Complete Elastic Constants and Giant Softening of c_{66} in Superconducting $La_{1.86}Sr_{0.14}CuO_4$

A. Migliori, William M. Visscher, and S. Wong
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

S. E. Brown
Department of Physics, University of Florida, Gainesville, Florida 32611

I. Tanaka and H. Kojima
Faculty of Engineering, Yamanashi University, Kofu 400, Japan

P. B. Allen
Department of Physics, State University of New York, Stony Brook, Stony Brook, New York 11794
(Received 29 January 1990)

A novel resonant ultrasound technique is used to measure all elastic constants and their temperature dependence in single-crystal $La_{1.86}Sr_{0.14}CuO_4$. The in-plane shear modulus c_{66} drops by nearly half upon cooling to 227 K, an effect attributed to order-parameter fluctuations (of 2D Gaussian character) near the tetragonal-orthorhombic phase boundary. Implications for current models of the structural phase transition are discussed, as well as the effect of domains in the low-temperature orthorhombic state.

PACS numbers: 74.70.Vy, 43.35.+d, 62.65.+k

The rich assortment of phases found in $La_{2-x}M_xCuO_4$ includes superconducting, magnetic, and structurally distorted materials. The relation between magnetic and superconducting phases is a critical issue that continues to attract attention.[1] A relation between the tetragonal-orthorhombic (TO) structural phase transition (SPT) and high-T_c superconductivity seemed less compelling until the recent work by Axe *et al.*[2] showed that a rearrangement of the structural distortion can destroy superconductivity. Here we report a surprisingly large elastic anomaly at the same SPT.

Studies on polycrystals[3,4] indicate that all the elastic moduli and their temperature dependences are important for modeling both the superconducting transition at T_c and the SPT at T_{TO} in La_2CuO_4. Bhattacharya *et al.*[4] found a break in slope of the shear-wave speed at T_c in sintered powders of $La_{1.85}Sr_{0.15}CuO_4$. Complicating the issue was the observation of similar behavior[5] at the same temperature in nonsuperconducting single-crystal La_2CuO_4 and features in the thermal expansion of nonsuperconducting polycrystal.[6] At higher temperatures, both shear and longitudinal velocities of the sintered superconductor exhibited an extremely large softening[7] ($\sim$15% near 200 K), in contrast to the weak temperature dependence of the insulator. This unusual softening could not be attributed unambiguously to the development of the tetragonal-orthorhombic SPT.[8] This Letter resolves some of these issues by reporting high-resolution measurements of all c_{ij} in a single-crystal sample of $La_{1.86}Sr_{0.14}CuO_4$. The measurements cover the temperature range 220–300 K, including T_{TO} (about 220 K in our sample). The most interesting feature observed is the monotonic and strong decrease of c_{66}. At 227 K, c_{66} has less than 60% of its room-temperature value, while the other c_{ij}'s show only small changes (c_{44} increases less than 0.8% over the same temperature range). We will show that the unusual elastic behavior can be understood from a Landau theory of the SPT.

The sample was prepared from a Cu-O flux using a traveling solvent floating-zone technique.[9] The crystal was aligned along the principal axes of the tetragonal cell and polished so the faces were parallel to within 1°, leaving a finished sample with dimensions $2.890\times2.816\times2.405$ mm^3 all ±0.01 mm, the shortest dimension corresponding to the tetragonal c axis. The density was measured to be 6.882 g/cm^3, consistent with the nominal strontium concentration. Although we do not study the superconducting transition here, our crystal had full shielding diamagnetism at 4 K and $B=10$ G and an onset temperature for superconductivity of 36 K in a field of 20 G, with a Meissner fraction of 6% for the c axis parallel to the field. Magnetization hysteresis loops evaluated at 5 K yielded critical currents of 10^5 A/cm^2. These measurements[10] indicate bulk superconductivity and good sample homogeneity.

