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Ultrasonic measurements on two single-phase polycrystalline $YBa_2Cu_4O_8$ superconducting samples

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Ultrasonic measurements in the MHz frequency range have been performed on two single-phase polycrystalline $YBa_2Cu_4O_8$ superconducting samples of different T_c and microstructure in a temperature region between 30 and 350 K. Both longitudinal and transverse modes are employed. A pronounced dissipation peak at about 260 K accompanied by an increase in velocity is observed. This anomaly is suggested to be caused by the formation of an antiferroelectric or ferroelectric state associated with the ordering of oxygen atoms in some off-center positions of the structure. Below 200 K a thermal hysteresis in velocity develops with no anomalous behavior observed in attenuation. The area of the thermal hysteresis loop seems to be mainly determined by both the percentage of pore volume in the sample, and by grain size. The hysteresis is explained in terms of the reversible defects created near grain boundaries during cooling, due to the unusual large anisotropic thermal expansion in the material. No anomaly is found at T_c in either sample at the available resolution. However, a large reproducible increase of velocity takes place at a temperature below T_c together with the appearance of an attenuation peak.

I. INTRODUCTION

Many elastic measurements have been reported for $YBa_2Cu_3O_{7-y}$ (Y 1:2:3). One characteristic of these reports is that they differ from one research group to another, except perhaps for the anomalies usually found around 240 K.[1] This is partly due to the fact that several extrinsic as well as intrinsic factors may contribute to the elastic properties of the system. In particular, it was discovered that the O(4) atoms in the CuO_{1-y} planes are highly mobile[2,3] leading to very rich phases in the Y-T phase diagram of Y 1:2:3. Another obvious reason is the lack of high-quality single crystals. The appearance[4] of bulk $YBa_2Cu_4O_8$, however, offers a very good reference system for Y 1:2:3 in studying elastic properties since bulk Y 1:2:4 samples are also superconducting with T_c about 80 K and have a structure similar to that of Y 1:2:3. The difference is that the single CuO chain parallel to the b axis in Y 1:2:3 is replaced in Y 1:2:4 by two CuO chains with one CuO chain shifted along the b axis direction by $\frac{1}{2}$ period.[5] The increase of the O(4) coordination in the CuO chain in Y 1:2:4 therefore makes oxygen more stable[4] in Y 1:2:4 than in Y 1:2:3. No oxygen vacancy is present in Y 1:2:4 and no twin structure is observed due to the absence of the tetragonal to the orthorhombic structural phase transition (SPT).[6] In this study, we examine the elastic properties of the Y-based cuprate superconductors, paying special attention to the elastic anomalies at around 260 K, the thermal hysteresis in velocity below 200 K, and the elastic behavior near T_c.

II. EXPERIMENT

Two polycrystalline Y 1:2:4 samples were used in this study. The one labeled Y124-1 with $T_c(\text{onset})=76$ K (ac-susceptibility measurement) is the same sample used in our previous work.[7] The other sample Y124-2 is prepared with the same method as that[7] for Y124-1 and has $T_c(\text{onset})=81$ K (ac-susceptibility measurement). Their bulk densities are 3.97 and 4.55 g/cm^3 for Y124-1 and Y124-2, respectively. X-ray measurements showed that both specimens are single phase without any trace of Y 1:2:3 or the $Y_2Ba_4Cu_7O_{15-y}$ phase.

A 36° Y-cut or 41° X-cut lithium niobate overtone polished transducer was bonded to one of the two parallel ends of the sample by Nonaq Stopcock grease. Standard Matec equipment and an automatic time-of-flight technique[8] were employed in the studies. For both compresssional and shear-wave measurements, at least four distinct, well-separated echo signals were visible over the whole temperature range. As the temperature is lowered, more reflection signals always appear. Both ultrasonic velocity and attenuation were recorded during cooling and heating. Temperature was regulated to within 0.5 mK of the set value. A change of 50 ppm in velocity could be detected.

III. RESULTS AND DISCUSSION

As a by-product of this study, first we report here some fundamental physical quantities such as longitudinal and transverse ultrasonic velocities (V_l, V_t), bulk modulus (B), Young's modulus (E), shear modulus (G), and Debye temperature (D_t) in Y 1:2:4 at 300 K (see Table I). Also included in the table are the values for a pore-free state calculated according to the method used in Ref. 9. The corresponding quantities for Y 1:2:3 are given for comparison. It is easily seen that the lattice of Y 1:2:4 is significantly softer than that of Y 1:2:3, a feature which must be caused by the additional CuO chain present in

TABLE I. Room-temperature elastic properties and Debye temperature of the Y 1:2:4 superconductor, together with calculated void-free values. Also included are the corresponding values of Y 1:2:3.

