Interplay between Lattice Softening and High-T_c Superconductivity in $La_{1.86}Sr_{0.14}CuO_4$

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High-resolution ultrasonic measurements have been performed on single-crystalline $La_{1.86}Sr_{0.14}CuO_4$ in magnetic fields H up to 14 T. We found that by reducing temperature the transverse elastic constant $(C_{11}-C_{12})/2$ starts to soften from about 50 K and continues to soften down to $T_c(H)$, even when $T_c(H)$ is reduced to 14 K by magnetic field. The softening turns to rapid hardening by the emergence of superconductivity. This behavior of $(C_{11}-C_{12})/2$ is a consequence of the structural instability of the orthorhombic phase and disappearance of the instability caused by emergence of the superconducting state.

There has been considerable interest in the relation between high-temperature superconductivity in copper oxides and structural instability which involves distortions of the Cu-O layers [1–9]. In the case of $La_{2-x}Sr_xCuO_4$ (LSCO), which is a model system of high-temperature superconductive oxide, superconductivity appears in the orthorhombic (OMT) phase with space group *Bmab* (OMT denotes orthorhombic at midtemperatures). 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 tetragonal (THT) phase with space group *I4/mmm* (THT denotes tetragonal at high temperatures). It is well known that the superconducting transition temperature T_c is considerably lowered by the structural transformation from the OMT phase to a second tetragonal (TLT) phase with space group $P4_2/ncm$ (TLT denotes tetragonal at low temperatures) in $La_{1.875}Ba_{0.125}CuO_4$ (LBCO) [1] or to a second orthorhombic (OLT) phase with space group *Pccn* (OLT denotes orthorhombic at low temperatures) in La_{2-x-y}-$Nd_ySr_xCuO_4$ [2]. Measurements of elastic constants [8,9], specific heat [8], and thermal expansion [10] point toward some structural anomalies at low temperatures in LSCO, although no additional transformation has been observed so far by diffraction techniques.

The purpose of this Letter is to demonstrate the presence of a novel structural instability in LSCO starting from a temperature above T_c, which, however, is quenched by the appearance of superconductivity, and to clarify the nature of this instability in terms of the anomalies of elastic constants for various ultrasonic modes. The elastic constants measured were longitudinal C_{11} and C_{33} and transverse $(C_{11}-C_{12})/2$, C_{66}, and C_{44} of single crystals in magnetic fields up to 14 T applied both parallel and perpendicular to the Cu-O layers. Here the elastic constants and corresponding strains are defined using crystalline coordinates in the THT phase. Among these elastic constants, only $(C_{11}-C_{12})/2$ exhibits remarkable softening in the OMT phase. The elastic constant $(C_{11}-C_{12})/2$ is a strain susceptibility to a

shearing strain $\varepsilon_{xx}-\varepsilon_{yy}$, by which the [100] axis (x) is stretched and the [010] axis (y) is shrunk and vice versa. It is worth noting that the elastic $(C_{11}-C_{12})/2$ mode is a pure shear mode with B_{1g} symmetry both in the THT and the OMT structure.

The single crystals of LSCO $(x=0.14)$ used here were grown by a traveling-solvent floating-zone method [11]. We determined the superconducting onset temperature of 36 K with a transition width of 4 K by using a superconducting quantum interference device magnetometer (Quantum Design model MPMS), and the Sr concentration of $x=0.138\pm0.03$ by electron-probe microanalysis (EPMA). The THT-OMT structural transition temperature is $T_d=210$ K according to the analysis of the temperature dependence of C_{66} which shows 70% softening toward T_d in the THT phase [12,13], consistent with the report by Migliori *et al.* [7]. For the measurements of $(C_{11}-C_{12})/2$, a pair of surfaces (110) were prepared on the sample with dimensions of [110]×[1$\bar{1}$0]×[001] $=3.482\times6.3\times2.9$ mm³. Transducers of x-cut $LiNbO_3$ with a fundamental frequency of 10 MHz were bonded onto each surface to enable sound to propagate in a [110] direction (k) with [1$\bar{1}$0] polarization (u). Sound velocity v was measured using a phase comparison method [14] with a frequency of 30 MHz and a relative resolution of better than 10^{-6}. The elastic constant was calculated from the relation $(C_{11}-C_{12})/2=\rho v^2$ using the room-temperature value of mass density $\rho=6.97$ g/cm³. No correction for contraction of the sample with temperature was made since it is expected to be 1 part in 10^3 over the entire temperature interval studied. The measurements in each magnetic field were performed on cooling from well above T_c using a superconducting magnet system (Oxford Instruments). It should be noted that thermal hysteresis was not detected within the experimental resolution.

