Unconventional lattice stiffening in superconducting $La_{2-x}Sr_xCuO_4$ single crystals

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Ultrasonic and specific-heat measurements have been performed on single crystals of $La_{2-x}Sr_xCuO_4$ (LSCO) with $x=0.09$, 0.14, and 0.19 across the superconducting transition temperature T_c. We observed jumplike decreases in the longitudinal elastic moduli at T_c, as are seen in conventional superconductors. Anisotropic strain dependence of T_c was estimated from both the jump in the elastic moduli and specific heat at T_c via the Ehrenfest relation. With further lowering temperature below T_c, we found a pronounced lattice stiffening in the elastic moduli of LSCO, which contrasts with the continuous softening observed in most of the conventional superconductors. Thermodynamic analysis revealed that the stiffening originates from the change in the superconducting condensation energy under the lattice strain. This unusual lattice stiffening in the superconducting state is possibly a common character of the high-T_c copper oxides.

I. INTRODUCTION

Electron-phonon coupling plays a fundamental role in conventional superconductors. Phonons mediate an attractive interaction between electrons which leads to the formation of Cooper pairs. For high transition temperature (T_c) oxide superconductors, it has been widely examined whether the electron-phonon coupling is essential to superconductivity.

Studies of superconductivity-induced changes in lattice properties provide a direct way to probe the relevant coupling of phonons with electrons. Measurements of ultrasonic sound velocity or elastic moduli in solids are one of the most sensitive methods to detect a change in the acoustic branch of dispersion in the low-frequency limit. Earlier ultrasonic studies[1] have revealed that in Nb, Pb, and V the elastic moduli decrease by less than 0.01% when the sample is cooled to the superconducting state. Subsequently, Shapiro, Shirane, and Axe[2] have shown by inelastic neutron scattering measurements for Nb that the phonon frequencies of the particular acoustic branch decrease by about 4% in the superconducting state. This lattice softening below T_c is expected according to the calculation of the phonon self-energy by Schuster.[3]

In the high-T_c oxide superconductors, changes of phonon frequencies in the superconducting state have been observed by Raman scattering, infrared reflection, and other techniques; the zone-center optic phonon mode at 330 cm^{-1} of $YBa_2Cu_3O_7$ shows softening due to superconductivity, whereas the mode at 440 cm^{-1} shows stiffening in the superconducting state.[4] These changes have been explained by the strong-coupling theory based on electron-phonon coupling.[5] Recently, Normand, Kohno, and Fukuyama[6] have provided a different interpretation on the viewpoint of spin-phonon coupling.

Lattice anomalies have been reported also in the normal state of the high-T_c oxide superconductors. Raman spectra[7] have exhibited an anomalous decrease of phonon frequency for $YBa_2Cu_4O_8$ well above T_c. Extended x-ray absorption spectroscopy (EXAFS), ion channeling, and inelastic neutron diffraction have shown the existence of local lattice distortions[8] due to the buckling motions of the CuO_2 planes. Moreover, dynamical changes of the distortions[9,10] due to the superconducting transition have been observed. Recently, we have found a novel lattice softening in the normal state of LSCO with $x=0.14$ in a particular elastic modulus $(C_{11}-C_{12})/2$.[11] The softening starts from a temperature appreciably above T_c, which, however, turns to stiffening by the appearance of superconductivity.

La-214 compounds, $La_{2-x}M_xCuO_4$ (M = Sr, Ba, etc.), are very well suited for the investigation of the relation between the lattice properties and high-T_c superconductivity. The buckling structure of the CuO_2 planes in which superconductivity occurs varies with temperature, doping, and other external parameters. In $La_{2-x}Sr_xCuO_4$ (LSCO), superconductivity appears in both the orthorhombic (OMT: space group *Bmab*. OMT denotes *orthorhombic* at midtemperatures) and the tetragonal phases (THT: $I4/mmm$. THT denotes *tetragonal* at high temperatures). The OMT phase emerges as a result of a second-order structural phase transition accompanied by cooperative tilting of the CuO_6 octahedra about either the [110] or $[1\bar{1}0]$ axis of the THT phase. $La_{2-x}Ba_xCuO_4$ exhibits an additional transformation[12–14] from the OMT to a second tetragonal phase (TLT: $P4_2/ncm$. TLT denotes *tetragonal* at low temperatures). A second orthorhombic phase (OLT: *Pccn*. OLT denotes *orthorhombic* at low temperatures) appears in $La_{2-x-y}Nd_ySr_xCuO_4$.[15] The superconducting transition temperature T_c is considerably lower in the TLT and OLT phases only if the carrier concentration is $p\sim\frac{1}{8}$.[16] Thus, it indicates an intimate coupling between the lattice strains and superconductivity in this system.

In this paper, we will present results of elastic-moduli and specific-heat measurements on single crystals of $La_{2-x}Sr_xCuO_4$ with $x=0.09$, 0.14, and 0.19. We observed anomalies around T_c in the longitudinal and transverse elastic moduli in various sound modes. The most peculiar feature observed is a pronounced increase of the elastic moduli at low temperatures. In striking contrast, the elastic moduli in conventional superconductors always decrease in the superconducting state.[1] We will show that the strain dependence of the superconducting condensation energy is crucial to the temperature dependence of the elastic moduli below T_c.

The structure of the paper is as follows: The characterization of the samples and the experimental procedures are presented in Sec. II. The results of the specific-heat and elastic-moduli measurements are shown in Secs. III and IV, respectively. In Sec. V, we perform thermodynamical analysis of the elastic data to clarify the origin of the peculiar lattice stiffening. We conclude in Sec. VI.

II. EXPERIMENTAL

Large and high-quality single crystals of $La_{2-x}Sr_xCuO_4$ with nominal Sr concentrations of $x=0.09$, 0.14, and 0.19 were grown by a traveling-solvent floating-zone method.[17] The Sr concentrations of the samples were determined by using an electron-probe microanalysis (EPMA) as summarized in Table I.

Because it is necessary for thermodynamic analysis of the ultrasonic data, we measured relative variation of isobaric specific heat c_P in detail by using an optical ac calorimeter (Sinku-Riko Inc, model ACC-VL1). The absolute values in c_P were calibrated by a conventional adiabatic calorimeter. Samples for the specific-heat measurements were cut from the crystals used for the ultrasonic measurements.

For ultrasonic measurements, the crystals were cut into parallelepipeds with (100) and (001) planes, and (110) and (001) planes. The dimensions of the samples are approximately $4\times4\times4$ mm^3. Ultrasonic measurements were performed with a homemade apparatus based on a phase comparison method.[18] Ultrasound in the frequency range between 10 and 50 MHz was generated and detected by $LiNbO_3$ transducers glued onto parallel surfaces of a sample. In the present measurements, the relative resolution of the sound velocity v was typically $\sim 10^{-6}$. The velocity v was converted to the elastic moduli by the relation of $C_{ii}=\rho v^2$ with mass density ρ. In Table II, we list the measured elastic moduli along with corresponding sound-propagating direction (q), polarization (u), and lattice strains (ε_i) induced by the sound wave. The measurements in a temperature range from 1.8 to 350 K were performed by using a ^{4}He cryostat. The measurements in each magnetic field were performed on cooling from well above T_c using a 16 T superconducting magnet system (Oxford Instruments).

