Solid State Communications, Vol.65,No.10, pp.1073-1077, 1988.
Printed in Great Britain.

0038-1098/88 $3.00 + .00
Pergamon Press plc

ELASTIC PROPERTIES OF POLYCRYSTALLINE $La_{2-x}Sr_xCuO_4$

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(Received October 9, 1987 by R.H. Silsbee)

We report on the temperature dependence of the shear (G) and Young's (E) moduli of polycrystalline $La_{1.85}Sr_{0.15}CuO_4$ and La_2CuO_4. We find that E~3G, implying that the single crystal shear moduli are small, so that the polycrystalline E and G are determined by the single crystal shear moduli only. Contrary to expectations, there are large, but sample dependent, drops in moduli at T_c for the superconducting Sr-alloy. The large shear softening associated with the tetragonal-orthorhombic transition at 180K is also very sample dependent, and does not appear simply related to the superconducting transition. The polycrystalline elastic moduli are very hysteretic below the structural transition, presumably due to the distortion driven variation in crystallite dimensions with temperature.

1. Introduction

Hoping to illuminate the mechanism of high temperature superconductivity in $La_{1.85}Sr_{0.15}CuO_4$ and related compounds,[1] a number of groups have reported measurements of the Young's modulus, E[2,3] and the modulus for the ultrasonic longitudinal mode, K'.[4] The motivation of the present investigation was initially to complement these studies with a measurement of the shear modulus, G. We found a very unusual hysteresis in the temperature dependence of G, which prompted us to intensively study the temperature dependence of E and G on a number of samples of $La_{1.85}Sr_{0.15}CuO_4$, as well as the parent compound, La_2CuO_4. While revealing interesting properties that may be related to the superconducting transition, these measurements also demonstrated the difficulty in interpreting experimental data on the elastic properties of such polycrystalline samples.

In general, changes in elastic constants give information on the thermodynamics of a phase transition. For a second-order Landau-type transition,[5] anomalies in the single crystal shear (C_{44}) and Young's ($E_z = 1/S_{33}$) moduli are related to those in the specific heat (c) and entropy (s), i.e.

$$\Delta E_z = -(\Delta c/T_c)(E_z\, dT_c/d\sigma_3)^2$$

while

$$\Delta C_{44} = (\Delta s)d^2T_c/d\varepsilon_4^2 \to 0,$$

so that only changes in the derivatives of the shear moduli are expected. Furthermore, care must be taken in extending the expression for the Young's modulus to polycrystals. While the polycrystalline shear modulus will be an average of single crystal shear moduli only, the polycrystalline Young's modulus will depend on single crystal moduli of all symmetries. In particular, we found that G~E/3, implying that the polycrystalline Young's modulus is mostly determined by the single crystal <u>shear</u> moduli. On the other hand, G drops sharply at T_c, in contrast to the behavior predicted above. While the moduli of $La_{1.85}Sr_{0.15}CuO_4$ decrease greatly below room temperature, presumably due to the tetragonal-orthorhombic distortion associated with canting of the CuO planes,[6] the magnitudes and temperatures of the decreases in elastic moduli vary enormously with sample and the softening does not appear to be correlated with the superconducting transition. Associated with the softening is a very unusual hysteresis, described in detail below.

2. Experimental Technique

Samples of typical dimensions 5x0.2x0.2 mm^3 were cut with a diamond saw fromm a pellet of $La_{1.85}Sr_{0.15}CuO_4$ prepared at the University of California, Berkeley, and of La_2CuO_4 prepared at the University of Kentucky. Elastic measurements were done using "vibrating reed" techniques described at length elsewhere.[7] In order to measure both Young's and shear moduli, one end of the sample was "clamped" with silver paint on a copper rod and a stiff metal wire was (usually) attached with silver paint to the free end. The wire lowered the flexural resonant frequency to experimentally desirable values (i.e. <10kHz) and also allowed torsional resonances to be excited. However, the magnitude of E was more precisely determined using a sample without the wire load; i.e. the fundamental flexural frequency is given by:[8]

$$f_E = 0.16 \frac{a}{L^2}(E/\rho)^{1/2}$$

while for the loaded reed, G can be found from:[8]

$$f_G = 2.0 f_E L/L' \left(\frac{G(4.1+M/M')}{E}\right)^{1/2} \quad .$$

Here, a, L,ρ,M and I are the thickness, length, density, mass and moment of inertia of the sample, and the primed quantities refer to the wire. In either case, relative changes of the modulus, given by twice the relative change in the resonant frequency, could be precisely measured. Flexural and torsional modes were excited by, respectively, centering and off-centering the electrostatically coupled drive and pick-up electrodes, and were distinguished by the different phase shifts of the resonant signals.[7] Measurements of the bandwidth and amplitude were made to determine the quality factor, Q, and internal friction, 1/Q; drive voltages were kept sufficiently small such that the quality factor and resonant frequency were independent of oscillation amplitude.[7] For some samples, a four-probe resistance measurement was simultaneously performed on a 2 mm length at the clamped end of the sample.

