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# Elastic softening and internal friction in $La_{2-x}Sr_xCuO_4$

W-K. Lee, M. Lew, and A. S. Nowick
*Henry Krumb School of Mines, Columbia University, New York, New York 10027*

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The Young's modulus $E$ and the internal friction of polycrystalline ceramic $La_{2-x}Sr_xCuO_4$ were measured over the composition range $0.05 \le x \le 0.30$. A striking elastic constant anomaly, reported previously, was observed, in which $E$ falls by 40% or more and the internal friction increases with decreasing temperature. The temperature region of the elastic softening falls rapidly with increasing Sr concentration $x$ and occurs near the tetragonal-orthorhombic ($T$-$O$) transition temperature. The "soft" modulus does not recover at lower temperatures but persists to at least $\sim 100$ K. This elastic softening and the accompanying internal friction are attributed to stress-induced migration of martensitic domain boundaries produced by the $T$-$O$ transition. It is also found that there is no correlation between the elastic softening and the occurrence of superconductivity.

## I. INTRODUCTION

The discovery of superconductivity in $La_{2-x}M_xCuO_4$ ($M$=Sr,Ba),[1] for $0.15 < x < 0.20$ has led to numerous studies of the properties both of the parent material ($La_2CuO_4$) and the doped systems. Pure $La_2CuO_4$ has the tetragonal $K_2NiF_4$ structure at elevated temperatures but undergoes a tetragonal to orthorhombic ($T$-$O$) structural phase transition at $\sim 500$ K (the exact temperature depending on oxygen stoichiometry).[2] The substitution of La by the alkaline-earth elements (Sr and Ba) stabilizes the tetragonal phase by sharply lowering the $T$-$O$ transition temperature.[3,4] A pronounced lattice softening with decreasing temperature in the vicinity of the $T$-$O$ transition was observed both for Sr- and Ba-doped systems, using techniques of neutron scattering,[5-7] Raman scattering,[8-10] ultrasonic pulse propagation,[11-16] and resonant frequency measurements.[17-19] The neutron and Raman observations were attributed to an optical mode softening associated with the $T$-$O$ transition. The elastic-constant anomaly, on the other hand, clearly involves acoustical vibrations at wave vectors, $q$, close to zero. In the case of $La_{1.85}Ba_{0.15}$,$CuO_4$, Fossheim *et al.*[12,14] showed that a partial restiffening of the elastic constants takes place at low temperatures ($< 63$ K), a result shown by Axe *et al.*[20] to be due to a return to the tetragonal phase.

Most of the previous work, with the exception of the neutron scattering work of Thurston *et al.*,[7] was limited to the narrow composition range that is optimal for superconductivity ($0.15 \le x \le 0.20$). In the present paper, we describe a study of elastic constants and internal friction of $La_{2-x}Sr_xCuO_4$ covering the wider composition range $0.05 \le x \le 0.30$. The prime objective is to determine to what extent the lattice softening phenomenon is related to the $T$-$O$ transition and to the occurrence of superconductivity. In addition, this work has led us to an interpretation of the elastic softening which differs from that given previously.

## II. EXPERIMENTAL

$La_{2-x}Sr_xCuO_4$ samples with $0 \le x \le 0.30$ were prepared by solid-state reaction in air. Stoichiometric proportions of $La_2O_3$, CuO, and $SrCO_3$ powders (all 99,99% pure from Johnson Matthey) were first calcined at 1000 °C for 24 h on platinum foil. The resulting mixture was pulverized and recalcined under the same conditions. The samples were then cold pressed and sintered at 1100 °C for 40 h in air. Sample densities were 65 to 75 % of the theoretical density. X-ray diffraction was used to confirm that a single phase had been achieved. Bar shape samples were then sliced for internal friction ($20 \times 2.5 \times 0.65$ mm$^3$) and resistivity ($5 \times 1 \times 1$ mm$^3$) measurements.