III. SPECIFIC HEAT

The specific heat c_P divided by T^2 of $La_{2-x}Sr_xCuO_4$ is shown in Fig. 1 as a function of temperature. A change in c_P was observed around T_c. In order to estimate a superconductivity-induced change $\Delta c_P(T)$ in c_P, we utilized a similar method adopted by Schnelle *et al.*;[19] we fitted an expression of the total specific heat, which consists of a smooth background and a contribution from superconductivity, to the obtained data. In the present analysis we assumed the background specific heat c_P^N is expressed by a polynomial, which contains both the phonon and normal-electron contributions,

$$\frac{c_P^N}{T^2}=\sum_{k=-2}^{2} A_k T^k , \tag{1}$$

TABLE I. Estimated values of x, T_c, $\Delta c_P(T_c)/T_c$, $\Delta C_{ii}(T_c)$, and $\Delta C_{ii}(0)$ for $x=0.09$, 0.14, and 0.19. Uniaxial strain and pressure dependence are calculated from the jump $\Delta c_P(T_c)/T_c$ and $\Delta C_{ii}(T_c)$. Strain dependence of the superconducting condensation energy, $(1/\phi)d^2\phi/d\varepsilon_i^2$, is estimated from $\Delta C_{ii}(0)$.

x (nominal)	0.09	0.14	0.19
x (analyzed)	0.091(4)	0.138(3)	0.190(4)
T_c (K)	25.8	35.0	28.7
$\Delta c_P(T_c)/T_c$ (mJ/K^2 mol)	5.2(5)	9.6(5)	10.2(5)
$\Delta C_{11}(T_c)$ (10^{-2} GPa)	−0.7	−10.0	−4.5
$\Delta C_{33}(T_c)$ (10^{-2} GPa)	−6.5	−19.0	−9.5
$\Delta C_{11}(0)$ (10^{-2} GPa)	+2.7	+32.0	+6.2
$\Delta C_{33}(0)$ (10^{-2} GPa)	−2.1	+17.0	+6.2
$d\ln T_c/d\varepsilon_{ab}$	−11	−22	−17
$d\ln T_c/d\varepsilon_c$	+33	+30	+25
dT_c/dP_{ab} (K/GPa)	+3.2	+3.8	+2.9
dT_c/dP_c (K/GPa)	−6.6	−6.5	−5.4
$(1/\phi)d^2\phi/d\varepsilon_{ab}^2$	−3600	−12000	−3400
$(1/\phi)d^2\phi/d\varepsilon_c^2$	+2800[a]	−6600	−3400
A (for C_{11})	−1500	−3600	−400
A (for C_{33})	+2600	+300	+1200

[a]Slight ambiguity remains on the sign because of the uncertainty of the choice of the background elastic constant.

TABLE II. Elastic moduli in the tetragonal lattice. Propagating direction q and polarization u of the corresponding ultrasound for the measurement of the elastic moduli are shown together with the elastic strain and its symmetry.

Elastic moduli	Propagating direction	Polarization	Strain	Symmetry Γ
C_{11}	$q\parallel[100]$	$u\parallel[100]$	ε_{xx}	$A_{1g}+B_{1g}$
C_{33}	$q\parallel[001]$	$u\parallel[001]$	ε_{zz}	A_{1g}
$(C_{11}-C_{12})/2$	$q\parallel[110]$	$u\parallel[1\bar{1}0]$	$\varepsilon_{xx}-\varepsilon_{yy}$	B_{1g}
C_{66}	$q\parallel[100]$	$u\parallel[010]$	ε_{xy}	B_{2g}
C_{44}	$q\parallel[001]$	$u\parallel[100]$	ε_{yz}, ε_{zx}	E_g

where A_k are fitting parameters listed in Table III. The mean-field contribution from superconductivity was approximated by a two-fluid model:[20]

$$\Delta c_P(T) = -\frac{\Delta c_P(T_c)}{2}\frac{T}{T_c}\left[1-\frac{3T^2}{T_c^2}\right] . \tag{2}$$

This choice of the model is just for simplification of the analysis, but our final conclusion does not depend critically on the model. The parameters A_k and the magnitude of the jump $\Delta c_P(T_c)$ were adjusted so as to fit our experimental data. The transition temperature T_c was estimated by an entropy balance so that the area-conserving rule is satisfied. The obtained background is represented by broken lines in Fig. 1. In Fig. 2, we show the difference $\Delta c_P/T$ after subtracting the background.

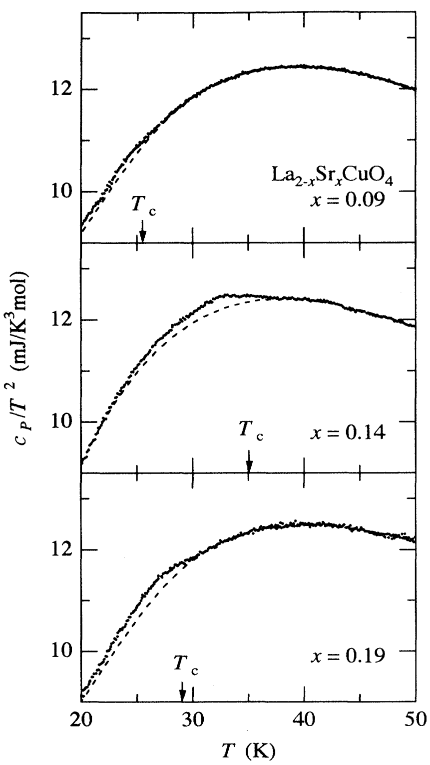

FIG. 1. Temperature dependence of the specific heat c_p over T^2 of $La_{2-x}Sr_xCuO_4$. The broken lines represent an estimated normal-state background.

The solid lines represent an estimated mean-field contribution. The values of T_c and $\Delta c_P(T_c)/T_c$ are summarized in Table I. The magnitude of $\Delta c_P(T_c)/T_c$ is comparable to that of powder samples,[21,22] suggesting the volume fractions of superconductivity of our samples are 60–70 %.

IV. ELASTIC MODULI

A. Elastic anomalies around the structural phase transition

In Figs. 3 and 4 we show an overall temperature dependence of various elastic moduli in $La_{2-x}Sr_xCuO_4$ with $x=0.09$, 0.14, and 0.19. The most remarkable feature in the longitudinal modes is a large softening in C_{11} around the temperature as indicated by arrows in Fig. 3. This softening is due to the structural phase transition from the THT to the OMT phase at a transition temperature of T_d. An anomaly is also seen in C_{33} around T_d. For the transverse modes, a softening of $\sim 70\%$ was observed in C_{66} above T_d as seen in Fig. 4. This softening was analyzed by a two-dimensional Gaussian model,[23] as proposed by Migliori *et al.*[24] The analysis allows us to determine T_d as ~ 300, ~ 200, and ~ 80 K for $x=0.09$, 0.14, and 0.19, respectively. Below T_d, measurements of C_{66} were prevented by heavy scattering of the sound wave of this particular mode by structural domain walls formed in the OMT phase. Changes in elastic moduli around T_d are also evident in $(C_{11}-C_{12})/2$ and C_{44} as seen from Fig. 4. Absolute values of the elastic moduli are listed in Table IV. Here, we employed the tetragonal representation for the elastic moduli even below T_d since the sample is in a pseudotetragonal lattice.