3. Results

The temperature dependence of the moduli and related internal friction of samples of $La_{1.85}Sr_{0.15}CuO_4$ are shown in Figures 1 and 2. As seen in Figure 1, E and G vary similarly for a given sample, but quantitatively vary for different samples. The temperature dependence of G for a typical (nonsuperconducting) sample of La_2CuO_4 is shown in the inset of Figure 1. Whereas the moduli of the superconducting material are strongly temperature dependent, with an anomalously large softening, the temperature dependence for La_2CuO_4 is much weaker. Our best estimates of the moduli of the polycrystalline samples of the strontium alloy, given uncertainties in dimensions and densitites (see below) are $E = (4.5\pm1.0)\times10^{11}$ dynes/cm^2 and $G = (.36\pm.03)E \sim 1.6\times10^{11}$ dyne/cm^2. For an isotropic sample, one must have[9] $E \leq 3G$, with the equality realized in the limit that the bulk

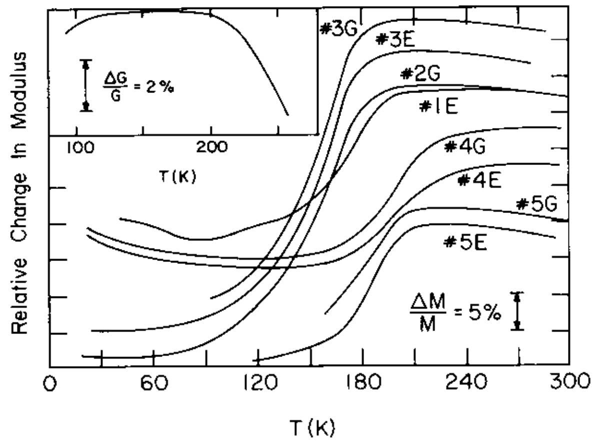

Figure 1--Relative change in moduli for several samples of $La_{1.85}Sr_{0.15}CuO_4$ vs. temperature; vertical offsets are arbitrary. "E" and "G" denote Young's and shear modulus respectively. Inset: Relative change in shear modulus vs. temperature for a La_2CuO_4 sample.

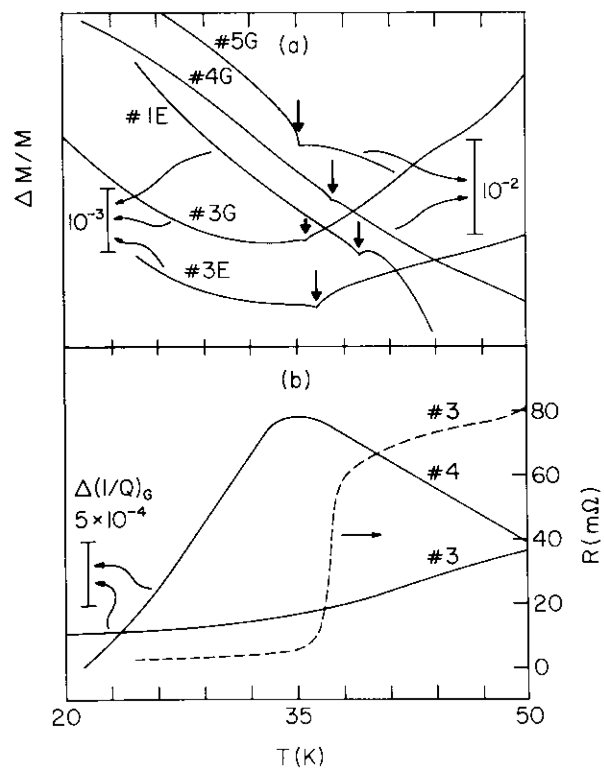

Figure 2--a) Relative changes in moduli for several samples of $La_{1.85}Sr_{0.15}CuO_4$ near their superconducting transitions, denoted with arrows. "E" and "G" denote Young's and shear modulus, respectively.