The variations of $(C_{11}-C_{12})/2$ with temperature are presented in Fig. 1. The elastic constant $(C_{11}-C_{12})/2$ hardens with decreasing the temperature from 300 K as it does for an ordinary solid [13]. The most remarkable feature of the zero-field measurements is that
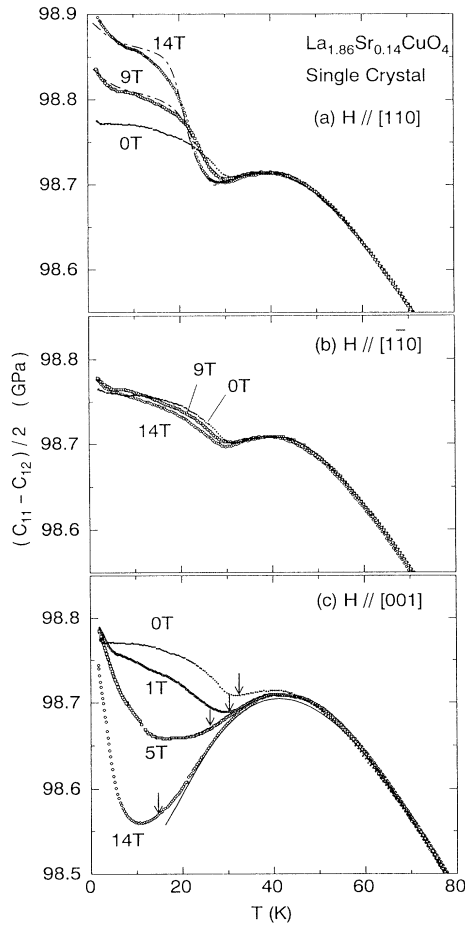
FIG. 1. Temperature dependence of the transverse elastic constant $(C_{11} - C_{12})/2$ in single-crystalline $La_{1.86}Sr_{0.14}CuO_4$ under magnetic fields. The field direction is (a) $H \| [110] \perp u$, (b) $H \| [1\bar{1}0] \| u$, and (c) $H \| [001] \perp u$. The dot-dashed lines in (a) are a theoretical prediction for the hardening due to the FL's pinning. Arrows in (c) indicate superconducting transition temperatures $T_c(H)$ in each magnetic field. The solid line is a calculated curve by Eq. (3).

$(C_{11} - C_{12})/2$ starts to soften at a temperature around 50 K, which is substantially higher than T_c, but starts to harden just below T_c. This is different from the behavior of other elastic constants, which do not show any corresponding anomaly above T_c [13,15].

First, we will examine whether this anomalous softening originates from superconductivity itself. A calculation of the variation of a transverse elastic constant caused by superconductivity consists of two contributions [16]: a mean-field contribution that gives a discontinuity of slope at T_c and a contribution from superconducting fluctuations near T_c. The former is related to the second-order strain dependence of T_c by the thermodynamic relation

$$\frac{dC_t}{dT}\bigg|_{T_c^+} - \frac{dC_t}{dT}\bigg|_{T_c^-} = -\frac{\Delta C_p}{T_c}\left(\frac{d^2T_c}{d\varepsilon_t^2} + \cdots\right), \quad (1)$$
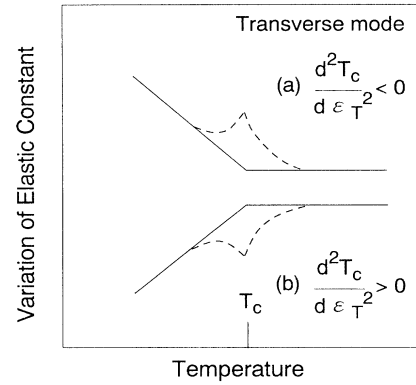