Phenomenological models of the structural phase transition have been discussed by many authors[13,14,25] for

TABLE III. Fitting parameters in Eqs. (1) and (2) for specific heat. Data between 20 and 50 K were used for the fitting.

x	0.09	0.14	0.19
$\Delta c_P(T_c)$ (mJ/K mol)	134	336	293
A_{-2} (mJ/K mol)	8906	4188	7556
A_{-1} (mJ/K^2 mol)	−1315	−801.8	−1125
A_0 (mJ/K^3 mol)	69.31	50.18	59.18
A_1 (mJ/K^4 mol)	−0.9245	−0.6282	−0.6993
A_2 (mJ/K^5 mol)	0.004647	0.002976	0.002949

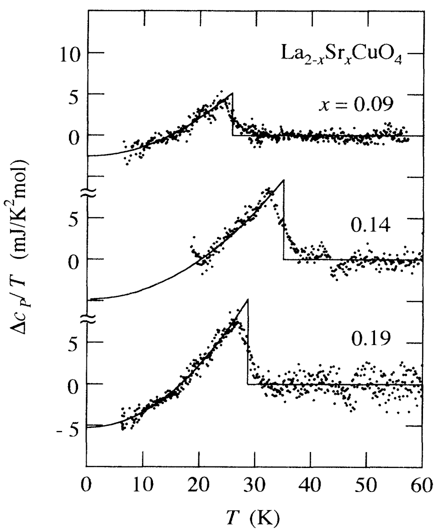

FIG. 2. Contribution of superconductivity to the specific heat c_P over T of $La_{2-x}Sr_xCuO_4$ after subtraction of the background. Solid lines represent a fit with the two-fluid model.

La-214 compounds within the framework of the Landau free energies. Using the results given in Ref. 25, we consider the coupling term between the order parameter and lattice strains in the Landau free energies,

$$F_C=\gamma_1(\varepsilon_{xx}+\varepsilon_{yy})(Q_1^2+Q_2^2)+\gamma_2\varepsilon_{zz}(Q_1^2+Q_2^2)+\gamma_3\varepsilon_{xy}(Q_1^2-Q_2^2)\ , \tag{3}$$

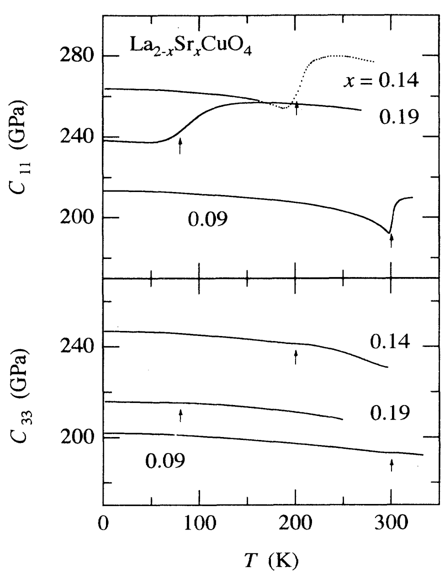

FIG. 3. Temperature dependence of the longitudinal elastic moduli C_{11} and C_{33} of $La_{2-x}Sr_xCuO_4$ measured by an ultrasound propagating along the a and c axes, respectively. The arrows indicate the THT-OMT structural phase transition temperature T_d.

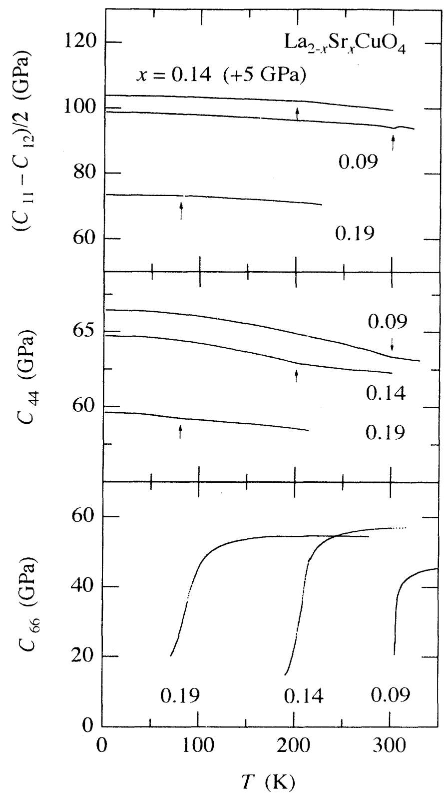

FIG. 4. Temperature dependence of the transverse elastic moduli $(C_{11}-C_{12})/2$, C_{44}, and C_{66} of $La_{2-x}Sr_xCuO_4$. Configuration of the measurements is shown in Table II. The arrows indicate the THT-OMT structural phase transition temperature T_d.

where Q_1 and Q_2 are the components of the order parameter and γ_j the coupling energies. The OMT phase is characterized by either $Q_1\neq 0$ and $Q_2=0$, or $Q_1=0$ and $Q_2\neq 0$, corresponding to the tilting of the CuO_6 octahedra around [110] or [1$\bar{1}$0] axes, respectively. The magnitudes of spontaneous strains which appear in the OMT phase, $\varepsilon_{xx}^S+\varepsilon_{yy}^S$, ε_{zz}^S, and ε_{xy}^S, depend linearly on the coupling energies γ_j in Eq. (3). C_{11}, C_{33}, and C_{66} are the susceptibilities to ε_{xx}, ε_{zz}, and ε_{xy}, respectively, because elastic moduli are second-order derivatives of free energy with respect to strain. The magnitude of softening of these elastic moduli at T_d depends quadratically on γ_j.[25]

TABLE IV. Elastic moduli for $La_{2-x}Sr_xCuO_4$ single crystals in GPa at 4.2 K. For C_{66}, values at highest temperature measured are shown since C_{66} was not measured below the structural phase transition temperature.

x	C_{11}	C_{33}	$(C_{11}-C_{12})/2$	C_{44}	C_{66}
0.09	213.4	202.0	98.7	59.6	54.4
0.14	263.8	246.8	98.8	66.4	66.4
0.19	238.1	238.1	73.4	64.7	64.7
0.14[a]	248	205	100	67.4	58.3

[a]See Ref. 24.

The significant softening observed in C_{11} and C_{66} suggests the first and last terms are dominant in Eq. (3). This is in accordance with the measurement of the lattice parameters in the OMT phase;[13,26] a significant expansion is observed in the ab plane (i.e., $\varepsilon_{xx}^S+\varepsilon_{yy}^S>0$) together with the orthorhombic distortion ($\varepsilon_{xy}^S\neq 0$). On the other hand, the c axis contracts slightly ($\varepsilon_{zz}^S<0$) in the OMT phase.[26] Anomalies are seen also in C_{44} and $(C_{11}-C_{12})/2$ at T_d suggesting that the higher-order coupling between the order parameter and the strains ε_{xz} and $\varepsilon_{xx}-\varepsilon_{yy}$ is not negligible.

The tilting of the CuO_6 octahedra induces both the orthorhombic distortion and the expansion of the ab plane. Correspondingly, both the bond angles and the bond lengths in the CuO_2 planes are modified. These changes are expected to alter the electronic states and correlations, and to affect superconductivity. A sound wave not only induces a uniform strain but also modifies the tilting of the CuO_6 octahedra via the coupling involved in Eq. (3). Hence, one can probe electronic states and superconductivity by measurements of elastic moduli.