	$YBa_2Cu_4O_8$		$YBa_2Cu_3O_{7-Y}$[a]	
Parameters	Specimen	Pore free	Specimen	Pore free
Density (g/cm^3)	3.97	6.11	5.36	6.3
Void fraction	0.35	0	0.15	0
V_l (m/s)	3048.3	4664.5	4664	5165
V_t (m/s)	1802.4	2612.4	2783	3061
B (GPa)	19.7	77.3	61.3	89.4
G (GPa)	12.9	41.7	41.5	59.0
E (GPa)	31.8	106.0	101.6	145.1
D_t (K)		364		426
T_c (K) (onset)	76		95	

[a] Data taken from Ref. 9.

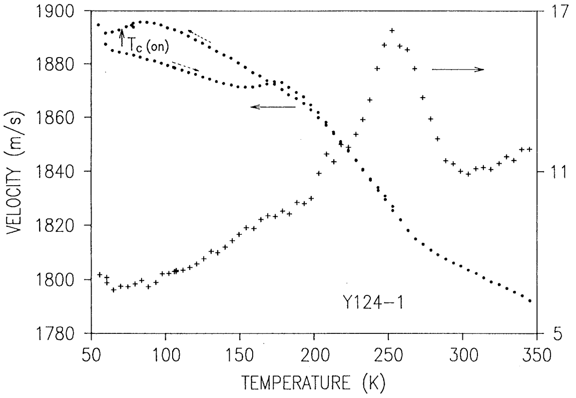

FIG. 2. Ultrasonic velocity and attenuation in Y124-1 measured with transverse waves at 10 MHz. The dashed-line arrows indicate the direction of the thermal cycle.

the Y 1:2:4 structure. This particular property will not be addressed further below.

A. The anomalies near 260 K

Our main results are shown in Figs. 1 and 2 for the Y124-1 sample. Measurements on Y124-2 show quite similar features. The longitudinal mode shows a pronounced attenuation peak at around 260 K accompanied by a change of slope in velocity vs temperature curve. The increase of velocity starts at 275 K and continues smoothly down to 240 K where a downward inflection occurs. The same anomalies were found for the shear mode (see Fig. 2). These features resemble the elastic anomalies of Y 1:2:3 near 240 K where an attenuation peak and a concomitant velocity change were reported by a number of groups.[10-14] It was assumed[7] that the anomalies in Y 1:2:4 at 260 K and in Y 1:2:3 at 240 K may originate from the same mechanism in view of the similarity of their structures. If so, our present results therefore rule out the possibility that the anomalies at 240 K in Y 1:2:3 are caused by the ordering of the oxygen vacancies in the CuO chains[10,12,15] or by the "oxygen breathing" taking place at grain boundaries or crystal surfaces[16-18] since there are no oxygen vacancies in Y 1:2:4. Nor will twin structure contribute to the anomalies.

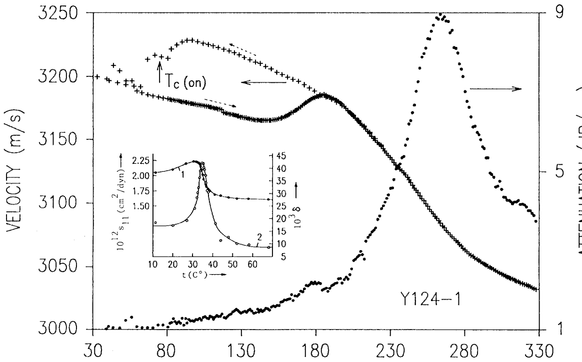

FIG. 1. Ultrasonic velocity and attenuation in Y124-1 measured with longitudinal waves at 14 MHz. The dashed-line arrows indicate the direction of the thermal cycle. The inset is the elastic data measured on $PbMg_{0.5}W_{0.5}O_3$: (1) for elastic compliance S_{11}, (2) for the energy dissipation of elastic waves (after Ref. 19).