FIG. 2. Schematics of the variation of transverse elastic constant with temperature near T_c caused by superconductivity. The solid lines represent mean-field behavior and the broken lines represent the contribution of Gaussian fluctuations. The change of slope and the fluctuation contribution depend on the sign of the second derivative of T_c with respect to strain.

where Δc_p (> 0) is the specific-heat jump at T_c, and C_t and ε_t are the transverse elastic constant and the shearing strain, respectively. This contribution is shown in Fig. 2 by solid lines. Concerning the fluctuation contribution, the expression for longitudinal modes was given by Millis and Rabe [16]. Extending their calculation to the transverse mode, we obtain as the fluctuation contribution

$$\Delta C_t^{fl}(T) \propto -\Delta C_p \frac{d^2T_c}{d\varepsilon_t^2} \frac{2-\alpha}{\alpha}\left[\frac{T}{T_c}-1\right]^{1-\alpha} \quad (2)$$

for $T > T_c$. Here, α is the critical exponent for specific heat and is expected to be $0 < \alpha \ll 1$. This contribution is added to the mean-field contribution as shown schematically in Fig. 2 by broken lines.

It is clear from the zero-field results in Fig. 1 that the slope of the $(C_{11} - C_{12})/2$ vs T curve changes across the superconducting transition region. In the context of the mean-field analysis, this change in slope is expressed by the left hand side of Eq. (1), which gives a positive value. Using a specific-heat jump of $\Delta c_p/T_c = 13$ mJ/mol K^2 [17], we obtain the second derivative at zero field to be $d^2T_c/d\varepsilon_t^2 \approx -3 \times 10^4$ K. The sign of the second derivative is negative and, as indicated by Eq. (2), the superconducting fluctuation would therefore contribute to an elastic hardening above T_c rather than to the observed softening. Thus the softening that starts substantially above T_c can neither be explained by simple thermodynamic calculations nor by superconducting fluctuations. Therefore the softening is attributed to an intrinsic property of the lattice in the normal state. We confirmed this interpretation by applying magnetic fields which reduce T_c, retaining the normal state to lower temperatures.

The results with three field directions of $H \| [110] \perp u$, $H \| [1\bar{1}0] \| u$, and $H \| [001] \perp u$ are shown in Figs. 1(a)–1(c), respectively. In the configuration of $H \| Cu$-O layers, the upper critical field $H_{c2}(0)$ is as high as about 100

T and T_c is almost unchanged even for $H=14$ T. The elastic constant $(C_{11}-C_{12})/2$ in $H\|[110]\perp u$ is shown in Fig. 1(a). The most remarkable effect of applied fields is the enhancement of $(C_{11}-C_{12})/2$ below about 30 K. According to high-field dc magnetization measurements, this temperature corresponds to the irreversibility temperature T^*, below which the flux lines (FL's) in the mixed state are rigidly pinned to the crystal lattice. Since the displacement u is perpendicular to the FL's in this configuration, the sound wave acts to tilt the FL's below T^*. Consequently the tilt modulus of FL's is superposed on the elastic constant of the crystal lattice [18]. The dot-dashed lines in Fig. 1(a) are theoretical curves using Eq. (6) of Ref. [18]. It shows good agreement with the observed hardening. Such a step in the elastic constant was not observed in the configuration of $H\|[1\bar{1}0]\|u$ as is seen in Fig. 1(b). This is reasonable since the displacement of the crystal lattice parallel to FL's does not deform the FL's. In the configuration of $H\|[001]$, the sound wave acts to shear a flux-line lattice (FLL) below T^* and a shear modulus of the FLL should be superposed on the elastic constant of the crystal lattice. However, a magnitude of the shear modulus of the FLL is considerably smaller than that of the tilt modulus [19], and the observed hardening below $T_c(H)$, shown in Fig. 1(c), is never explained by the FLL contribution as discussed later.