B. Elastic moduli in the superconducting state

Our main data are displayed in Figs. 5–8. Figure 5 shows the low-temperature behavior of the elastic modulus C_{33} for the longitudinal sound wave propagating along the c axis in LSCO. In the normal state, C_{33} increases monotonically with decreasing temperature. In zero field, C_{33} exhibits a steplike decrease in the vicinity of T_c. The magnitude of the jump $\Delta C_{33}(T_c)/C_{33}$ ranges from 30 to 770 ppm depending on x. These values are comparable with those reported in polycrystalline samples of LSCO,[27] but are much larger than the observed values of several ppm in conventional superconductors. With further lowering temperature, we found quite unusual behavior; C_{33} of LSCO starts to increase in contrast with a continuous decrease observed in conventional superconductors.

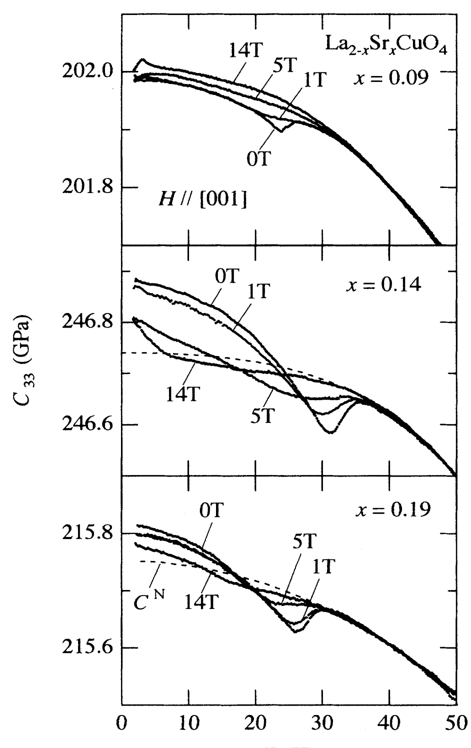

FIG. 5. Temperature dependence of the longitudinal elastic modulus C_{33} of $La_{2-x}Sr_xCuO_4$ in magnetic field $H\|c$. The broken lines are an estimated elastic modulus in the normal state.

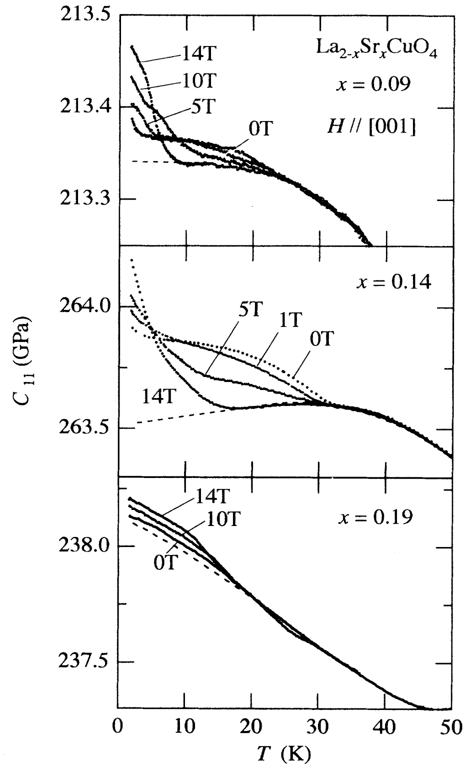

FIG. 6. Temperature dependence of the longitudinal elastic modulus C_{11} of $La_{2-x}Sr_xCuO_4$ in magnetic field $H\|c$. The broken lines are an estimated elastic modulus in the normal state.

We need to estimate a normal-state elastic modulus below T_c to determine the superconductivity-induced changes in elastic modulus. We applied magnetic field H along the c axis by which T_c is significantly lowered. In the normal state of LSCO with $x=0.14$ and 0.19, C_{33} varies as T^4 below about 60 K as we reported in Ref. 23. This T^4 dependence is ascribed to the phonon contribution. A T^2 contribution from normal electrons becomes important at lower temperatures.[28] Thus, the normal-state elastic modulus in the temperature range under consideration is expressed by

$$C^N=C_0+C_2T^2+C_4T^4 . \quad (4)$$

We estimated the constants C_0, C_2, and C_4 from the data taken in the magnetic field of 14 T applied along the c axis in which the normal state persists to the lowered T_c. The broken lines in Fig. 5 represent the estimated back-

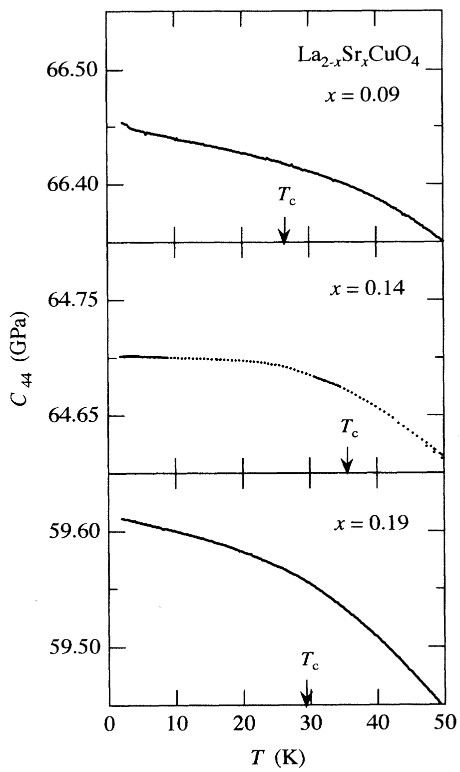

FIG. 7. Temperature dependence of the transverse elastic modulus C_{44} of $La_{2-x}Sr_xCuO_4$. No anomalies are visible around T_c.

grounds. For $x = 0.09$, the data at 14 T itself are used for background since the fit with Eq. (4) was not satisfactory. The superconductivity-induced change, $\Delta C_{33} = C_{33}(0T) - C^N$, is plotted in Fig. 9 as a function of temperature. Now it is clear that C_{33} exhibits negative jump at T_c and starts to increase at lower temperatures. We will discuss this anomalous temperature dependence of ΔC_{33} in Sec. V B.

In Fig. 6 we show the elastic modulus C_{11} for the longitudinal sound wave propagating along the [100] axis in LSCO under magnetic fields $H \| c$. For $x = 0.19$, a jump-like decrease is observed at T_c in the zero field. The jump at T_c is less obvious for $x = 0.09$ and 0.14, likely due to the effects of domain structure formed in the OMT phase.