During the elastic constant and internal friction measurements, samples were suspended at their nodal positions for free-free flexural vibration on thin stainless-steel wires inside a vacuum chamber ($< 30$ mtorr). Electrostatic excitation and detection of vibrations was used. Detailed experimental procedures are described elsewhere.[21] Measurements were done primarily upon cooling (below room temperature) or heating (above room temperature). Sufficient time was allowed to achieve a stable temperature before any measurement was taken. The temperature interval between each measurement was about 5 K or less. Only the fundamental mode of resonance was excited and detected. The relationship between the resonant frequency $f_r$ and Young's modulus $E$ is given by[22]

$$f_r = 1.03(h/l^2)(E/\rho)^{1/2} \tag{1}$$

where $h$ is the sample thickness and $l$ its length. The internal friction was measured as the logarithmic decrement $\delta$ in free decay, which is related to the commonly used parameter $Q^{-1}$ by

$$Q^{-1} = \delta/\pi \ . \tag{2}$$

A four-probe dc method was employed for resistivity measurements in the temperature range from 4 to 300 K. Silver paint (Englehard SC4004) and platinum wire were used for the electrode contacts and leads, respectively.

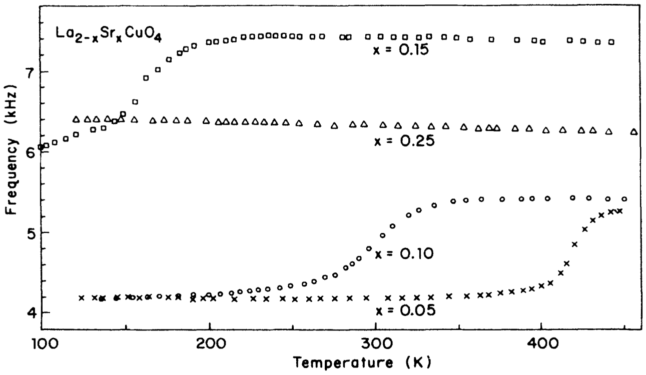

FIG. 1. Variation of resonant frequency with temperature for $La_{2-x}Sr_xCuO_4$ samples of compositions $x=0.05$, 0.10, 0.15, and 0.25.

## III. RESULTS

The resonant frequencies as a function of temperature for samples of various compositions are shown in Fig. 1. A pronounced drop ($\gtrsim 20\%$) in the resonant frequency $f_r$ with decreasing temperature was observed for compositions $x=0.05$, 0.10, and 0.15 while no similar anomaly was detected for $x=0.25$ and also for $x=0.30$ (not shown in Fig. 1). The frequency drop occurs at a lower temperature the higher the value of $x$. In view of the relation between $f_r$ and Young's modulus $E$ given by Eq. (1), these frequency drops imply decreases in $E$ of greater than 40%, thus representing considerable softening of the elastic properties of the lattice. These effects are much larger than those observed by ultrasonic pulse methods, although they occur in the same temperature region for the same composition. Furthermore, no restiffening of the lattice at still lower temperatures (down to 100 K) was observed. In particular, for the composition $x=0.05$, the "soft" modulus persists over a temperature range from $\sim 400$ to 100 K. No appreciable temperature shift of the frequency drop was found by heating instead of cooling.

The data of Fig. 1 also suggest that the value of $E$ in the higher temperature region (before the softening) goes through a maximum as a function of the Sr concentration, $x$. We are reluctant, however, to draw conclusions from the absolute values of $f_r$ of different samples, because such values are subject to variability due to differences in texture (preferred orientation of grains) and density of the different ceramic samples. This matter, therefore, requires further investigation.

A rapid increase in the internal friction $Q^{-1}$ is associated with the lattice softening and occurs in the same temperature range, as evidenced in Fig. 2 for $x=0.10$. (The two treatments covered in this figure will be discussed later). After the $\gtrsim 20\%$ drop in frequency is completed, $Q^{-1}$ increases to a maximum. Then it begins to decrease gradually as the temperature is lowered further but remains high relative to the values that exist before the softening starts. This result is typical of what is observed for other compositions as well. It is worth noting that the internal friction is somewhat erratic throughout this temperature range.