The crystal was mounted into the resonant-ultrasound cell as shown in the inset of Fig. 1. Diametrically opposite corners contact two transducers that serve as driver and receiver. The transducer contact force is 10^4 dyn. The transducers have a lowest resonant frequency above 5 MHz, well above the range of frequencies we used, thereby ensuring that all resonances observed are associated with the sample.

An example of the output appears in Fig. 1. The amplitudes of resonances are influenced by mounting and corner imperfections. Therefore, only resonance frequencies f_i are used. The f_i, density, and dimensions of the sample overdetermine the shear moduli c_{44},c_{66}, enabling us to check for consistency. However, the four moduli c_{11},c_{22},c_{12},c_{23} are underdetermined by one constraint, which we take from the bulk-modulus data of Ledbetter *et al.*[6] In previous work on La_2CuO_4, where

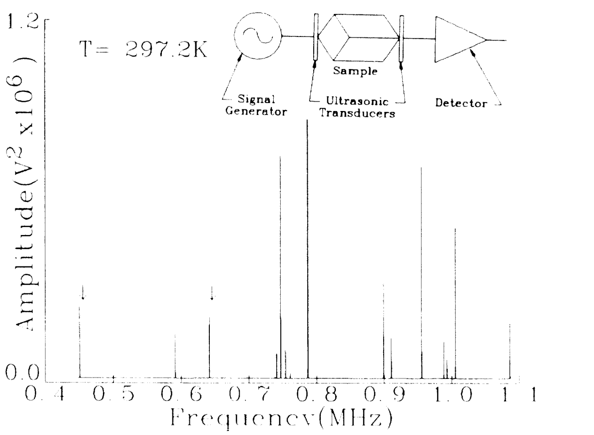

FIG. 1. Resonant response spectrum of the $La_{1.86}Sr_{0.14}CuO_4$ sample at 297 K. The two modes with behavior dominated by c_{66} are marked by arrows. Inset: The experimental configuration.

we did determine all nine moduli,[5] the bulk modulus agreed well with Ref. 6. Our data do show that the four moduli $c_{11}, c_{22}, c_{12}, c_{23}$ display only minimal temperature dependence, and a huge increase in the quantity of data taken would be required to provide the last constraint ourselves.

The data were analyzed using a method developed by Demarest[11] and Ohno.[12] Our modified procedure relies on minimizing the free-surface Lagrangian to obtain eigenfrequencies and eigenmodes in terms of c_{ij}. An optimization using simulated annealing[13] fits c_{ij} to measured f_i's, with an accuracy determined partly by dimensional errors. Results at ambient temperature are summarized in Table I. Because the crystal is tetragonal[14] (space group D_{4h}^{17}), there are six independent elastic constants, as opposed to the nine that are necessary to describe the elastic properties of orthorhombic La_2CuO_4 (space group D_{2h}^{18}). Compared to the latter, we and others[6,15] observe that Sr-doped materials are stiffer (after proper rotation of axes), contrary to the usual trend for charge carriers to soften elastic waves by screening. For reasons that will become clear later, we attribute the stiffening to the suppressed onset of the low-temperature orthorhombic phase in the doped material.

Several resonances exhibit a large softening with decreasing temperature below 300 K. Two of these, noted by the arrows in Fig. 1, drop to 60% of their 300-K values before a loss of signal causes them to be unobservable below 227 K. Analysis of these modes showed them to be dominated by the in-plane shear modulus c_{66}; the temperature dependence of c_{66} (essentially the same as for the mode at the upper arrow) is plotted in Fig. 2(a), and the associated increase in loss, plotted as the reciprocal of the quality factor Q of the mode at the upper arrow, is shown in Fig. 2(b). In Figs. 3(a) and 3(b) we show similar plots for the out-of-plane shear modulus c_{44}, a modulus that does not couple to the order parameter of the SPT. The insets in Figs. 2(a) and 3(a) show the deformations at resonance of the dominant eigenmode.