It is not straightforward to estimate a normal-state background C^N of this mode because of a coupling between the ultrasound and flux lines (FL's) in the mixed state. A field-induced enhancement of C_{11} is obvious at low temperatures as seen in Fig. 6. This enhancement is attributed to the elastic modulus of the FL's. Since the displacement ($u \| [100]$) in the sound wave of the C_{11} mode is perpendicular to the FL's ($H \| [001]$) in this configuration, the sound wave compresses (and expands) the FL's which are rigidly pinned to the crystal lattice below the irreversibility temperature T^*. Consequently, the compressional modulus of the FL's is superposed on the elastic modulus of the crystal lattice.[29] The compressional modulus of the FL's, $\mu_0 H^2$, gives an enhancement of the elastic modulus of ~ 0.16 GPa for 14 T, consistent

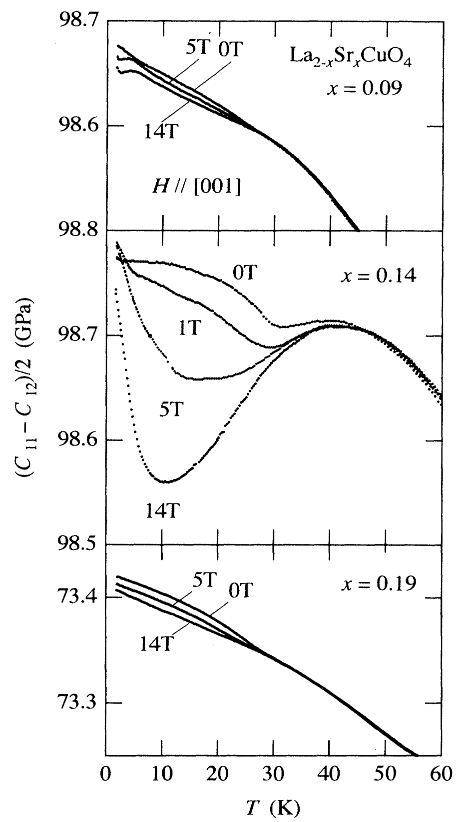

FIG. 8. Temperature dependence of the transverse elastic modulus $(C_{11} - C_{12})/2$ of $La_{2-x}Sr_xCuO_4$ in magnetic fields $H \| c$.

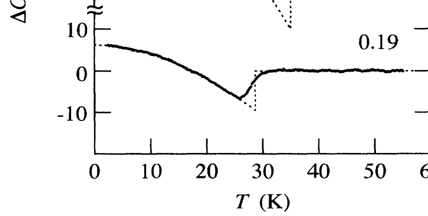

FIG. 9. The difference in the longitudinal elastic modulus C_{33} ($q \| c$) of $La_{2-x}Sr_xCuO_4$ between the normal and superconducting states as a function of temperature. The broken lines represent a fit with a thermodynamic model.

with the observation. A lack of such a field-induced enhancement in C_{33} under $H \| c$ is natural because $q \| H$ in the C_{33} mode and the sound wave does not deform the FL's.

The normal-state background C^N for $x = 0.09$ and 0.19 was estimated in the same manner as we applied for the analysis of C_{33}. The estimated C^N is shown in Fig. 6 by the broken lines. For $x = 0.14$, C_{11} exhibits slight softening below about 30 K in 14 T. Since we cannot apply Eq. (4) for an estimation of the background, C^N is assumed to follow an extrapolated curve shown by the broken line in Fig. 6. The superconductivity-induced changes $\Delta C_{11} = C_{11}(0T) - C^N$ are plotted in Fig. 10 as a function of the temperature. The lattice stiffens in the superconducting state.

Figure 7 show the elastic modulus C_{44} for the transverse sound wave propagating along the [001] direction with the [100] polarization for $x = 0.09$, 0.14, and 0.19. No appreciable changes are seen at T_c within the experimental resolution ($\Delta C_{ij}/C_{ij} \sim 10^{-6}$). This suggests that the shear strain ε_{zx}, which slides the CuO_2 planes relative to each other, scarcely couples with the superconducting state.

In Fig. 8, we show the variation with temperature of the elastic modulus $(C_{11} - C_{12})/2$ for the transverse sound wave propagating along the [110] direction with the $[1\bar{1}0]$ polarization (u). The most remarkable feature is that only for $x = 0.14$ $(C_{11} - C_{12})/2$ starts to soften at a temperature around 50 K, which is substantially higher than T_c, but shows a turn to a stiffening just below T_c. A corresponding softening was not observed for $x = 0.09$ and 0.19. Thus the softening in the normal state is seen in a narrow range of x around the optimum doping.

This is different from the behavior of the other elastic modes which show no corresponding anomaly above T_c (see Figs. 5–7). It is clear that $(C_{11} - C_{12})/2$ continues to soften as long as the sample is in the normal state under magnetic fields up to 14 T along the c axis, which reduce T_c from 35 to 14 K. Therefore, the softening is an intrinsic property of the lattice in the normal state. The rapid recovery of stiffness starting just below T_c indicates a disappearance of the lattice instability in the CuO_2 plane. Thus, there exists an interference between the lattice softening and superconductivity as we described in detail previously.[11] Aside from this unusual softening in the normal state, the lattice stiffening is also observed in this mode below T_c as is clear for $x = 0.09$ and 0.19.

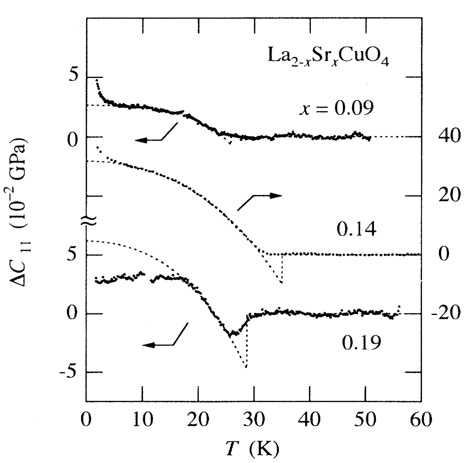

FIG. 10. The difference in the longitudinal elastic modulus C_{11} ($q \| a$) of $La_{2-x}Sr_xCuO_4$ between the normal and superconducting states as a function of temperature. The broken lines represent a fit with a thermodynamic model.

V. DISCUSSION

A. Thermodynamics of elastic moduli in the superconducting state

Opposite to the behavior of conventional superconductors, the lattice of LSCO stiffens in the superconducting state as presented in Sec. IV. How can one understand this difference? A number of calculations are available to describe the change in the elastic moduli in the superconducting state.[30] Generally, these results are restricted to a mean-field treatment within a temperature range close to T_c. In the following, we describe thermodynamic relations of elastic moduli applicable to all $T < T_c$, which we will apply to the analysis of C_{ij} of LSCO.

Let us first consider the relations for the longitudinal elastic moduli. The difference in the Helmholtz free energy F per volume between the superconducting and normal states can be written as

$$\Delta F = F_s - F_n = -\tfrac{1}{2}\mu_0 H_c^2 , \tag{5}$$

where H_c is the thermodynamic critical field. The temperature dependence of the difference in longitudinal elastic moduli, $\Delta C_{ii}(T)$, is thermodynamically given as a second-order derivative of the difference in the Helmholtz free energy with respect to strain ε_i:

$$\Delta C_{ii}(T) = -\mu_0 \left[H_c \frac{d^2 H_c}{d\varepsilon_i^2} + \left[\frac{dH_c}{d\varepsilon_i} \right]^2 \right] . \tag{6}$$