To explore the relationship between the tetragonal-to-orthorhombic ($T$-$O$) transition and the lattice softening, Fig. 3 compares the ($T$-$O$) transition temperatures taken from the literature with the temperature ranges over

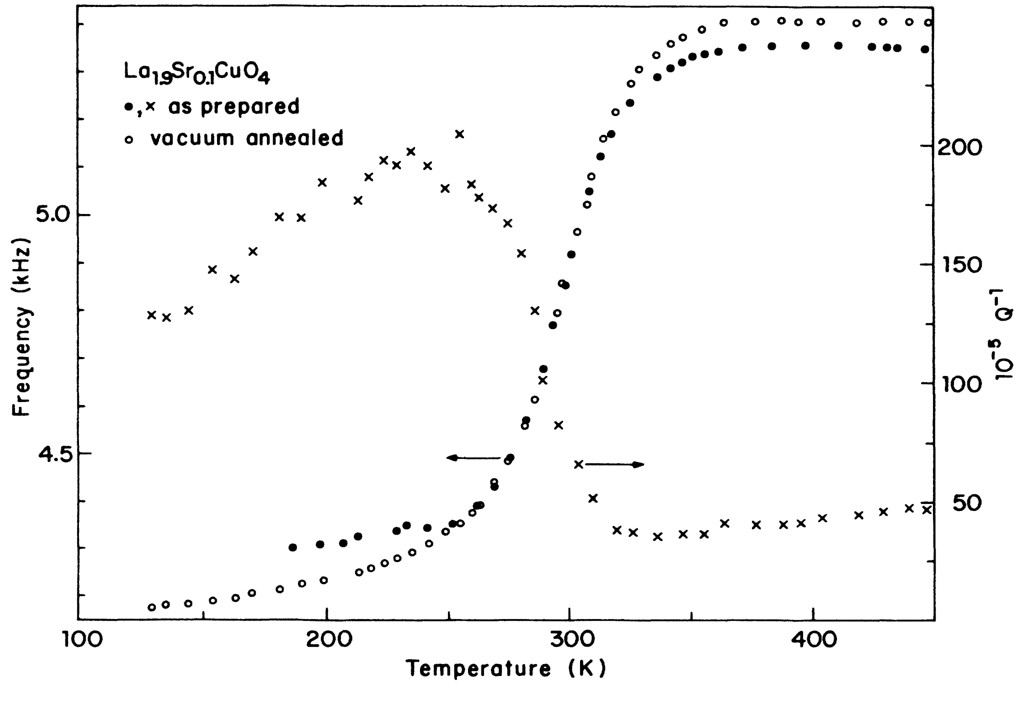

FIG. 2. Resonant frequency and internal friction as a function of temperature for a sample of composition $x=0.10$. The resonant frequency data compares samples that were treated in air ("as-prepared") and in vacuum (solid and open circles, respectively).

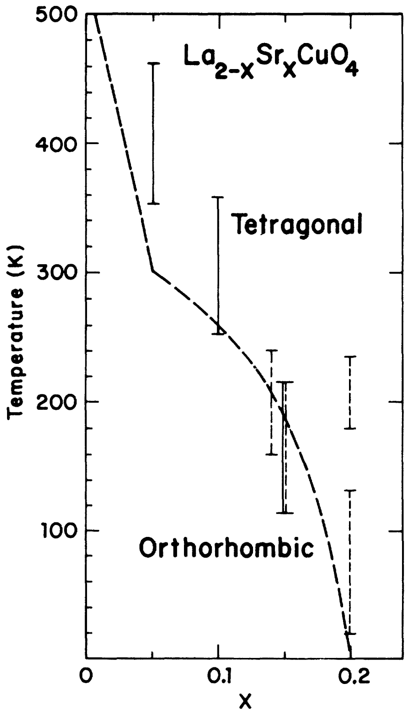

FIG. 3. The *T-O* transition temperature as a function of Sr composition $x$ is shown by the broken curve. (Data are from Ref. 3). The vertical bars show the range of temperature over which elastic softening occurs, the solid ones from the present work, and the dashed ones from Refs. 11, 13, 17, and 18.