The tetragonal-orthorhombic SPT[1,16] at T_{TO} is described by a two-component order parameter (q_1, q_2), where (q_1, q_2) are the amplitudes of rotation of copper-oxygen octahedra around the [110] and [1$\bar{1}$0] axes, respectively. Higher-than-quadratic terms in (q_1, q_2) break 2D rotational symmetry in favor of the degenerate solutions $(q,0)$ (domains of type A) or $(0,q)$ (domains of type B). Heavily twinned mixtures of A and B are normally found below T_{TO}. Coupling to strains ϵ_{ij} occurs through terms of the type $q^2\epsilon$. After choosing a preferred direction for (q_1, q_2) and a single strain component, the Landau free energy has the form

$$F - F_0 = \tfrac{1}{2} a (T - T_{TO}) q^2 + \tfrac{1}{4} \beta q^4 + \tfrac{1}{2} c_{el} \epsilon^2 + \xi q^2 \epsilon \,. \quad (1)$$

The presence of a nonzero strain coupling coefficient ξ has four consequences at the level of mean-field theory. (1) The quartic coefficient β is renormalized to $\beta_{eff} = \beta - 2\xi^2/c_{el}$; (2) a spontaneous strain $\bar{\epsilon} = -\xi_a (T_{TO} - T)/\beta_{eff} c_{el}$ develops below T_{TO}; (3) the transition temperature T_{TO} is sensitive to externally applied strain: $\partial T_{TO}/\partial\epsilon = 2\xi/a$; (4) below T_{TO}, the elastic modulus c_{el} is renormalized,

$$c_{eff} = \begin{cases} c_{el}, & T > T_{TO}, \\ c_{el} - 2\xi^2/\beta, & T < T_{TO}. \end{cases} \quad (2)$$

This predicted step discontinuity in c_{el} is similar in origin (but opposite in sign) to the discontinuity $\Delta C_v = T_{TO} a^2 / 2\beta_{eff}$ of the specific heat C_v. When a complete treatment of elastic strains is made based on the Landau theory, the mean-field shift of the elastic-modulus tensor at the phase boundary is $\Delta c_{ij} = -2\xi_i \xi_j/\beta$. Because $\xi_1 = \xi_2$, c_{11} and c_{12} have the same shift and $c_{11} - c_{12}$ is unaffected, as well as c_{44} (because $\xi_4 = \xi_5 = 0$). These relations may be

TABLE I. Elastic constants for single-crystal La_2CuO_4 and $La_{1.86}Sr_{0.14}CuO_4$ at 297 K in 10^{12} dyn/cm^2. Absolute accuracies for the latter are dependent on Ref. 6 for $c_{11}, c_{33}, c_{23}, c_{12}$, while for c_{44}, c_{66} the accuracy is determined purely by our work and is $\pm 0.2\%$. Note that a rotation of axes is required for proper comparison of the tetragonal and orthorhombic moduli in the Cu-O plane.

	c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{31}	c_{12}	c_{23}	B[a]	B[b]
La_2CuO_4	1.72	1.71	2.00	0.656	0.658	0.968	0.73	0.90	0.73	1.13	1.15
$(La\text{-}Sr)_2CuO_4$	2.48		2.05	0.674		0.583		0.48	0.65		1.17

[a]Bulk modulus for a single crystal, Ref. 5. [b]Bulk modulus for sintered powder, Ref. 6.

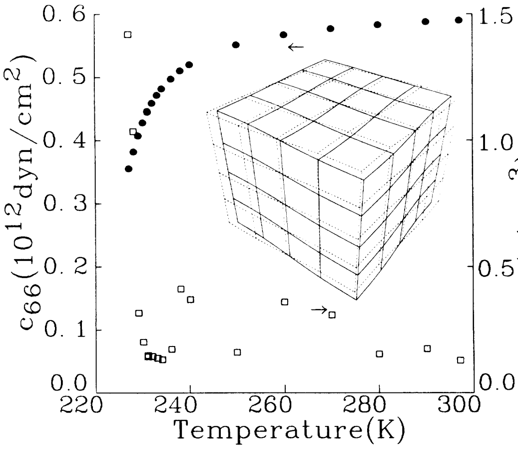

FIG. 2. c_{66} and reciprocal quality factor $(1/Q)$ vs temperature associated with the 640-kHz line marked in Fig. 1. Inset: The deformation for the 640-kHz eigenmode.

