RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 16 1 JUNE 1987

Elasticity studies of $La_{2-x}Sr_xCuO_4$

L. C. Bourne and A. Zettl
Department of Physics, University of California, Berkeley, California 94720

K. J. Chang and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Angelica M. Stacy and W. K. Ham
Department of Chemistry, University of California, Berkeley, California 94720
and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 12 March 1987)

We report measurements of Young's modulus Y and internal friction δ of the high-T_c superconductor $La_{2-x}Sr_xCuO_4$. For $x=0.15$, anomalies in Y and δ at $T_c=40$ K are preceded by a dramatic decrease in Y, indicative of a soft phonon mode beginning near 200 K. For $x=0.30$, the softening is absent. The magnetic field dependence of Y and δ is investigated, and predictions are made for ΔC_p and $\partial H_{c2}/\partial T$.

The recent discovery of superconductivity above 30 K in the La-Ba-Cu-O system[1] has initiated a major research effort directed toward an understanding of material parameters, mechanisms of high-transition-temperature (T_c) superconductivity and a search for similar compounds.

High-T_c superconductivity is usually explained in terms of strong electron-phonon interactions[2] or a high density of states at the Fermi energy. The strong electron-phonon coupling is often associated with soft phonon modes which can also induce structural phase transitions. For example, in most A-15 compounds, cubic-to-tetragonal phase transitions[3] are observed, and the soft mode causing the structural changes is considered to be associated with the high-T_c superconducting mechanism. We present evidence for similar behavior occurring in the $La_{2-x}Sr_xCuO_4$ system.

We have prepared samples of $La_{2-x}Sr_xCuO_4$ by both coprecipitation techniques and by mechanical mixing of La_2O_3, CuO, and $SrCO_3$. Pressed pellets of the starting materials were sintered at 1100 °C in air for 44 h. The polycrystalline samples were characterized by magnetic-susceptibility measurements [employing a superconducting quantum interference device (SQUID) magnetometer] and dc-electrical-resistivity measurements; for the $x=0.15$ and 0.30 samples we observed, respectively, a 100% and a 1.5% diamagnetic effect. Samples with $x=0.15$ indicated a superconducting transition near $T_c=35$–37 K, while those with $x=0.3$ had $T_c=20$ K. The transition temperatures are in agreement with previous studies.[4]

Elasticity measurements were performed using a resonant vibration technique described in detail elsewhere.[5] Polycrystalline samples with approximate dimensions of $5\times0.5\times0.5$ mm^3 were cut from the sintered pellets with a diamond saw and rigidly clamped at one end, and flexural vibrations were induced in the sample and detected with a capacitive technique. On occasion, a weight (a blob of silver paint) was attached to the free end of the sample to produce a system with a resonant vibration in the experimentally accessible frequency range. All measurements were performed in the range of 2–7 kHz. Changes in Young's modulus Y are determined directly from changes in vibration frequency, and the internal friction δ is inversely proportional to the vibration amplitude.[5]

Elasticity data for a $La_{2-x}Sr_xCuO_4$ sample with $x=0.15$ are shown in Fig. 1. As the sample is cooled from 300 K, the normal increase of Young's modulus from thermal contraction is observed. At about 200 K, Y shows an anomalous turnover and decreases with decreasing temperature until about 100 K, where Y saturates abruptly. The total change in Y from 200 to 100 K is 14%. At lower temperatures, Y begins to rise again, and the internal friction (inverse of the amplitude) shows a strong dip

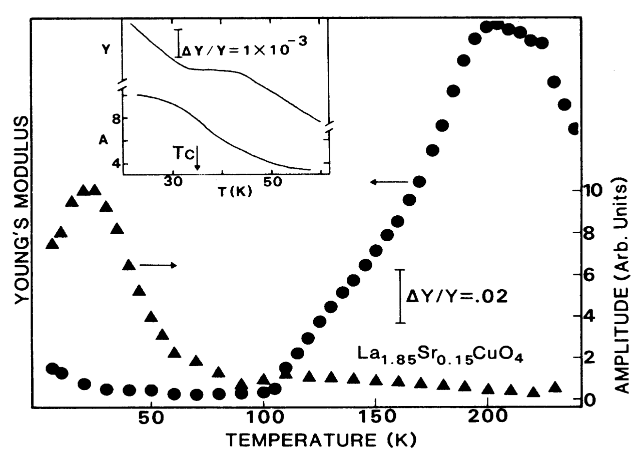

FIG. 1. Young's modulus Y and resonance amplitude A ($\propto 1/\delta$) in $La_{1.85}Sr_{0.15}CuO_4$. The inset shows the superconducting transition region in detail. T_c is indicated by an arrow.

near 25 K. For a given sample, the saturation point in Y (near 100 K in Fig. 1) was found to be very reproducible from run to run. The inset to Fig. 1 shows the results of a careful measurement of Y and δ near the superconducting transition temperature $T_c = 35$ K (as determined from susceptibility measurements). At T_c there exist well-defined anomalies in both Y and δ; these features will be discussed shortly.