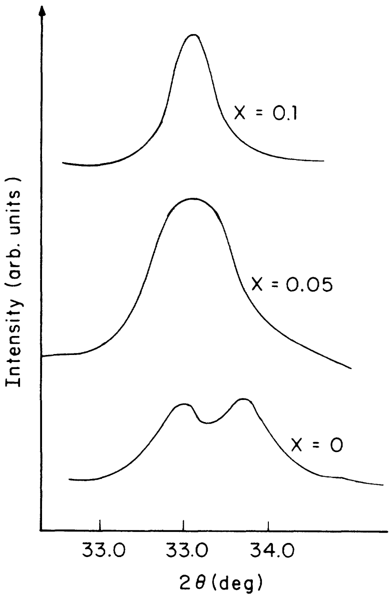

FIG. 4. X-ray diffraction in the vicinity of the tetragonal (110) reflection for the three compositions $x=0$, 0.05, and 0.10.

which elastic softening occurs, both plotted as a function of the Sr concentration. The plot of $T_0$ versus Sr concentration, marked by a dashed line, is taken from Ref. 3. Other workers, using single crystals, have reported higher $T_0$ values in the range of $x < 0.1$.[4] Data showing the range of temperature of the elastic softening are shown as vertical bars, the solid ones taken from the present measurements for $x=0.05$, 0.10, and 0.15, while the dashed ones for $x=0.14$,[13] 0.15,[11,17] and 0.20,[15,18] are taken from previous work. Excellent agreement in the softening ranges between the present work and earlier studies is observed for $x=0.15$; however, for $x=0.20$, a discrepancy exists between the two previous studies. The temperature range of the lattice softening decreases sharply with the Sr concentration, as does the *T-O* transition temperature. At 0.14 and 0.15, the *T-O* transition temperatures lie within the temperature range of the drop in elastic constants, but for $x=0.05$ and 0.10 the frequency drop seems to lie almost entirely in the range of the tetragonal phase. To investigate this point further, we have carried out x-ray diffraction at room temperature on the same samples that were used in the frequency measurements. The (110) tetragonal reflection, which splits to form the (020)-(200) doublet of the orthorhombic phase,[3] was studied carefully by x-ray diffraction at room temperature (~25 °C) for the compositions $x=0$, 0.05, and 0.10. The results are shown in Fig. 4. The orthorhombic splitting is clearly shown for $x=0$, while the peak for $x=0.05$ is enough broadened to suggest the orthorhombic phase. On the other hand, no orthorhombic splitting was observed for $x=0.10$. These observations imply that the $x=0.10$ composition is tetragonal at room temperature, while the *T-O* transition temperature for $x=0.05$ falls somewhat above room temperature. Comparison with the dashed curve of Fig. 3 suggests that this curve might be moved upward by 10 to 20 K, but not more. In any case, there is little doubt that much of the elastic softening occurs in the tetragonal phase region.