The details were discussed by Seraphim and Marcus[31] to explain $\Delta C_{ii}(T)$ of superconducting tantalum. Temperature dependence of $\Delta C_{ii}(T)$ is represented more clearly when the difference in the Helmholtz fee energy is expressed in the form of

$$\Delta F = -\phi(\varepsilon_i) f[T/T_c(\varepsilon_i)] . \tag{7}$$

Here f is a function of T/T_c normalized as $f(0) = 1$ and $f(1) = 0$, $\phi = (\frac{1}{2})\mu_0 H_c^2(0)$ is a superconducting condensation energy at $T = 0$, and only ϕ and T_c depend on the lattice strains ε_i. The function f may be expressed by the BCS scaling, a two-fluid model, or other models, but the form of f is assumed to be independent of ε_i. Irrespective of the form of f, the difference in the longitudinal elastic modulus in Eq. (6) is rewritten as[32]

$$\Delta C_{ii}(T) = -\left[\frac{d\ln T_c}{d\varepsilon_i}\right]^2 \frac{T\Delta c_p(T)}{V_{\rm mol}} + AT\Delta s(T) + \frac{1}{\phi}\frac{d^2\phi}{d\varepsilon_i^2}\Delta F(T) , \quad (8)$$

with

$$A = \frac{d^2 \ln T_c}{d\varepsilon_i^2} + 2\frac{d\ln T_c}{d\varepsilon_i}\frac{d\ln\phi}{d\varepsilon_i} - \left[\frac{d\ln T_c}{d\varepsilon_i}\right]^2 . \quad (9)$$

Here $\Delta c_P / V_{\rm mol}$ and Δs are the differences of specific heat and entropy per volume, respectively. We used the molar volume $V_{\rm mol} = 5.73$, 5.71, and 5.70×10^{-5} m^3/mol for $x = 0.09$, 0.14, and 0.19, respectively, based on the x-ray diffraction data near T_c. Equation (8) reduces to the Ehrenfest relation for $T = T_c$:

$$\left[\frac{dT_c}{d\varepsilon_i}\right]^2 = -\frac{V_{\rm mol} T_c \Delta C_{ii}(T_c)}{\Delta c_p(T_c)} . \quad (10)$$

The mean-field contribution gives a negative jump in C_{ii} at T_c as shown schematically in Fig. 11 because the jump Δc_P in specific heat at T_c is always positive. At lower temperatures, the last term in Eq. (8) becomes dominant. The difference at $T = 0$ is related to the second-order strain dependence $\Delta C_{ii}(0) = d^2\phi/d\varepsilon_i^2$. Thus, whether the lattice softens or stiffens in the superconducting state predominantly depends on the sign of $d^2\phi/d\varepsilon_i^2$. The negative value of $d^2\phi/d\varepsilon_i^2$ leads to a net stiffening, $C_{ii}(0) > C^N(0)$.

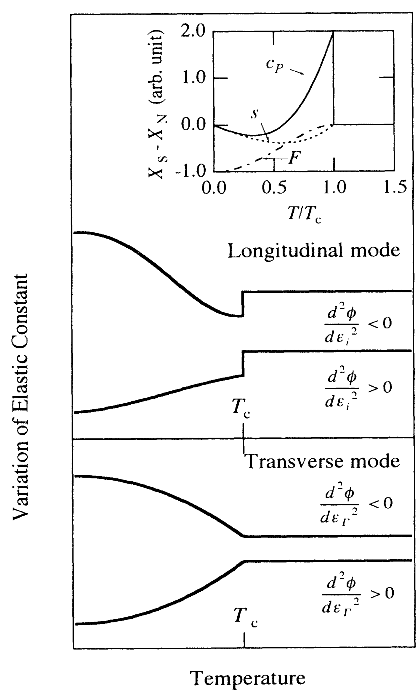

FIG. 11. Schematics of a variation of elastic moduli in the superconducting state. The longitudinal elastic moduli exhibit hardening below T_c when the second-order derivative $d^2\phi/d\varepsilon_i^2$ is negative, following the discontinuous jump at T_c. No jump is seen at T_c in the transverse elastic moduli. The inset shows variations of the Helmholtz free energy F, entropy s, and specific heat c_P in the superconducting state.

Next, the relations are somewhat modified for pure transverse elastic moduli C_Γ, linear response to shear strain ε_Γ with symmetry Γ. The first-order derivatives of T_c and ϕ with respect to ε_Γ vanish in Eqs. (8) and (9) since $+\varepsilon_\Gamma$ and $-\varepsilon_\Gamma$ give the same energy state. The difference in C_Γ between the superconducting and normal states is given by

$$\Delta C_\Gamma(T) = \frac{1}{T_c}\frac{d^2 T_c}{d\varepsilon_\Gamma^2} T\Delta s(T) + \frac{1}{\phi}\frac{d^2\phi}{d\varepsilon_\Gamma^2}\Delta F(T) . \quad (11)$$

At T_c, transverse elastic moduli exhibit no jump but a discontinuous change in the slope dC_Γ/dT, which corresponds to Δc_P ($\propto T\partial\Delta s/\partial T$):

$$\left.\frac{dC_\Gamma}{dT}\right|_{T_c^+} - \left.\frac{dC_\Gamma}{dT}\right|_{T_c^-} = -\frac{\Delta c_P(T_c)}{V_{\rm mol} T_c}\left[\frac{d^2 T_c}{d\varepsilon_\Gamma^2} + \cdots\right] . \quad (12)$$

Generally, $d^2\phi/d\varepsilon_\Gamma^2$ and $d^2T_c/d\varepsilon_\Gamma^2$ have the same sign since $\phi = (\frac{1}{8})T_c^2(\Delta c_P(T_c)/T_c)$ and $\Delta c_P(T_c)/T_c$ depend little on ε_Γ. Therefore, lattice stiffening is expected if $d^2\phi/d\varepsilon_\Gamma^2$ is negative.

B. Lattice stiffening in the superconducting state

In order to obtain a specific temperature dependence for elastic moduli in the superconducting state, we take a two-fluid form for the Helmholtz free energy in Eq. (7):

$$f = [1 - T^2/T_c^2(\varepsilon_i)]^2 . \quad (13)$$

We performed a least-squares fit to determine the coefficients in each term in Eq. (8) for C_{11} and C_{33} noticing that $\Delta C_{ii}(T_c) = -(dT_c/d\varepsilon_i)^2 \Delta c_P(T_c)/T_c V_{\rm mol}$, A and $\Delta C_{ii}(0) = -d^2\phi/d\varepsilon_i^2$. The broken lines shown in Figs. 10 and 9 represent a fit with Eq. (8). It shows good agreement with the experimental data except for the region of the transition width. The estimated parameters are listed in Table I.

As we have emphasized, the most remarkable feature is the unusual stiffening in the superconducting state. Furthermore, there exist indications that such a stiffening is common to the high-T_c superconductors. A similar stiffening has been reported for $YBa_2Cu_3O_{6+y}$,[33] although the sample was polycrystalline. Ledbetter[34] has pointed out that in most of the high-T_c copper oxides, T_c increases as the Debye frequency increases. This correlation suggests that lattice stiffening is preferable for high-T_c superconductivity. The different sign of $d^2\phi/d\varepsilon_i^2$ indicates that the copper oxides form a class of superconductors which involves different coupling between the lattice and electrons from that in conventional superconductors.