A new mechanism was proposed in a previous work[7] to account for the anomalies in both Y 1:2:4 and Y 1:2:3. In short, it was suggested that above the anomaly temperature O(4) atoms are randomly distributed between the two potential wells[7] in the direction transverse to the CuO chains along the *a* axis, while below the anomaly temperature O(4) atoms order in a periodic, antiferrodistortive manner. Since an electric dipole is associated with each CuO pair, this type of ordering may therefore be viewed as a phase transition from a paraelectric (PE) state to an antiferroelectric (AFE) state. This PE to AFE phase transition associated with the ordering of the O(4) atoms of the CuO chains is believed to be responsible for the elastic anomalies in Y 1:2:4 at 260 K and in Y 1:2:3 at 240 K. In other words, the elastic anomalies are considered to be created by the piezoelectric or electrostrictive coupling between acoustic waves and the polarization of CuO dipoles. In fact, elastic anomalies due to the PE to AFE phase transition had been observed in $PbMg_{0.5}W_{0.5}O_3$ a long time ago[19] as illustrated in the inset of Fig. 1.

A mechanism similar to what we proposed above has also been suggested recently[20] to explain the dissipation peak observed at lower temperatures in Y 1:2:3. In that paper it was noted that other off-center positions in the Y 1:2:3 structure could give rise to an AFE or even a ferroelectric (FE) state, leading to the formation of a domain structure. However, from our present measurements we believe that AFE or FE domains are unlikely to exist in Y 1:2:4 below 260 K. The reason for this is that once the domain structure appears in the AFE state, the attenuation will remain very large below the phase transition due to the scattering from domain boundaries, a phenomenon that is in contradiction with the experimental results (see

Figs. 1 and 2). We agree, however, that other off-center positions such as the displacement of the O(4) atoms along the *c* direction[21–23] can induce an AFE state. Our experimental results can also not conclusively exclude the possibility that the phase transition is a result of the correlated flipping of the buckled Cu-O-Cu links along either *a* or *b* directions in the CuO plane, which was suggested in Ref. 24 as a mechanism for the structural phase transition at 220 K for Y 1:2:3.

The physical consequences of our proposed mechanism are the following.

(1) In the mechanism we proposed, the system is considered to exhibit a uniaxial electric polarization due to the ordering of oxygen atoms in some off-center positions of the structure below 260 K. Suppose that the ordering of O(4) atoms takes place in the double CuO chains. In such a case of uniaxial electric polarization, the interactions between the CuO electric dipoles in the CuO chains are dominated by long-range dipole-dipole interactions. Large fluctuations are thus partially suppressed.[25] Therefore, energy dissipation of the acoustic waves comes mainly from the Landau-Khalatnikov damping mechanism which is characterized by a Debye-like relaxation peak. The partial suppression of fluctuations may also weaken the corresponding anomaly in specific heat.

(2) It is expected that the attenuation and velocity variation of ultrasonic waves have a very strong directional dependence if piezoelectric coupling governs the interactions between ultrasonic waves and the CuO dipoles. In particular, for the Y 1:2:3 case where FE domains can form below the transition temperature,[20] the elastic anomalies occur only when the acoustic wave vector is perpendicular to the polar axis.[26] So it is expected that sound waves propagating parallel to the polar axis should have no anomaly due to piezoelectric coupling. Experimental evidence for the existence of such strong directional dependence is available. In an ultrasonic measurement made on a sinter-forged Y 1:2:3 sample,[27] an attenuation peak at 250 K was found when propagating the 12-MHz compressional waves perpendicular to the forging axis (*c* axis). Interestingly, as expected, the 250 K peak disappeared completely when passing the waves parallel to the forging axis. This result indicated that in that sample the O(4) atoms are ordered along the *c* direction. This phenomenon is reflected clearly in the measurement of ultrasonic velocity too. Longitudinal waves propagating along the *c* direction showed no upward inflexion in velocity. However, when the direction of propagation was parallel to the basal plane, the anomaly in velocity emerged.[28] These observations actually are the direct consequence of point (1) above. The reason is as follows: When longitudinal waves propagate along the *c* direction, ultrasonic attenuation is expected to be caused by the thermal fluctuations of CuO dipoles alone. This fluctuation is, however, suppressed strongly in Y 1:2:3 due to the long-range dipole-dipole interactions [see also, point (3)]. Thus, elastic anomalies are not seen in this case. On the other hand, if waves propagate along the basal plane, piezoelectric coupling between ultrasonic waves and CuO dipoles is allowed, leading to the anomalies in velocity and attenuation.