The interplay between superconductivity and lattice softening was also explored. As shown in Fig. 5, the as-prepared sample with $x=0.05$ is semiconducting; nevertheless, lattice softening is still observed (Fig. 1). Figure 5 also shows the resistivity plot of a sample with $x=0.10$ under different treatments. The as-prepared sample shows the onset of superconductivity at around 31 K and zero resistance at 12 K. For the vacuum-annealed sample, the normal-state resistivity increases about fivefold. The resistivity still shows a drop at around 30 K, but remains finite down to the lowest temperature of measurement (10 K). The variation of resonant frequency with temperature for the $x=0.10$ sample, both for the as-prepared and vacuum-annealed conditions, are shown in Fig. 2. The temperature region of the frequency drop in both cases is nearly identical, the only difference being that the drop in frequency is greater by about 10% for the vacuum treated sample. The internal friction $Q^{-1}$ is also about the same for both cases (not shown in the figure). For the $x=0.05$ sample, there is again no apparent shift in the frequency drop between the air- and vacuum-annealed samples. However, $Q^{-1}$ for the vacuum treated sample is appreciably lower than that of the air-annealed sample. By contrast, for the $x=0.15$ sample the temperature region of the frequency drop is shifted by about 15 K toward higher temperatures after vacuum annealing, as shown in Fig. 6. The internal friction of the vacuum-annealed sample is also somewhat lower than

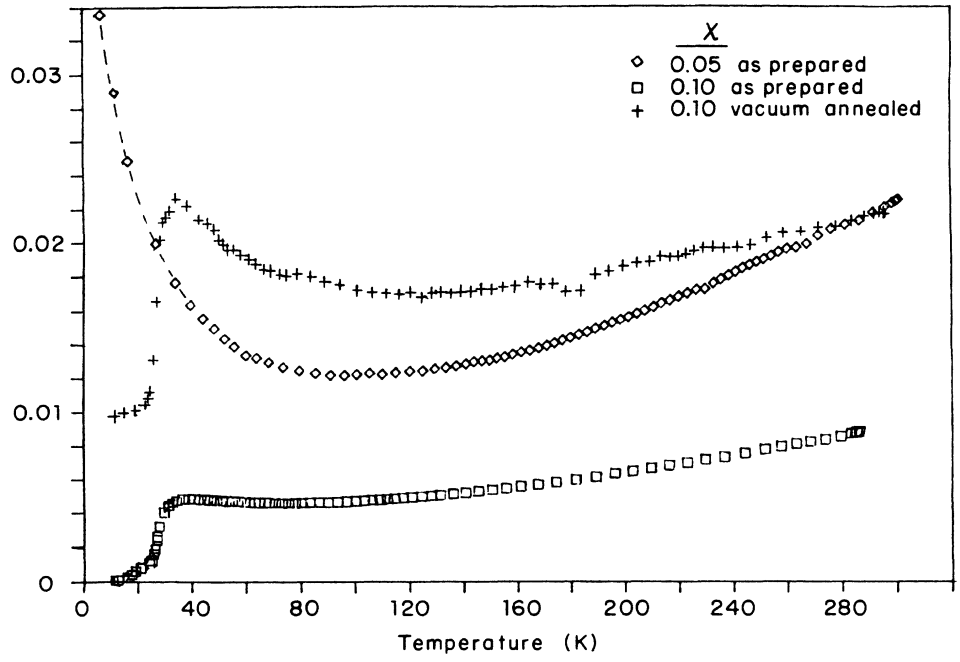

FIG. 5. Electrical resistivity as a function of temperature for the as-prepared $x=0.05$ sample, and for the $x=0.10$ sample as prepared and after vacuum annealing.

that of the air-treated sample. It is not clear as to why this difference in frequency behavior exists between the samples for $x=0.05$ and 0.10 on the one hand, and that for $x=0.15$ on the other.

## IV. DISCUSSION

The striking drop in resonant frequency with decreasing temperature observed in this work for compositions $x=0.05$, 0.10, and 0.15 corresponds to a decrease in the Young's modulus $E$ of 40% or more. This manifestation of elastic "softening" is considerably larger than that observed by ultrasonic methods,[11–16] although it takes place in the same temperature range. The reciprocal Young's modulus $E^{-1}$ for a tetragonal crystal of arbitrary orientation is related to the six independent elastic compliance constants, $S_{ij}$, of such a crystal. In particular, it involves the three shear constants: $S_{11}-S_{12}$, $S_{44}$, and $S_{66}$. In the absence of single-crystal data, it is not possible to state which of these shear constants goes "soft." An important clue, however, comes from the results of Fig. 3 which shows that the elastic softening varies with strontium concentration very nearly as the *T-O* transformation temperature, $T_0$. The crystallography of the *T-O* transition, which shows that the orthorhombic $a$ and $b$ axes lie along the tetragonal ⟨110⟩ axes,[23] strongly suggests that is must be the $S_{66}$ shear constant that undergoes the softening, i.e., that this compliance becomes extremely large near $T_0$. On this basis, the Young's modulus of a grain oriented in a ⟨110⟩ direction which is given by[22]