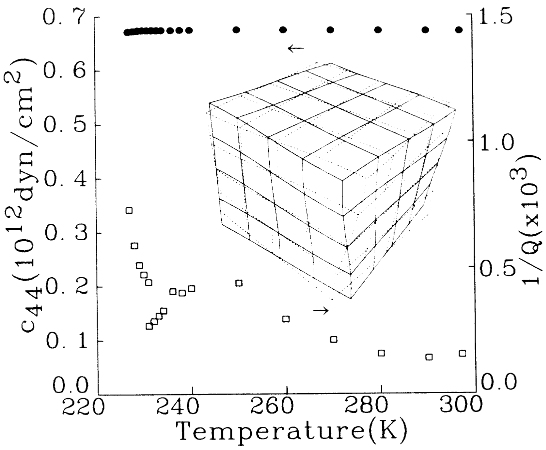

FIG. 3. c_{44} and reciprocal quality factor $(1/Q)$ vs temperature associated with the 591-kHz line of Fig. 1. Inset: The deformation for the 591-kHz eigenmode.

useful for semiquantitative estimates, but experiments show that mean-field behavior is strongly modified by fluctuations.

The leading effect of order-parameter fluctuations can be estimated by the usual Ginzburg-Gaussian approximation[17] (below $T_{\rm TO}$, a is replaced by $2a$)

$$F-F_0=\tfrac{1}{2}c_{\rm el}\epsilon^2-\tfrac{1}{2}k_BT\sum_{\mathbf{Q}}\ln\left(\frac{\pi k_BT}{a\,|T-T_{\rm TO}|+\Gamma_{\alpha\beta}Q_\alpha Q_\beta-2\xi\epsilon}\right), \tag{3}$$

where the tensor $\mathbf{\Gamma}$ is the coefficient of the gradient term in the Landau expansion, $\frac{1}{2}\Gamma_{\alpha\beta}\nabla_\alpha q\nabla_\beta q$. The expression $a\,|T_{\rm TO}-T|+\Gamma_{\alpha\beta}Q_\alpha Q_\beta$ has the interpretation $I\omega_Q^2$, where I is the moment of inertia and ω_Q is the harmonic frequency for the octahedron rotation, with Q measured from the $(\pi/a)(110)$ or X point of the Brillouin zone. Inelastic neutron scattering[18] has determined the temperature dependence of this frequency. The elastic modulus in the Gaussian approximation is

$$c_{\rm eff}=c_{\rm el}-2k_BT\sum_{\mathbf{Q}}\frac{\xi^2}{(a\,|T-T_{\rm TO}|+\Gamma_{\alpha\beta}Q_\alpha Q_\beta)^2}. \tag{4}$$

The sum over $\mathbf{Q}$ depends on the dimensionality of Γ. For example, if the dispersion is negligible in the $\hat{\mathbf{c}}$ direction, then the corresponding eigenvalue of Γ vanishes; there are thus two nonzero eigenvalues γ and the order-parameter fluctuations are two dimensional,

$$c_{\rm eff}-c_{\rm el}=-k_BT\xi^2d^2/2\pi\gamma a\,|T-T_{\rm TO}|\,, \tag{5}$$

where d is a characteristic lattice spacing. If there are three nonzero eigenvalues, the result is

$$c_{\rm eff}-c_{\rm el}=-k_BT\xi^2d^3/4\pi\gamma^{3/2}a^{1/2}\,|T-T_{\rm TO}|^{1/2}. \tag{6}$$

These formulas are completely parallel but opposite in sign to the Gaussian formulas for the specific heat.[17]

The Gaussian exponents $\frac{1}{2}$, 1 do not survive arbitrarily close to $T_{\rm TO}$. Instead, the predicted critical exponent β for a two-component order parameter in three dimensions is $\beta\approx 0.37$.[19] We do not yet have enough information to estimate the critical range; therefore we attempted to fit our data by

$$c_{66}(T)=c_{66}^0-A(T-T_{\rm TO})^{-\beta}, \tag{7}$$

where c_{66}^0 is the background elastic constant and $\beta=0.37$, 0.5, and 1.0.