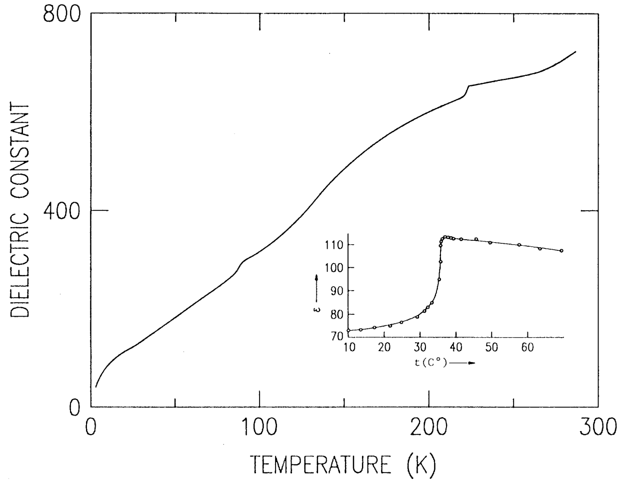

FIG. 3. Static dielectric constant vs temperature for a tetragonal Y 1:2:3 ceramic (after Ref. 31). The inset is the corresponding data measured on $PbMg_{0.5}W_{0.5}O_3$ (after Ref. 19).

The elastic anomalies near 240 K have been observed[29,30] also in Y 1:2:3 single crystals. Unfortunately it was not checked if the anomalies depended on the direction of propagation.

(3) The anomalies should be directly detectable from measurements of the static dielectric constant and pyroelectric voltage. Indeed an anomaly in the static dielectric constant was discovered[31] in a tetragonal Y 1:2:3 polycrystalline sample at 220 K as shown in Fig. 3. It looks remarkably similar to the anomaly found near the PE to AFE phase transition temperature in $PbMg_{0.5}W_{0.5}O_3$ (see the inset of Fig. 3). Furthermore, recent measurements[55,56] of the pyroelectric voltage in a Y 1:2:3 single crystal revealed a spontaneous polarization along the *c* axis at around 220 K. This observation supports strongly the ideas presented in point (2) above. The mechanism proposed here may be responsible also for the anomalies observed at around 240 K in Raman scattering[32,33] and thermal expansion[35] measurements in Y 1:2:3.

Further measurements of the frequency dependence of the attenuation peak position show unexpected behavior. It is clearly seen from Figs. 1 and 2 that the position of the attenuation peak is shifted by about 6 K to the lower temperature when the probing frequency is changed from 14 to 10 MHz. This tendency was checked further by performing compressional mode measurements on Y124-2 at 10 MHz. In this case the attenuation peak appeared at around 245 K, a downward shift in temperature of 15 K. These results are unexpected in the following sense: in order-disorder or displacive phase transitions, there are two mechanisms which contribute to the dynamic response of the system. One is the critical scattering caused by the fluctuations of the order parameter. The other is the well-known Landau-Khalatnikov relaxation damping. Therefore, ultrasonic attenuation due to the phase transition should be given by the superposition of the two contributions. Of these two contributions, only the Landau-Khalatnikov process will shift the attenuation peak to lower temperature with increasing frequency below the phase transition temperature. Thus, the position of the attenuation peak should exhibit weak frequency dependence even in the cases where the fluctuation contribution is completely suppressed, since the relaxation time of the order parameter of the phase transition changes significantly only near the transition temperature. On the other hand, if the phase transition is induced by applied ultrasonic waves, the influence of the probing frequency on the location of the attenuation peak could be quite strong. Upon increasing frequency, the position of the peak must move to a higher temperature, a way which is opposite to that in the Landau-Khalatnikov case. It is worth pointing out here that the reasons given above are generally true only for a system, such as potassium dihydrogen phosphate (KDP), where there is no localized lattice distortion associated with the electric dipoles. The validity of this condition, however, is in doubt for Y-based compounds.

Finally, we must emphasize here that although ultrasonic measurements are very sensitive to phase transitions, it is very difficult to assign a detailed mechanism to explain the observed anomalies from the ultrasonic measurement alone.

B. The thermal hysteresis in velocity

Now let us turn our attention to the lower-temperature region (below about 200 K) where a velocity hysteresis in both longitudinal and transverse cases was observed (see Figs. 1 and 2). Similar behavior has been found in Y 1:2:3.[1] As in Y 1:2:3,[10,11] the hysteresis does not show up until the temperature is lowered down to T_h, which is defined as the temperature where the velocity reaches its maximum value. Below T_h, a continuous softening of the sample begins. This softening is not so pronounced in the Y124-2 sample (see Fig. 4). The area of the hysteresis loop, which is a way of evaluating the strength of the thermal hysteresis, increases with the decrease of the lowest temperature in each run. Below 70 K, sample Y124-1 shows a scattering in velocity data while sample Y124-2 exhibits a sharp increase in velocity (we will return to the discussion of this behavior in Y124-2 and the attenuation data later). When heating up, sample Y124-1 remains soft up to a temperature T_l where an upward inflection takes place, whereas sample Y124-2 shows a linear decrease in velocity. The thermal hysteresis in velocity (abbreviated "the hysteresis") in both samples closes at around 200 K. It is noticed that the area of the hysteresis is larger in sample Y124-1 than in Y124-2.