$$E^{-1}=\tfrac{1}{4}[2(S_{11}+S_{12})+S_{66}]$$

may go to zero at the *T-O* transition, in the limiting case when $S_{66}\rightarrow\infty$. For a polycrystalline aggregate, the observed modulus is an average over grains of all orientations, most of which retain higher values of $E$. Nevertheless, the large elastic anomaly observed in the present work can be understood on the basis of $S_{66}$ becoming very large. It is also understandable that the softening observed through ultrasonic techniques is smaller, since in those cases the elastic stiffness coefficients $C_{ij}$ are involved. Specifically, the velocity $v$ of a longitudinal ultrasonic wave along the ⟨110⟩ direction is given by[22]

$$\rho v^2=\tfrac{1}{2}(C_{11}+C_{12})+C_{66}$$

where $\rho$ is the density. Thus $v$ does not vanish even in the limiting case when $C_{66}\rightarrow 0$.

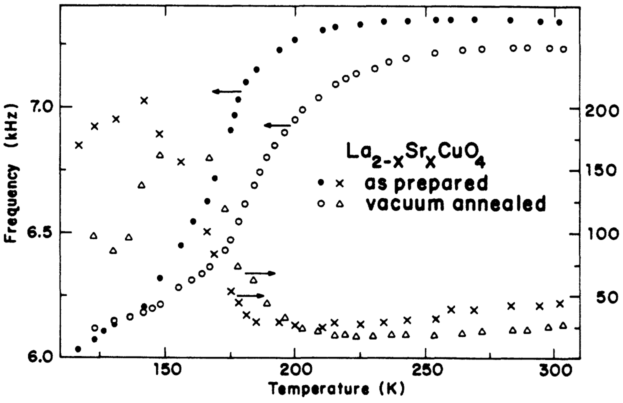

FIG. 6. Resonant frequency and internal friction as a function of temperature for a sample with $x=0.15$ both after air annealing and vacuum annealing.

While the present measurements deal with softening of acoustic modes of the lattice, previous work utilizing other techniques, particularly neutron scattering[5-7] and Raman scattering,[8-10] also show lattice softening which has been related to the *T-O* transition. The extensive work on inelastic neutron scattering on single crystals, by the Brookhaven and MIT groups, has shown the presence of a low-lying transverse-optical lattice mode that goes soft as the *T-O* transition is approached.[6] It is then important to understand the connection between the present elastic-constant (acoustical mode at $q=0$) softening and the optical-mode softening. According to the prevalent viewpoint, this coupling may take place through an order parameter $Q$ that is used to describe the *T-O* transformation (e.g., $Q$ being nonzero in the tetragonal phase and vanishing in the orthorhomibic phase).[7,16] The present work shows that there are several problems with this viewpoint. First, coupling of elastic strain to an order parameter should be strongest just at the transformation temperature $T_0$, and therefore gives rise to a cusp in the elastic constants and the internal friction[22] rather than to a monotonic elastic transition and persistent high internal friction as observed here. In fact, the optical soft mode rehardens to some extent below $T_0$,[6] but there is no evidence for any recovery of Young's modulus in the orthorhombic phase as the temperature decreases (most strikingly, for the $x=0.05$ and 0.10 compositions; see Fig. 1). Furthermore, it was shown previously[24] that, in a centrosymmetric crystal, coupling between optical and acoustic modes vanishes as $q \rightarrow 0$. For example, in the case of $KTaO_3$ crystals, even though transverse optic modes are greatly softened, elastic properties are unaffected.[24] In the present case, the tetragonal phase, in which must of the softening occurs, is indeed centrosymmetric.