Our best fit $(\beta=1)$ corresponding to 2D Gaussian fluctuations also required the least number of free parameters: i.e., c_{66}^0 is taken to be independent of temperature. The fit appears in Fig. 4 for the higher of the resonances highlighted by the arrows in Fig. 1. We were, however, able to obtain reasonable fits with $\beta=0.37$ (3D x-y model[17]) and $\beta=0.5$ (3D Gaussian). The fits with $\beta=0.37$ and $\beta=0.5$ required an additional free parameter: c_{66}^0 must be temperature dependent. By itself, that is not unreasonable, but the required dependences for exponents other than unity were very large, stiffening nearly 3% on cooling from 300 to 227 K for both cases, unlike the trend for c_{44}, an elastic constant uncoupled to the order parameter.

As shown in Fig. 2, the drop in c_{66} is accompanied by a large drop in the quality factor Q of associated resonances. Even though our fits yield a transition temperature of ~223 K, we were unable to measure the resonances that determine c_{66} below 227 K because of the loss of signal. This increase in loss is typical of relaxation effects, and therefore we do not expect the large softening of c_{66} to show up in neutron-scattering studies[18] because such studies probe at frequencies higher than the probable relaxation rates. We refrain from a relaxational analysis, because it is clear from Fig. 3(b)

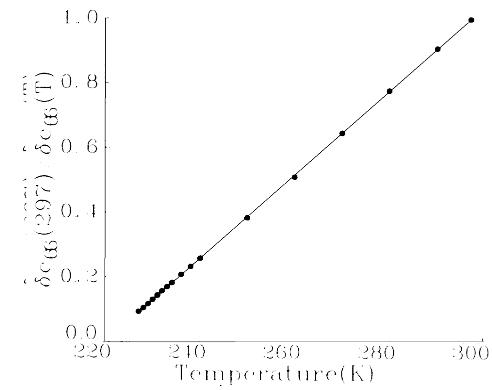

FIG. 4. $\delta c_{66}(297)/\delta c_{66}(T)$ vs temperature, where $\delta c_{66}(T)$ is defined as $c_{66}^0 - c_{66}(T)$. c_{66}^0 is the background elastic constant that we have chosen to give the best fit with a straight line (solid curve).

that above 235 K, other mechanisms dominate the acoustic loss, and we were unable to get close enough to the T_{TO} to measure the transition-induced loss peak.

The low-temperature phase also exhibits high ultrasound attenuation, with Q's similar to those observed in La_2CuO_4 below T_{TO}, and nearly 2 orders of magnitude lower than at 300 K. We believe that this is attributable to the formation of domain walls (twin boundaries) between the two types of domains (each domain has two possible "phases") allowed by the two-component order parameter. Strong acoustic coupling to domains produces losses associated with the motion of the walls. We believe that the motion of these domain walls is the dominant mechanism for ultrasonic losses in the orthorhombic state and leads to the greater intrinsic attenuation in La_2CuO_4 at ambient temperatures.