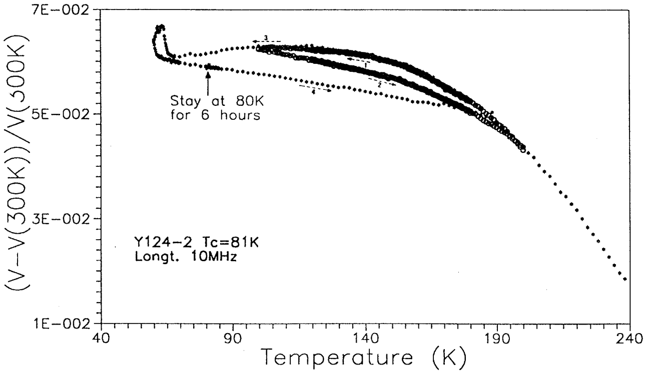

FIG. 4. The thermal hysteresis in velocity for the longitudinal mode in Y124-2, measured at 10 MHz. The dashed-line arrows indicate the direction of the thermal cycle.

This behavior of velocity resembles that of Y 1:2:3 [Refs. 10, 28, 36, and 37] in many ways, except that in the Y 1:2:3 case one or two attenuation peaks are usually found in this temperature region[10,13,27,38,39] and sometimes the velocity does not recover entirely even up to room temperature.[12,40–42] In addition, a partial isothermal recovery of elastic moduli was revealed in Y 1:2:3,[10,41,43] which was not observed in our measurements. We have measured the velocity at 80 K at 2-h intervals on the sample Y124-2, staying at this temperature for a total of 6 h during the heating run. No change was detected (see Fig. 4). Unlike Y 1:2:3,[37] in Y 1:2:4 the hysteresis was reproducible in spite of several different cooling rates between 4 and 30 K/h. These observations imply that at least part of the mechanism responsible for the hysteresis in Y 1:2:4 is different from that in Y 1:2:3.

Usually, the hysteresis can arise from two sources.[36] One is the nonchemical free energy from the elastic strain generated at the interface. The other is a barrier to nucleate a new phase. The latter source seems to be quite unlikely to occur in the present case since no significant attenuation anomaly was found in Y 1:2:4 for either longitudinal or transverse modes. This observation indicates that there are no significant structural or ordering phase changes in this temperature region. This idea is corroborated by X-ray measurements.[44,45] It is noted, however, that small irregular changes in attenuation appeared sometimes around 170 K (see, for instance, the small attenuation peak in Fig. 1 or a shoulder in attenuation in Fig. 2). Nevertheless, we believe that the hysteresis is induced dominantly by the first source.

In Y 1:2:3, Ewert and co-workers[46] found that the hysteresis disappeared in a fine-grain sample with grain size of 4 μm and a density of 92%. The result was later confirmed by other groups.[15,47,48] It was concluded[37,48] that grain size is the main controlling factor for the hysteresis. This explanation seems to be too simple to account for the present experimental results. We notice that in the literature there were no elastic measurements on a sample with small grain size and large amount of porosity (a characteristic possessed by both of our samples). For Y124-1, the SEM photograph shows that the average grain size is about 3 μm and the grain is relatively round shaped with a pore size from about 1 up to 10 μm, in contrast with Y124-2 where the shape of the grains are mostly platelike [Figs. 5(a) and 5(b)]. Although the grain size is larger in Y124-2, it is more compact. In view of the fact that the area of the hysteresis loop in Y124-1 is larger than in Y124-2, the possibility that grain size is the only important factor governing the strength of the hysteresis is excluded. The difference in the shape of the grain does not seem to be of any importance to the strength of the hysteresis since Y124-1 has a shape of grains similar to the one used by Ewert *et al.*[46]