Accordingly, we consider an alternative viewpoint which still accepts the concept that the occurrence of a soft-phonon mode drives the displacive *T-O* phase transition, but regards that the elastic-constant anomaly and the internal friction are both manifestations of the occurrence of a martensitic transformation, as has often been observed in metallic alloy systems such as $Nb_3Sn$ and Au-48% Cd.[25,26] According to this viewpoint the low elastic constants are due to the stress-induced movement of domain walls in the transformed (martensite) phase, rather than to low values of the second derivatives of atomic potentials or free energies. The internal friction, correspondingly, results from the hysteresis loss involved in these domain-wall motions. In this way, we readily explain (a) the large magnitude of the drop in $E$; (b) the stability of the "soft behavior" of the elastic constants over a wide range of temperature in the orthorhombic phase (Fig. 1); and (c) the rise in $Q^{-1}$ which begins close to $T_0$ and remains at a high level throughout the orthorhombic phase (as shown in Fig. 2). On the other hand, the existence of a broad peak in the internal friction and its erratic nature (see Fig. 2) is suggestive of the formation of thermoelastic martensite.[27] This means that the application of stress can induce a change in the amount of martensite as well as to reorient originally existing martensite plates. However, the present measurements did not show the amplitude dependence that should characterize such internal friction, possibly because of the very low strain amplitudes employed. The question of heating or cooling rate dependence was also not tested in the present work.

Comparison of the resistivity measurements in Fig. 5 with the lattice softening results of Fig. 2 enables us to examine two key questions. The first is the relationship between lattice softening and superconductivity. Here we see that vacuum treatment of the sample with $x=0.10$, which causes a loss of superconductivity, has hardly any effect on the lattice softening. In addition, as previously noted, the sample with $x=0.05$, which is not superconducting, shows lattice softening. These results both imply that the occurrence of lattice softening near $T_0$ is not a sufficient condition for the existence of superconductivity at lower temperatures. It may also be concluded that lattice softening is not a necessary condition for superconductivity, since we failed to observe[28] any elastic anomaly in the case of the electron superconductor $Nd_{1.85}Ce_{0.15}CuO_4$ whose structure is closely related to that of the present material.[29] Accordingly, we conclude that there is no direct connection between lattice softening and superconductivity. A similar conclusion was arrived at by other authors for different reasons.[30,7] The second question concerns the effect of oxygen stoichiometry on the lattice softening. We vary the stoichiometry by using both vacuum and air treatments. While composition plays an important role in the existence of superconductivity[31] (as also shown in Fig. 5), and is also alleged to affect the *T-O* transition at least for the case of $x=0$,[2,32] it appears to have little effect on the elastic softening of the $x=0.05$ or 0.10 compositions (see Fig. 2). On the other hand, for $x=0.15$, the elastic softening of the vacuum-annealed sample shows an appreciable shift toward higher temperatures.

## V. CONCLUSIONS

(i) A large decrease in Young's modulus $E$ (as much as $\gtrsim 40\%$) is observed in crossing the temperature range of the *T-O* transition in $La_{2-x}Sr_xCuO_4$. Further, $E$ remains low as the temperature decreases further, showing no recovery down to 100 K.

(ii) This elastic anomaly is accompanied by a large increase in internal friction, which remains high throughout the orthorhombic-phase region.

(iii) Both the soft elastic constant and the internal friction in the orthorhombic phase are interpreted as resulting from stress-induced migration of martensite domain boundaries.

(iv) There is no correlation between elastic softening and the occurrence of superconductivity.

(v) Elastic softening in this system is not strongly sensitive to the changes in composition produced by vacuum annealing.

## ACKNOWLEDGMENTS

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