The anomalous high-temperature lattice softening near 200 K in $La_{2-x}Sr_xCuO_4$ was investigated both for different values of x and for fixed x, but with different high-temperature sample annealing conditions. Additional annealing of the sample at 900 °C resulted in an increase in T_c to 37 K; the corresponding elastic properties showed behavior similar to that displayed in Fig. 1, but the drop in Y was increased to 20%, and the saturation point in Y was reduced to 70 K.

Changes in x were found to have a dramatic effect on Y and δ. Figure 2 shows Y for a $La_{2-x}Sr_xCuO_4$ sample with $x = 0.3$ ($T_c = 20$ K). Both cooling and heating curves are shown (vertically offset for clarity). It is apparent that a dramatic lattice softening is not observed for $x = 0.3$. Instead, there are smaller anomalies in Y at 220 and 80 K; the anomaly at 220 K is hysteretic and is suggestive of a first-order phase transition. The internal friction for this sample was observed to decrease gradually with decreasing temperature, with no obvious structure.

The elastic behavior described above is remarkably similar to that observed in the A-15 compounds.[3] In these materials, decreases in Y with decreasing temperature have been interpreted as reflecting a soft phonon mode signaling a tendency toward structural phase transformation. The compounds are intrinsically unstable, and this structural instability is tied to both the elastic properties and to the superconductivity mechanism.

Recently, it was suggested[6-9] that the tetragonal K_2NiF_4-type phase in $La_{2-x}A_xCuO_4$ compounds also has soft phonon modes which can be responsible for the high superconducting temperature within the framework of conventional BCS superconductivity. This softening of the phonon modes is related to a two-dimensional Fermi surface nesting and a resulting Peierls-like instability. Although the undoped compound La_2CuO_4 crystalizes in an orthorhombic structure at temperatures below 530 K, alkaline-earth substitutes for the La^{3+} ions suppress the Peierls' distortions. In the doped samples, the superconducting tetragonal phase was found even at low temperatures around 10 K.[10] The Sr^{2+} ion is the best substitute for the La^{3+} ion, resulting in a relatively strain-free lattice.

Our observed softening of the Young's modulus for the sample with $x = 0.15$ can be interpreted as a result of phonon mode softening. This suggests that the sample has a large portion with a single phase which is most likely responsible for the superconductivity. Hence, it can be inferred that the lattice is close to an instability and that a characteristic incipient structural transformation and its associated soft mode enhance the superconducting temperature. As shown in Fig. 2, the softening of the modulus disappears when $x = 0.3$, which indicates that a part of the sample has the structural distortions which reduce the mode softening. This is confirmed by magnetic susceptibility measurements on the $x = 0.3$ sample, which show a very small diamagnetic effect below T_c. Recent magnetic-susceptibility measurements[11] have shown that the fraction of the sample which is superconducting varies with composition and a strong peak exists near $x = 0.15$, in accord with our elasticity measurements.

We consider now in more detail the elastic anomalies near T_c. From the inset in Fig. 1, there exists at T_c an anomaly in Y of magnitude $\Delta Y/Y = 10^{-3}$. From thermodynamic considerations, this may be related to a discontinuity in the specific heat[12]

$$\Delta C_p = \left(\frac{-\Delta Y}{Y}\right) \frac{T_c}{Y(\partial T_c/\partial\sigma)^2} , \tag{1}$$

where σ is the uniaxial stress. The porosity of our poly-

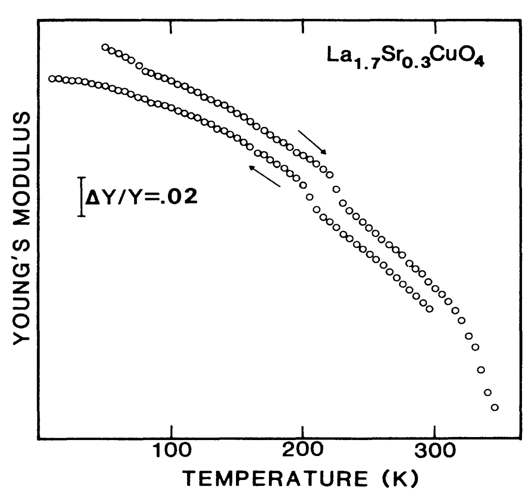

FIG. 2. Young's modulus Y for $La_{1.7}Sr_{0.3}CuO_4$. The cooling and warming curves have been vertically offset.