b) Change in internal friction (for shear modes) for two samples of $La_{1.85}Sr_{0.15}CuO_4$ (solid lines) and of resistance (dashed line) vs. temperature near T_c.

modulus, $K\to\infty$. Hence, our result ($E\sim3G$) suggests that the samples may be slightly "textured"; i.e. have a statistically anisotropic distribution of the crystallographic directions of the individual crytallites.[9]

For different samples, T_{max} and T_{min}, the temperatures at which the moduli take their maximum and minimum values, vary from 210K to 270K and from 35K to 135K, respectively. The amount of softening varies from 15% to 40%. It is also striking that the anomalies at T_c (Figure 2a) vary by an order of magnitude (from $2x10^{-4}$ to $2x10^{-3}$), although all samples have transition temperatures between 36K and 39K. Qualitatively, two very different types of behavior are observed for the internal friction, shown in Figure 2b. In no case was the unusual strong minimum in 1/Q at T_c, reported in Reference (2), observed. It is likely that the internal friction for these samples is dominated by friction at the grain boundaries, and is not related to damping in the individual crystallites.

The resonant frequencies for both modes also showed hysteretic and time dependent behavior, shown in Figure 3. Generally, the resonant frequency increased slowly with time, i.e. ~ 0.01%/hr; such time dependent stiffening was also observed for La_2CuO_4. Since the samples are sintered powders with large holes (see below), such time dependence is not surprising and can be understood as a settling of grains into low energy, "stiff" positions, with sample vibration. In addition to this stiffening, more anomalous hysteretic behavior is observed in the superconducting Sr-alloy. In particular, the resonant frequency increased rapidly (up to 0.005%/min.) by an amount f_H (see Figure 3b) as the temperature was cooled slightly after a slow warming, i.e. when trying to stablize the temperature. (In some cases, also shown in Figure 3, similar behavior was observed after cooling the sample.) f_H increased with the magnitude of the previous temperature change, and could be as large as 0.03%. This hysteretic behavior was observed at all temperatures near or between T_{min} and T_{max}. For example, significant hysteresis was observed below 30K for a sample (#3) having T_{min} = 35K (Figure 3a), but no hysteresis was observed below 50K for a sample (#4) with T_{min} = 135K (not shown). It should be noted that, as shown in Figure 3a, no hysteresis in T_c was observed, indicating that the sample temperature is not lagging behind that of the thermometer.

After completing the elastic measurements, scanning electron microscope studies were made on specimens of both materials. Both exterior