A more consistent explanation, we suggest, is the following: It has been observed that Y 1:2:4 displayed large anisotropic compressibility and expansivity along the three crystallographic directions.[44,45] The compressibility and expansivity along the *a* direction were triple[45] and double,[44] respectively, of those along the *b* direction. The differences between *c* and *a* or *b* were even much larger.[44] It was noted that such strong anisotropy had not been discovered in other high-T_c superconductors before.[45] If a polycrystalline Y 1:2:4 sample is cooled down, the different thermal expansion coefficients along the three crystallographic directions lead to an anisotropic change of grain size. Each grain inside the sample will change in a different manner because of the different crystallographic orientations. Due to the presence of grain boundaries, the change of grain size is hindered and a stress field is thus created near grain boundaries. This stress field is enhanced gradually with decreasing temperature down to T_h where the stress becomes large enough to create some reversible defects near the interconnecting region so as to relieve part of the gathered elastic energy. Consequently, we observe a decrease of velocity. This process goes on continuously until the thermal expansion coefficients of the sample along the three principal directions become relatively stable with respect to temperature at about 60 K (see Fig. 1 of Ref. 44). Further cooling therefore produces less thermal hysteresis. When heating back to 60 K, the velocity remains low until T_l where the reversible defects start to be annihilated gradually. This process is completed near 200 K where the velocity is recovered completely. It must be emphasized that it is the reversible defect generated by the large anisotropic thermal expansion along three different crystallographic axes in each grain which is mainly responsible for the observed hysteresis in Y 1:2:4.

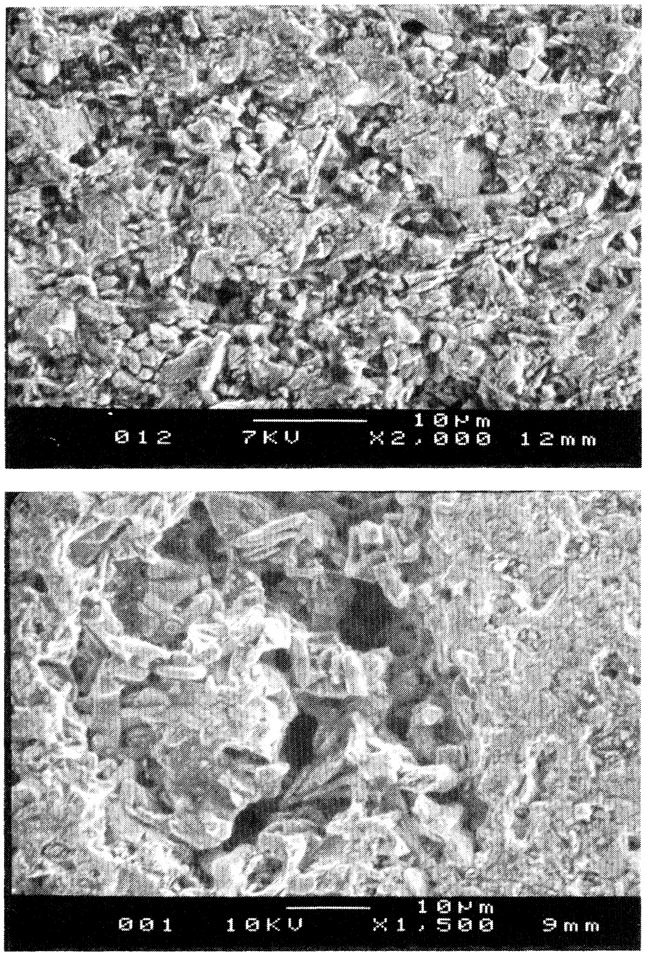

FIG. 5. SEM pictures of (a) Y124-1 (the upper figure) and (b) Y124-2.

Within the above model, we now try to explain our experimental results. For the Y124-1 sample, although the grains are small the percentage of pore volume is large. It is therefore easier to create some reversible defects, such as a small tilting or rotation of grains or the formation of gaps near grain boundaries, inside the sample. In Y124-2, it is relatively more compact and thus the excitation energy for the creation of the reversible defects in Y124-2 is relatively higher. Since in Y124-2, the grain size does not differ significantly from that of Y124-1, the strength of the hysteresis is expected therefore a little smaller than that of Y124-1.

So, from our model, we expect that the samples with a large percentage of pore volume and grain size will display the most pronounced hysteresis. If the formation energy of the defects exceeds the coupling energy between interface of grains, the velocity may not recover even at room temperature, nor will the hysteresis be observed in small-grained and compact samples. The latter expectation has been verified recently by ultrasonic measurements on a Ca-doped Y 1:2:4 sample.[34]

It is noted that the phase transition at 260 K will not contribute to the thermal hysteresis since there is no strain created by the PE to AFE phase transition. However, if the phase transition is from PF to FE, the hysteresis could be affected.

Naturally, our model does not predict that the sound velocity depends on the cooling rate nor on the partial isothermal recovery of elastic moduli, provided that the sample reaches thermal equilibrium at each measuring point, as it does in our measurements. The smaller strength of the hysteresis in Fig. 4 is also a logical consequence of the present model, since in this case the sample was only cooled down to 100 K. Thus, fewer amounts and less serious reversible defects were formed.