The second feature of interest is the magnitude of the stiffening $\Delta C_{ii}(0)$. $\Delta C_{ii}(0)$ for LSCO is much larger than those in conventional superconductors. For instance, $\Delta C_{33}(0)/C_{33} \approx 0.8 \times 10^{-3}$ for LSCO with $x = 0.14$ while $10^{-5}-10^{-6}$ for conventional superconductors. This indicates the phonons in LSCO are strongly affected by the change in the electronic state. Kresin[35] has pointed out the importance of the parameter $\Delta(0)/E_F$, the gap energy divided by the Fermi energy. An analysis of the phonon self-energy leads to the expression for change in the elastic moduli in the superconducting state;[36] $\Delta C_{ii}(0)/C_{ii} \sim \Delta(0)^2/E_F^2$. For the conventional superconductors, $\Delta \sim 1$ meV and $E_F = 5-10$ eV lead to the correction of elastic modulus $\Delta C_{ii}(0)/C_{ii} \sim 10^{-7}$. On the other hand, $\Delta(0)/E_F$ is much larger in the high-T_c cuprates since $\Delta \sim 10$ meV and $E_F = 0.1-1$ eV, which leads to $\Delta C_{ii}(0)/C_{ii} = 10^{-2}-10^{-4}$, consistent with our observation.

C. Uniaxial strain dependence of T_c

We determined strain dependence of T_c from the jump in elastic moduli and specific heat at T_c using Eq. (10) as summarized in Table I. From elastic moduli, however, one can only determine the magnitude of $dT_c/d\varepsilon_i$. The sign of $dT_c/d\varepsilon_i$ must be determined consistently with other experiments. The strain dependence is related to the uniaxial pressure (P_i) dependence of T_c by the following formula:

$$\frac{dT_c}{d\varepsilon_i} = -\sum_j C_{ij} \frac{dT_c}{dP_j} . \tag{14}$$

Schnelle *et al.*[19] obtained $dT_c/dP_{ab} = +6.2$ K/GPa and $dT_c/dP_c = -6.7$ K/GPa for $La_{1.88}Sr_{0.12}CuO_4$ from a thermal-expansion measurement. Maeno *et al.*[37] reported $dT_c/dP_{ab} = +3$ K/GPa and $dT_c/dP_c = -2$ K/GPa from a thermal-expansion measurement for the same sample of $La_{1.86}Sr_{0.14}CuO_4$ that is used in the present work. A recent thermal-expansion measurement by Gugenberger *et al.*[38] gives $dT_c/dP_a = +2.5$ K/GPa, $dT_c/dP_b = +4.9$ K/GPa, and $dT_c/dP_c = -6.8$ K/GPa for $x = 0.15$. The signs of the pressure dependencies of T_c are opposite along the *a* and *c* axes, while the magnitude differs slightly. We obtained dT_c/dP_i using C_{ij} reported in Ref. 24 as listed in Table I. The obtained magnitude is in the same order with the reported values, suggesting the validity of our estimate of the jump $\Delta C_{ii}(T_c)$.

In LSCO, both $dT_c/d\varepsilon_a$ and $dT_c/d\varepsilon_c$ depend only weakly on *x* and hence on the carrier concentration as seen in Fig. 12. Results from the recent data[38] are shown together. In many oxide superconductors, the sign of the strain dependence of T_c depends on the carrier concentration *p* and where it is placed on the bell-shaped T_c-p curve. This is because one of the dominant effects of the strain is a charge redistribution from the blocking layers to the CuO_2 planes predominantly due to the contraction of the *c* axis.[39] This scenario successfully explains the pressure dependence of T_c for $YBa_2Cu_3O_{6+y}$, in which $dT_c/d\varepsilon_c$ is negative for the underdoped samples and is ~ 0 for the samples with optimized T_c.[40,41] In contrast, positive values of $dT_c/d\varepsilon_c$ regardless of doping *x* in LSCO suggest an importance of other effects than the charge redistribution.

The strain dependence of T_c in LSCO is possibly dominated by a coupling between strains and tilting of the CuO_6 octahedra. Yamada and Ido[42] claimed from thermal-expansion measurements under hydrostatic pressure that T_c increases when the tilting of the CuO_6 octahedra is reduced. The reduction of the tilting accompanies a contraction of the *ab* plane ($\varepsilon_{ab} < 0$) and an expansion of the *c* axis ($\varepsilon_c > 0$) as we discussed in Sec. IV A. Therefore, $dT_c/d\varepsilon_{ab} < 0$ and $dT_c/d\varepsilon_c > 0$ obtained in this study support the dependence of T_c on the tilting. The coupling between the tilting of the CuO_6 octahedra and superconductivity is also suggested by neutron and thermal-expansion measurements in $La_{1.87}Sr_{0.13}CuO_4$ (Ref. 26). According to a band calculation,[43] the tilting about the [110] axis causes little change in the electronic structure around the Fermi level; however, it is plausible that a change in Cu-O bond angles and lengths by the tilting alters the electronic correlations and changes T_c.

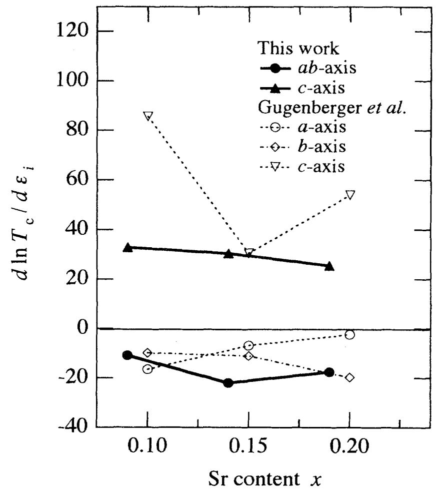

FIG. 12. Anisotropic strain dependencies $d\ln T_c/d\varepsilon_i$ ($i = ab$ and c) calculated from $\Delta C_{ii}(T_c)$ and $\Delta c_p(T_c)$ via the Ehrenfest relation. For comparison we show the $d\ln T_c/d\varepsilon_i$ estimated from Ref. 38.

VI. CONCLUSIONS

The high quality single crystals, high-resolution sound-velocity measurements, and strong magnetic fields allowed us to explore the peculiar features in the elastic properties of $La_{2-x}Sr_xCuO_4$. We measured both the elastic moduli and specific heat for $x = 0.09$, 0.14, and 0.19. From the jumplike decrease in the longitudinal elastic moduli C_{33} and C_{11} and the specific-heat jump at T_c, we estimated the anisotropic strain dependence of T_c. The values of $dT_c/d\varepsilon_i$ ($i = ab$ and c) are almost independent of the doping *x*. This suggests that the charge transfer from the blocking layers to the CuO_2 planes is not the origin of the strain dependence of T_c. The opposite signs of $dT_c/d\varepsilon_{ab}$ and $dT_c/d\varepsilon_c$ are attributed to the tilting of the CuO_6 octahedra induced by the lattice strains ε_i.

Thermodynamic analysis was developed to explain the temperature dependence of the elastic moduli of superconducting LSCO. The anomalous increase of the elastic moduli at low temperatures is ascribed to the strain dependence of the superconducting condensation energy ϕ; $d^2\phi/d\varepsilon_i^2$ is negative in LSCO while positive in most of the conventional superconductors. Understanding of the physical implication of these second-order derivatives may involve a proper treatment of lattice inharmonicity. Although the microscopic origin of the lattice stiffening in the superconducting state still remains to be investigated, we believe this finding provides an important key for the mechanism of high-T_c superconductivity.

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[1] G. A. Alers and D. L. Waldorf, Phys. Rev. Lett. **6**, 677 (1961).

[2] S. M. Shapiro, G. Shirane, and J. D. Axe, Phys. Rev. B **12**, 4899 (1975).

[3] H. G. Schuster, Solid State Commun. **13**, 1559 (1973).