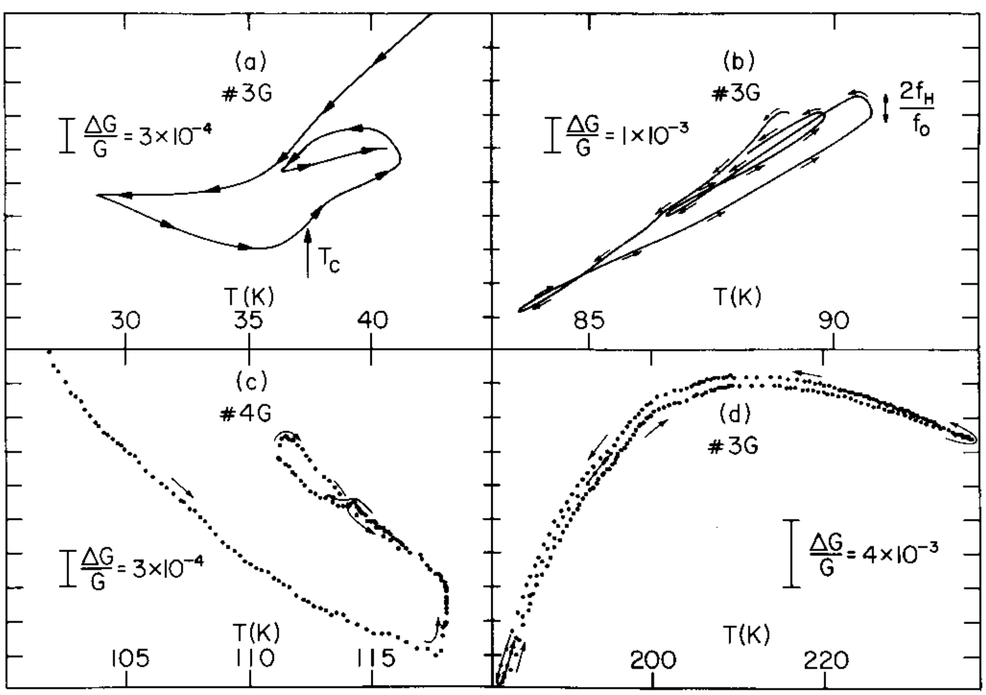

Figure 3--Typical hysteresis loops in the temperature dependence of the shear modulus of $La_{1.85}Sr_{0.15}CuO_4$. The arrows indicate the direction of time flow; in (c) and (d), the data points were taken at 50 second intervals. The increase in frequency, f_H, when reversing the sign of dT/dt is defined in (b). The closing of the hysteresis loop for $T>T_{max}$ is shown in (d). The independence of the superconducting transition temperature on the hysteresis is shown in (a).

and fresh fractured interior surfaces were examined. The former have large, flat, dense, areas covered in part with ~ 2μm diameter "balls". Energy dispersive x-ray analysis showed that the exterior surfaces of the superconducting material were very heterogeneous chemically, with strontium-depeleted regions. On the other hand, the fresh fractured surfaces for both materials appear as dense material pierced with holes 1-20 μm in diameter. A micrograph of an interior surface of $La_{1.85}Sr_{0.15}CuO_4$ is shown in Figure 4; the

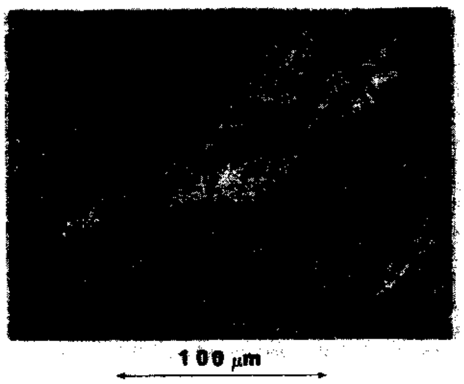

Figure 4--SEM micrograph of an internal (fresh-fractured) surface of $La_{1.85}Sr_{0.15}CuO_4$.

interior surface appears very different from that of $YBa_2Cu_3O_7$, for which the individual crystallites are more obvious.[10] The measured density of the $La_{1.85}Sr_{0.15}CuO_4$ and La_2CuO_4 specimens were only 60% and 70% of the theoretical densities, respectively. X-ray analysis of the fresh fractured surfaces (i.e. the bulk of the specimen) indicated considerably less chemical heterogeneity (~20%); however, the uncertainty connected with this value is difficult to estimate due to the complicated morphology of the surface and the very different atomic numbers of the metals analyzed.

4. Discussion

It is very difficult to analyze the temperature dependence of elastic properties of polycrystals. Even without considering the complications caused by the large voids present in these samples, the temperature dependence of different samples can vary enormously depending on the boundry conditions satisfied by the crystallites. Generally, the elastic constants of an isotropic polycrystal are bounded by the Reuss (continuous strain) and Voigt (continuous stress) limits.[8,9]

It is very surprising that despite the different temperature dependences observed for different samples, the variation of G and E were so similar for each sample, as these generally involve very different averages over the single crystal elastic constants. However, if the single crystal shear moduli are small, then the isotropic polycrystalline B~3G, and both E and G will depend only on the single crystal shear moduli, while the bulk modulus will depend on longitudinal moduli, with K >> G. For example, for crystals of cubic symmetry,[9] in the Voigt limit

$$G_V = [(C_{11}-C_{12}) + 3C_{44}]/5$$

and in the Reuss limit,

$$G_R = 5[(C_{11}-C_{12})/4+C_{44}/3],$$

while in either limit $K = (C_{11} + 2C_{12})/3$ and $G/E = 1/3 + G/9K$. For noncubic systems, C_{11}, C_{12}, and C_{44} must be replaced with the appropriate averages of elastic moduli (or compliances in the Reuss limit).[9] Thus, the similar temperature dependences of G and E implies in itself that K>>G, so that B~3G, consistent with our measured value. Ultrasonic measurements of the longitudinal sound velocity determine the effective modulus $K' = K+4G/3$;[9] previous measurements[4] give $K' = 1.9x10^{12}$dyne/cm^2, and hence K~0.9K'~10G.

While all the above results give a consistent picture of the elastic properties of the samples, a few caveats must be kept in mind:

1) It is not clear if the samples are in fact isotropic, i.e. to what extent they may be textured.