We believe that at least part of the hysteresis observed in Y 1:2:3 could originate from the present mechanism. In fact, the importance of the reversible defects for explaining the hysteresis in Y 1:2:3 was noted already in 1990, when they were considered as a result of a phase transition of weak first order.[43] As mentioned above, for Y 1:2:3 samples it is plausible that another mechanism, such as the possible phase transition related to the ordering of oxygen vacancies[49] near 150 K, could contribute to the hysteresis too. However, what percentage of the hysteresis comes from the latter source cannot be predicted at this moment.

C. Elastic anomalies near T_c

As is easily seen from Figs. 1 and 2, no noticeable changes in velocity and attenuation were observed in all runs except for one run where a small dip was revealed at T_c (see Fig. 1). This result is not surprising if we compare our results with the results obtained from other kinds of measurements using thermodynamic relations. From the well-known Ehrenfest's relations, the following expression is easily deduced:

$$\frac{dT_c}{dP}=\left[-\frac{\Delta B}{B^2}\cdot\frac{VT_c}{\Delta C_p}\right]^{1/2} . \tag{1}$$

Here B is the bulk modulus, C_p is the specific heat at constant pressure, and V is the volume of the sample. ΔB and ΔC_p are defined as the differences in B and C_p between superconducting and normal states. It has been observed[50] that Y 1:2:4 has a strong pressure dependence of T_c ($dT_c/dP=0.55$ K/kbars). Unlike in Y 1:2:3 where the reported $\Delta C_p/(VT_c)$ values deviate a lot, in Y 1:2:4, a $\Delta C_p/(VT_c)$ value of 12–16 mJ/(mol K^2) is generally observed (see Ref. 51). If we take a maximum value 16 mJ/mol K^2) for $\Delta C_p/(VT_c)$, 0.55 K/kbars for dT_c/dP, and utilize the value of B in Table I, from the thermodynamic relation we get a $\Delta B/B$ value of 7.81 ppm for Y 1:2:4. For shear modes, it is expected from a thermodynamic argument[52] that no step change in velocity can occur at T_c. Therefore, the following relation holds:

$$\frac{\Delta B}{B}\approx\frac{V_l^2(2\Delta V_l/V_l)}{V_l^2-(4V_t^2/3)} . \tag{2}$$

Using data from Table I and inserting them into the above expression, we get $\Delta V_l/V_l=2.3$ ppm at T_c for Y 1:2:4 in an ideal case. This value is well below the resolution of our apparatus.

Inspecting Fig. 1, a small attenuation peak at around 55 K could be found. A continuous increase of attenuation below 60 K is also seen from the transverse mode (see Fig. 2). This feature was also observed in Y 1:2:3 (Ref. 1) and attention has been drawn to similar phenomena in heavy-fermion superconductors.[53]

Finally, we point out the striking increase of velocity at around 60 K shown in Fig. 6. Similar but less pronounced behavior was also observed in Y 1:2:3.[1] This anomaly seems to be one of the typical features for Y-based cuprate superconductors. It has been interpreted as due to reentrant softening.[54] Using the same model, we are unable to fit our experimental data. The difficulties are (1) the large stiffening occurs at a temperature well below the center of T_c (onset) (see Fig. 6), (2) there is no noticeable softening at T_c, and (3) a small thermal hysteresis is associated with the stiffening. Furthermore, when it was heated back to 85 K and cooled down again, the stiffening did not appear at the same temperature as before. This irreversible behavior is also difficult to explain by the reentrant softening model. At the present time, we do not know how to explain this anomaly. Further structural and elastic measurements on pure and Ca-doped samples are needed.

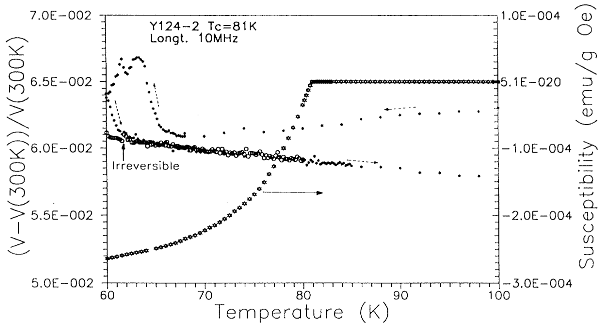

FIG. 6. A closeup look of the velocity data in the low-temperature region in Y124-2. The small thermal hysteresis associated with the anomalous increase in velocity below about 65 K can be easily seen. When the sample was heated back from 60 to 80 K and then cooled down again, the velocity showed an irreversible behavior with respect to temperature as indicated. Susceptibility data on the same sample are also shown. No change in velocity at T_c was observed. The dashed-line arrows indicate the direction of the thermal cycle.

