y. F. Yan *et al.*, Mod. Phys. Lett. B **2**, 571 (1988).

[26] R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1174 (1988).

[27] H. M. Shen, J. Wu, K. M. Tan, Z. Yu, J. S. Zhu, and Y. N. Wang, Superconduct. Sci. Technol. **2**, 52 (1989).

[28] L. H. Sun, Y. N. Wang, H. M. Shen, and X. H. Chen, Phys. Rev. B **38**, 5114 (1988).