[4] C. Thomsen, M. Cardona, B. Friedl, C. O. Rodriguez, I. I. Mazin, and O. K. Andersen, Solid State Commun. **75**, 219 (1990).

[5] R. Zeyher and G. Zwicknagl, Z. Phys. B **78**, 175 (1990).

[6] B. Normand, H. Kohno, and H. Fukuyama (unpublished).

[7] A. P. Litvinchuk, C. Thomsen, and M. Cardona, Solid State Commun. **83**, 343 (1992).

[8] L. E. Rehn, R. P. Sharma, and P. M. Baldo, in *Lattice Effects in High-T_c Superconductors,* edited by Y. Bar-Yam, T. Egami, J. Mustre-de Leon, and A. R. Bishop (World Scientific, Singapore, 1992), p. 27; K. Yamaya, T. Haga, and Y. Abe, *ibid.*, p. 33; A. Bianconi, S. Della Longa, M. Missori, I. Pettiti, and M. Pompa, *ibid.*, p. 65; S. J. L. Billinge and T. Egami, *ibid.*, p. 105.

[9] B. H. Toby, T. Egami, J. D. Jorgensen, and M. A. Subramanian, Phys. Rev. Lett. **64**, 2414 (1990).

[10] M. Arai, K. Yamada, Y. Hidaka, S. Itoh, Z. A. Bowden, A. D. Taylor, and Y. Endoh, Phys. Rev. Lett. **69**, 359 (1992).

[11] M. Nohara, T. Suzuki, Y. Maeno, T. Fujita, I. Tanaka, and H. Kojima, Phys. Rev. Lett. **70**, 3447 (1993).

[12] A. R. Moodenbaugh, Y. Xu, M. Suenaga, T. J. Folkerts, and R. N. Shelton, Phys. Rev. B **38**, 4596 (1988).

[13] T. Suzuki and T. Fujita, Physica C **159**, 111 (1989).

[14] J. D. Axe, A. H. Moudden, D. Hohlwein, D. E. Cox, K. M. Mohanty, A. R. Moodenbaugh, and Y. Xu, Phys. Rev. Lett. **62**, 2751 (1989).

[15] M. K. Crawford, R. L. Harlow, E. M. McCarron, W. E. Farneth, J. D. Axe, H. Chou, and Q. Huang, Phys. Rev. B **44**, 7749 (1991).

[16] Y. Maeno, N. Kakehi, M. Kato, and T. Fujita, Phys. Rev. B **44**, 7753 (1991).

[17] I. Tanaka and H. Kojima, Nature (London) **337**, 21 (1989); I. Tanaka, K. Yamane, and H. Kojima, J. Cryst. Growth **96**, 711 (1989).

[18] T. J. Moran and B. Lüthi, Phys. Rev. **187**, 710 (1969); T. Goto, T. Suzuki, A. Tamaki, Y. Ohe, S. Nakamura, and T. Fujimura, *The Bulletin of the Research Institute for Scientific Measurement* (Tohoku University, Sendai, Japan, 1989), Vol. 38, p. 65.

[19] W. Schnelle, O. Hoffels, E. Braun, H. Broicher, and D. Wohlleben, in *Physics and Materials Science of High Temperature Superconductors II, Vol. 209 of NATO Advanced Study Institute, Series E,* edited by R. Kossowsky, B. Raveau, D. Wohlleben, and S. Patapis (Kluwer Academic, Dordrecht, 1992), p. 151.

[20] Equation (2) is derived from the Helmholtz free energy given in Eq. (7) assuming its temperature dependence to Eq. (13).

[21] N. Wada, T. Obana, Y. Nakamura, and K. Kumagai, Physica B **165 & 166**, 1341 (1990).

[22] A. Amato, R. A. Fisher, N. E. Phillips, and J. B. Torrance, Physica B **165&166**, 1337 (1990).

[23] M. Nohara, T. Suzuki, Y. Maeno, T. Fujita, I. Tanaka, and H. Kojima, in *The Physics and Chemistry of Oxide Superconductors,* edited by Y. Iye and H. Yasuoka (Springer-Verlag, Berlin, 1992), p. 213.

[24] A. Migliori, W. M. Visscher, S. Wong, S. E. Brown, I. Tanaka, H. Kojima, and P. B. Allen, Phys. Rev. Lett. **64**, 2458 (1990).

[25] Wu Ting, K. Fossheim, and T. Lægreid, Solid State Commun. **75**, 727 (1990).

[26] M. Braden, O. Hoffels, W. Schnelle, B. Büchner, G. Heger, B. Hennion, I. Tanaka, and H. Kojima, Phys. Rev. B **47**, 12 288 (1993).

[27] Y. Horie, Y. Terashi, T. Fukami, and S. Mase, Physica C **166**, 87 (1990).

[28] G. A. Alers, in *Physical Acoustics,* edited by W. P. Mason (Academic, New York, 1966), Vol. 4A, p. 277.

[29] P. Lemmens, P. Fröning, S. Ewert, J. Pankert, G. Marbach, and A. Comberg, Physica C **174**, 289 (1991).

[30] For example, D. Shoenberg, in *Superconductivity* (Cambridge Univ. Press, New York, 1952), p. 75; L. R. Testardi, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. X, p. 193.

[31] D. P. Seraphim and P. M. Marcus, IBM J. Res. Dev. **6**, 94 (1962).

[32] L. R. Testardi, Phys. Rev. B **12**, 3849 (1975).

[33] For a review, see M. Levy, M. -F. Xu, B. K. Sarma, and K. J. Sun, in *Physical Acoustics,* edited by M. Levy (Academic, New York, 1992), Vol. XX, p. 237.

[34] H. Ledbetter, Physica C **235-240**, 1325 (1994).

[35] V. Z. Kresin, in *Physical Acoustics* (Ref. 33), Vol. XX, p. 435.

[36] J. Bardeen and M. Stephen, Phys. Rev. **136**, 1485 (1964).

[37] Y. Maeno, S. Nakayama, M. Irie, Y. Tanaka, S. Nishizaki, M. Nohara, Y. Omori, Y. Kitano, and T. Fujita, in *Advances in Superconductivity VI,* edited by T. Fujita and Y. Shiohara (Springer-Verlag, Berlin, 1994), Vol. 1, p. 103.

[38] Frank Gugenberger, Christoph Meingast, Georg Roth, Kai

Grube, Volker Breit, Thomas Weber, Helmut Wühl, S. Uchida, and Y. Nakamura, Phys. Rev. B **49**, 13 137 (1994).
[39]C. Murayama, Y. Iye, T. Enomoto, N. Môri, Y. Yamada, T. Matsumoto, Y. Kubo, Y. Shimakawa, and T. Manako, Physica C **183**, 277 (1991).
[40]U. Welp, M. Grimsditch, S. Fleshler, W. Nessler, J. Downey, G. W. Crabtree, and J. Guimpel, Phys. Rev. Lett. **69**, 2130 (1992).
[41]O. Kraut, C. Meingast, G. Bräuchle, H. Claus, A. Erb, G. Müller-Vogt, and H. Wühl, Physica C **205**, 139 (1993).
[42]N. Yamada and M. Ido, Physica C **203**, 240 (1992).
[43]R. E. Cohen, W. E. Pickett, D. Papaconstantopoulos, and H. Krakauer, in *Lattice Effects in High-T_c Superconductors* (Ref. 8), p. 223.