In the configuration of $H\|[001]$, it is important to note that T_c is substantially reduced by H. We determined $T_c(H)$ in magnetic fields by analyzing the temperature dependence of C_{33} [15] which exhibits a discontinuity at T_c corresponding to the specific-heat jump. With increasing H, $T_c(H)$ decreases from 32 K at 0 T to 30 K at 1 T, 26 K at 5 T, and 14 K at 14 T, as indicated by arrows in Fig. 1(c). The elastic constant $(C_{11}-C_{12})/2$ continues to soften as long as the system remains in the normal state, but exhibits a rapid hardening when superconductivity appears. The persistence of the softening below $T_c(H)$ is most likely because of the competition between the softening in the normal state and the hardening in the superconducting state. Thus the anomalous softening above $T_c(H)$ is ascribed to the intrinsic nature of the normal state.

The softening of $(C_{11}-C_{12})/2$ below 50 K indicates a growth of a structural fluctuation (i.e., a structural instability) related to the shearing strain $\varepsilon_{xx}-\varepsilon_{yy}$. Important information of this instability can be gained by tracing the positions of oxygen ions in the Cu-O layers as the strain is induced by the sound propagation. As seen from Fig. 3(a), all in-plane oxygen sites are equivalent in the OMT structure. As evident in Fig. 3(b) in contrast, there are two distinctive sites in the structure induced by $\varepsilon_{xx}-\varepsilon_{yy}$. The displacement of the in-plane oxygens toward the [001] axis from the Cu-O plane is different for half of the oxygen ions along the [100] axis and for the other half along the [010] axis. In connection with the TLT phase of LBCO, several authors argued both experi-
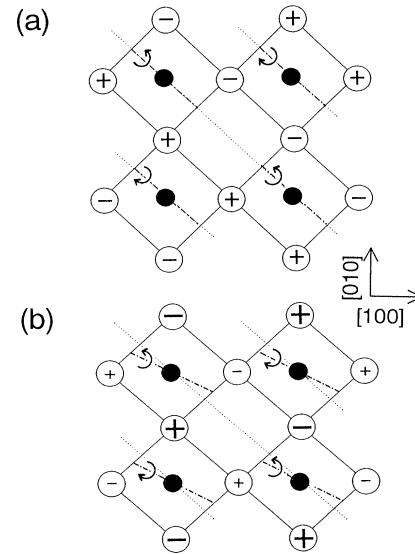

FIG. 3. Top view of Cu-O layers in (a) the OMT and (b) the structure induced by $\varepsilon_{xx}-\varepsilon_{yy}$. The closed circles indicate copper atoms in the center of the CuO_6 octahedra. The open circles with $+$ or $-$ indicate in-plane oxygen atoms slightly above or below the plane, respectively. The tilt is reduced along the [100] axis and is enhanced along the [010] axis by $\varepsilon_{xx}-\varepsilon_{yy}$, and the buckling changes as shown in (b). In the structure induced by $\varepsilon_{xx}-\varepsilon_{yy}$ there are distinctive sites for the in-plane oxygen ions.

mentally and theoretically that the existence of distinctive sites of oxygen leads to development of an additional gap structure at the Fermi level E_F in the so-called "in-gap state" (the states within the charge-transfer gap) [3–6]. The shearing strain $\varepsilon_{xx}-\varepsilon_{yy}$ does lift the degeneracy of the oxygen sites and splits the bands. In this case the instability is regarded as a Peierls-type instability [4,5]. The softening of $(C_{11}-C_{12})/2$ follows naturally from this coupling between the electronic states $\varepsilon_{xx}-\varepsilon_{yy}$ as described below.

Consider simple rectangular bands with density of state (DOS) N and bandwidth 2Γ centered at E_F, in which the electronic level splits into $E_k=E_k^0\pm d(\varepsilon_{xx}-\varepsilon_{yy})$ in response to the shearing strain. Here, E_k^0 is an electronic energy without the shearing strain and d is a coupling energy between electrons and strain. In this model, the deviation of the elastic constant from the background $C^0(T)$, the value in the absence of the coupling, is given by the following formula [20]:

$$\Delta(C_{11}-C_{12})/2 = -2d^2N(1-e^{-\Gamma/k_BT}),\qquad(3)$$

where k_B is the Boltzmann constant. As seen from Eq. (3), $(C_{11}-C_{12})/2$ should exhibit softening. The solid line in Fig. 1(c) is the fit with Eq. (3) assuming an appropriate linear background $C^0(T)$. A bandwidth of $2\Gamma=80$ K and a coupling parameter $d^2N=9.7\times10^7$ J/m³ were used in the present fitting. It shows a good agreement with the experimental observation in the field

of $H = 14$ T and temperature interval of 20–80 K, in which the sample is in the normal state. The obtained bandwidth 2Γ seems to be small, indicating an existence of narrow bands. Electronic van Hove singularity (vHs), which has been assumed to explain high-T_c superconductivity, effectively has a narrow bandwidth because of its logarithmically diverging DOS. Our preliminary analysis assuming vHs shows that the elastic constant exhibits significant softening when the singularity is close to E_F.

Now consider the origin of the hardening of $(C_{11} - C_{12})/2$ below $T_c(H)$ in Fig. 1(c). In the superconducting state, $(C_{11} - C_{12})/2$ consists of at least three components: contributions from superconductivity itself $\Delta C^S(T)$, from FLL $\Delta C^F(T)$, and from crystal lattice $C^L(T)$. Since $\Delta C^S(0) \propto T_c \Delta c_p$ [21], this contribution should be reduced by H. As we noted before, the contribution $\Delta C^F(T)$ is negligible in this configuration. In the normal state, $C^L(T)$ is the observed $(C_{11} - C_{12})/2$, which is softened by the instability. If this instability persists in the superconducting state, $C^L(T)$ should continue to soften or at least retain the value at $T_c(H)$. In this case, $C^L(T) + \Delta C^S(T)$ cannot explain the observed $(C_{11} - C_{12})/2$, which tends to the same value independent of H at the lowest temperature. Therefore the observed feature can be explained only when the structural instability disappears in the superconducting state and $C^L(T)$ is restored to the background value $C^0(T)$.

In LSCO we believe that the total energy may be reduced more by forming a superconducting gap rather than by forming a gap structure induced by the shearing strain. In such a situation, the instability of the OMT structure disappears as superconductivity emerges. This argument is consistent with the discussion by Pickett et al. [6] that a relevant fluctuation is very low in energy and is affected by the onset of the superconducting transition.

Interplay between local structural symmetry and superconductivity has been observed on $Tl_2Ba_2CaCu_2O_8$ [22] and $YBa_2Cu_3O_7$ (YBCO) [23]. In these compounds the Cu-O layers exhibit a dynamical change from a TLT-like to an OMT-like buckling structure below T_c. Although the Cu-O layers of YBCO are buckled in the orthorhombic phase, its in-plane oxygen sites are equivalent as in the case of the OMT phase of LSCO. It may be a common aspect of the high-T_c superconductors that the buckling motion of the Cu-O layers, which makes oxygen sites distinctive (as in TLT, OLT, and the structure induced by $\varepsilon_{xx} - \varepsilon_{yy}$), is unfavorable to superconductivity.

In conclusion, we found that the transverse elastic constant $(C_{11} - C_{12})/2$ of LSCO ($x = 0.14$) exhibits a remarkable softening starting from about 50 K and a rapid hardening below $T_c(H)$. This softening clearly indicates the existence of a structural instability of the OMT phase in the normal state. We propose that a Peierls-type instability caused by coupling between the shearing strain $\varepsilon_{xx} - \varepsilon_{yy}$ and the electronic states is responsible for the softening of $(C_{11} - C_{12})/2$. The rapid hardening of

$(C_{11} - C_{12})/2$ below $T_c(H)$ is most likely a signature of the disappearance of the structural instability due to the emergence of the superconducting state. Our observation gives evidence for a strong interplay between lattice instability and high-T_c superconductivity in LSCO and provides novel information of the bands responsible for the instability: The bands are considerably narrow and peaked near the Fermi level. Moreover they are restricted to coupling with the shearing strain $\varepsilon_{xx} - \varepsilon_{yy}$ with B_{1g} symmetry. These results appear to be important with respect to the mechanism of high-T_c superconductivity.

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