IV. SUMMARY

Ultrasonic measurements in the MHz frequency range have been performed on two single-phase polycrystalline Y 1:2:4 samples with different microstructure. The measurements covered the temperature region from 30 to 350 K and employed both compressional and transverse modes. The following information was obtained.

(1) Several basic elastic parameters of Y 1:2:4 are reported. It turns out that the lattice of Y 1:2:4 is markedly softer than that of Y 1:2:3.

(2) A pronounced dissipation peak at about 260 K with a simultaneous change of slope in velocity is observed for both compressional and shear modes. The anomalies are interpreted as the result of the formation of the AFE or FE state associated the ordering of oxygen atoms in some off-center positions in the structure. The physical implications of this interpretation are discussed. Good agreement with the existent experimental observations is found. It is suggested that a similar phenomenon could take place near 240 K in Y 1:2:3.

(3) Thermal hysteresis in velocity (abbreviated "the hysteresis") is studied and discussed in detail. Ultrasonic and SEM measurements on a sample with 3 μm grain size and 35% volume of porosity reveal convincingly that both percentage of pore volume in the sample and grain size govern the area of the hysteresis loop.

(4) A mechanism based on the unusually large anisotropic thermal expansion in Y 1:2:4 is proposed to explain the hysteresis. It is pointed out that the creation of some reversible defects, such as a small tilting or rotation of grains or the formation of gaps near grain boundaries, is essential for the hysteresis. For Y 1:2:3, however, other mechanisms, for instance, a possible structural phase transition at 150 K, could contribute to the hysteresis in addition.

(5) No reproducible anomaly in velocity is detected at T_c, which is consistent with the result of the specific-heat

measurements using thermodynamic relations. A small attenuation peak at around 55 K was noted.

(6) An enormously large increase of velocity at a temperature below T_c is probed in Y124-2. The anomaly is difficult to account for by the reentrant softening model.[54] It is found that the large stiffening is associated with a small thermal hysteresis and the anomaly is irreversible with respect to temperature.

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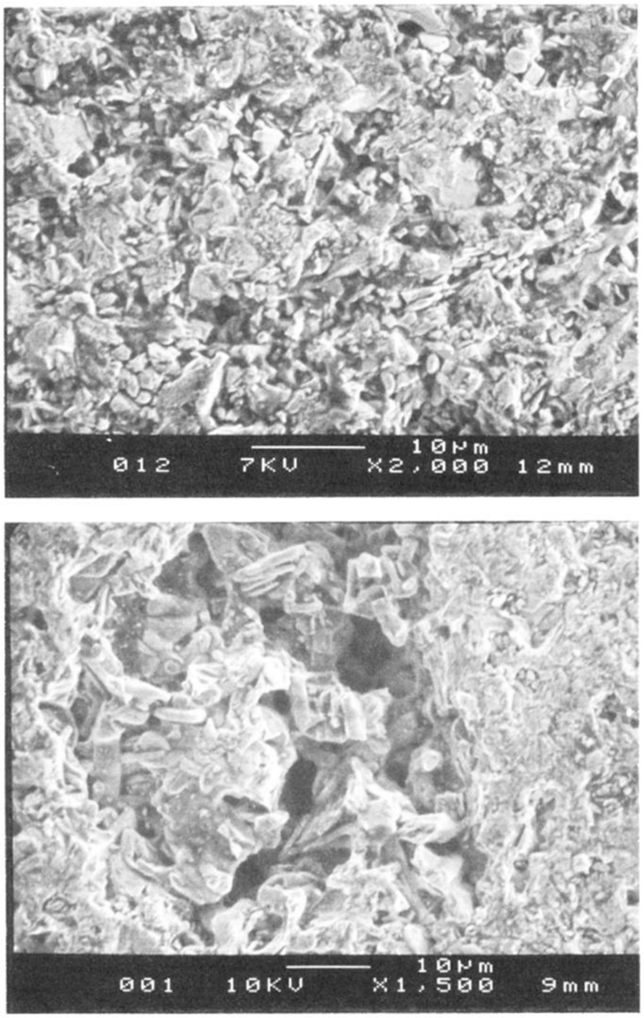

FIG. 5. SEM pictures of (a) Y124-1 (the upper figure) and (b) Y124-2.