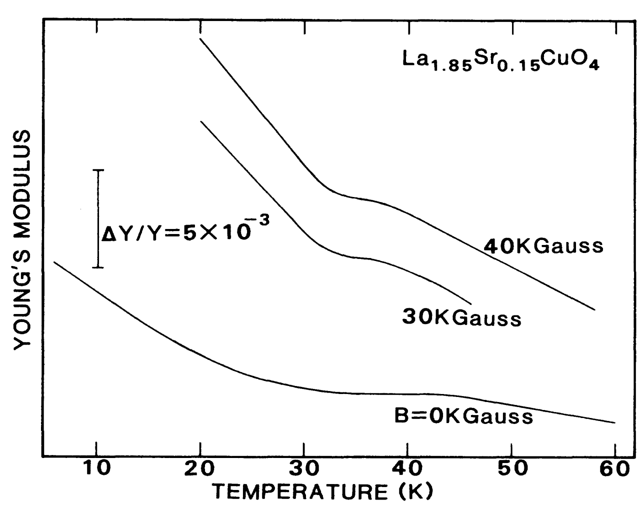

FIG. 3. Young's modulus Y for $La_{1.85}Sr_{0.15}CuO_4$ for selected values of magnetic field.

crystalline samples makes an absolute determination of Y difficult, and there is no published stress dependence of T_c for $La_{1.85}Sr_{0.15}CuO_4$. However, if we assume $Y \approx 10^{12}$ dyne/cm^2 and $\partial T_c/\partial P \approx 1$ K/kbar (as is appropriate for the La-Ba-Cu-O system[13]), we may estimate $\Delta C_p = 4$ mJ/K cm^3). A specific-heat anomaly of this magnitude should be experimentally accessible.

Finally, we consider the effect of an external magnetic field H on the elastic properties of $La_{2-x}Sr_xCuO_4$. Figure 3 shows Y near the superconducting transition for a $La_{1.85}Sr_{0.15}CuO_4$ sample. In the absence of field, the anomaly in Y is approximately 10 K wide. A major effect of H is to decrease the width of the Young's modulus anomaly; however, the magnitude of the anomaly $\Delta Y/Y$ at T_c is little affected up to $H = 40$ kG. Figure 3 also shows that the position of the elastic anomaly (which we associate with T_c) is rather insensitive to H. For example, within a resolution of 0.5 K, an increase in H from 30 to 40 kG does not affect the acoustic anomaly. This sets a lower bound to $\partial H_{c_2}/\partial T$ of 20 kG/K. The initial narrowing of the transition with increasing H could be due to partial destruction of mixed-gap superconductivity or to suppression of superconducting fluctuations above T_c.

This research was supported by National Science Foundation Grants No. DMR-82-19024 (K.J.C. and M.L.C.), No. CHE-83-51881 (A.M.S.), and No. DMR-84-00041 (A.Z.), and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A.Z. also acknowledges support from the Alfred P. Sloan Foundation.

[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2]P. B. Allen and B. Mitrovic, Solid State Phys. **37**, 1 (1982).

[3]L. R. Testardi, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1973), Vol. 10, p. 193; L. R. Testardi, Rev. Mod. Phys. **47**, 637 (1975).

[4]R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman, Phys. Rev. Lett. **58**, 408 (1987); S. Kanbe, K. Kishio, K. Kitazawa, K. Fueki, H. Takagi, and S. Tanaka, Chem. Lett. (to be published).

[5]L. C. Bourne and A. Zettl, Solid State Commun. **60**, 789 (1986); Phys. Rev. B (to be published).

[6]L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[7]J. J. Yu, A. J. Freeman, and J.-H. Xu, Phys. Rev. Lett. **58**, 1035 (1987).

[8]H.-B. Schuttler, J. D. Jorgensen, D. G. Hinks, D. W. Capone II, and D. J. Scalapino (unpublished).

[9]W. Weber, Phys. Rev. Lett. **58**, 1371 (1987); **58**, 2154(E) (1987).

[10]J. D. Jorgensen, D. G. Hinks, D. W. Capone II, K. Zhang, H.-B. Schuttler, and M. B. Brodsky (unpublished).

[11]R. B. van Dover, R. J. Cava, B. Batlogg, and E. A. Rietman, Phys. Rev. B **35**, 5337 (1987).

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

[13]C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, Phys. Rev. Lett. **58**, 405 (1987).