Recent measurements in polycrystalline bars of $La_{2-x}Sr_xCuO_4$ for $x=0.05$, 0.10, 0.15, and 0.25 by Lee, Lew, and Nowick[20] also display large (40%) softenings of Young's modulus E (which is mostly shear) between T_{TO} and $T_{TO}+100$ K. Lee, Lew, and Nowick were unable to attribute the softening to any particular elastic modulus of course, but they guess correctly that c_{66} is responsible. Although they produce no absolute numbers, they are able to track E below T_{TO} into the orthorhombic phase. They find that E does not restiffen below T_{TO} as would be expected based on a Landau theory. Based on this, they argue against coupling of strain to the order parameter of the TO transition, but propose instead that stress-induced domain-wall motion is responsible for the softening. However, their model cannot be correct above T_{TO} where no domain walls exist, but most of the softening occurs. Nevertheless, the Landau picture of fluctuating order parameter above T_{TO} merges naturally with the concept of moving domain walls below T_{TO} because a domain wall is a phase slip in the order parameter, and thus domain-wall motion is a phase fluctuation. Thus the model of Lee, Lew, and Nowick[20] below T_{TO} and our model above T_{TO} combine to produce a complete picture of the elastic behavior.

Our measurements of all elastic constants for the tetragonal phase of $La_{1.85}Sr_{0.15}CuO_4$ provide new information about the SPT, and doping. Doped material is stiffer than its undoped counterpart La_2CuO_4, and has lower ultrasonic attenuation in the tetragonal phase than in the orthorhombic phase, a conclusion presumably valid for the undoped material as well. We attribute differences in moduli primarily to the formation of the orthorhombic phase. Structural studies are planned to confirm the two-dimensional nature of the SPT, and explore the elastic moduli near the superconducting transition.

We thank J. D. Axe for discussions. The work at Los Alamos was performed under the auspices of the U.S. Department of Energy. The work of P.B.A. was supported in part by NSF Grant No. DMR 88-14311.

[1]See, for example, P. B. Allen, Z. Fisk, and A. Migliori, in *Physical Properties of High Temperature Superconductors*, edited by D. M. Ginsberg (World Scientific, Teaneck, NJ, 1989), p. 213.

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

[3]M. Lang *et al.*, Europhys. Lett. **4**, 1145 (1987).

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

[5]A. Migliori *et al.*, Phys. Rev. B **41**, 2098 (1990).

[6]H. Ledbetter, S. A. Kim, C. E. Violet, and J. D. Thompson, Physica (Amsterdam) **162–164C**, 460 (1989).

[7]S. Bhattacharya *et al.*, Phys. Rev. B **37**, 5901 (1988).

[8]J. M. Longo and P. M. Raccah, J. Solid State Chem. **6**, 526 (1973).

[9]I. Tanaka and H. Kojima, Nature (London) **337**, 21 (1989).

[10]M. McHenry (private communication).

[11]R. H. Demarest, J. Acoust. Soc. Amer. **49**, 768 (1971).

[12]I. Ohno, J. Phys. Earth **24**, 355 (1976).

[13]S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science **220**, 671 (1983).

[14]See, for example, U. Geiser *et al.*, Phys. Rev. B **35**, 6721 (1987).

[15]T. J. Kim *et al.*, J. Magn. Magn. Mater. **76&77**, 604 (1988).

[16]T. Goto, B. Lüthi, R. Geick, and K. Strobel, Phys. Rev. B **22**, 3452 (1980), and references therein.

[17]V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) **2**, 2031 (1960) [Sov. Phys. Solid State **2**, 1824 (1960)]; S.-k. Ma, *Modern Theory of Critical Phenomena* (Benjamin, Reading, MA, 1976), Chap. III.

[18]P. Böni, J. D. Axe, G. Shirane, R. J. Birgeneau, D. R. Gabbe, H. P. Jensen, M. A. Kastner, C. J. Peters, P. J. Picone, and T. R. Thursten, Phys. Rev. B **38**, 185 (1988).

[19]T. Suzuki, M. Yoshizawa, T. Goto, T. Yamakami, M. Takahashi, and T. Fujimura, J. Phys. Soc. Jpn. **52**, 1669 (1983).

[20]W-K. Lee, M. Lew, and A. S. Nowick, Phys. Rev. B **41**, 149 (1990).