2) Samples measured by others may differ from ours in morphology, density, and chemical heterogeneity. In particular, the samples discussed in Reference (2) were prepared differently.

3) Other groups have measured[3] $E = 1.9x10^{12}$dyne/cm^2~K', and estimated[11] (from Brillouin scattering) G~$7x10^{11}$dyne/cm^2, much greater than our values, and inconsistent with the "identical" temperature dependences of E and G for a given sample.

4) Qualitatively, K' has a temperature dependence similar to that of G.[4] Since the quantitative dependence of G is extremely sample dependent, it is desirable to measure K' and G (or E) for the same sample, as they are certainly not expected to be quantitatively the same. (For example, for $YBa_2Cu_3O_7$,[12-14] they are qualitatively very different.)

5) The effect of voids is difficult to estimate; they tend to make the experimental Young's and bulk moduli more strongly dependent on the single crystal shear moduli than on longitudinal moduli.[15] (This may help explain caveat (4) above.)

At T_c, we observe a large variation in the magnitude of elastic anomalies, with ΔG/G varying from $-2x10^{-4}$ (#4) to $-2x10^{-3}$ (#5). It is not clear if this variation is due to heterogeneity in crystallite packing or to chemical heterogeneity, i.e. the fraction of superconducting material. It should be noted (Figure 2) that the elastic anomaly coincides with the resistive drop, but the former, while very sharp (ΔT<1K), depends on the distribution of critical temperatures throughout the sample rather than the existence of a percolative path. The largest elastic change observed is an order of magnitude less than that observed for the shear modulus of YBa_2Cu_3O7,[14] but is still dramatically large; as discussed above, no anomaly in volume-conserving shear moduli is expected for a Landau-type second-order phase transition, and none is observed in "conventional" superconductors.[5] Unlike the case for $YBa_2Cu_3O_7$, however,[14] there is no anomalous increase in the loss, $1/Q$, in the superconducting state.

The strong increase in the shear modulus below T_c is also very surprising. Stiffening of the longitudinal moduli is expected from the Bohm-Stever relation,[13] but much greater increases than expected (i.e. also~1%) have been observed in ultrasonic measurements as well.[4]

The large shear softening below room temperature is probably due to the canting of the Cu-O planes and resulting tetragonal to orthorhombic distortion.[6] In $La_{1.85}Sr_{0.15}CuO_4$, this distortion has an onset at 180K and saturates at 60K,[16] but both temperatures have been shown to depend extremely strongly on Sr concentration,[17] explaining the ranges of values we observe. It is noteworthy that the superconducting transition temperature (i.e. as indicated by the "bulk" elastic measurement) is unaffected by the large variation in T_{min}, ranging from T_c to 100K higher, indicating that the superconductivity is not simply related to an incipient soft mode.

The observed elastic hysteresis between T_{min} and T_{max} cannot be viewed as superheating or supercooling, as the samples' elastic properties lag behind their "equilibrium" values, and probably does not reflect hysteresis in the single crystal elastic properties. The simplest explanation is that the "creep" and hysteresis are due to a distortion driven, slow resettling of the crystallites into low-energy, "stiff" positions, analogous to the slower and smaller drifts with time also observed for the La_2CuO_4 sample. Due to the temperature dependent distortion and "random" crystallite orientations, these "stiff" positions change with tempreature. In particular, the coefficients of thermal expansion are very anisotropic at these temperatures,[16] with $\Delta b/b \sim \Delta c/c \sim -\Delta a/a$! That neighboring crystallites may also differ in Sr concentration and distortion amplitude will further enhance the degree of resettling. However, it is interesting that the slow settling mostly occurs when cooling after (but not during) a "long" warming interval, i.e. when increasing the lattice distortion after a slow decrease. In fact, if the slow cool during an "f_H rise" is stopped and the sample is slowly warmed again, the frequency change seems to reverse itself (not shown in the Figure). It is obviously of interest to measure elastic properties of single crystals, not only to see if the hysteresis in fact still occurs, but also to determine the "true" amount of elastic softening which accompanies both the tetragonal to orthorhombic and superconducting phase transitions.

In summary, we have demonstrated the difficulty in understanding the elastic properties of these polycrystalline materials, especially in view of the fact that the low temperature structural distortions depend very critically on Sr doping concentration. Nevertheless, we conclude that the single crystal elastic moduli will be very anisotropic; i.e. the shear moduli will be small, resulting in $K \sim 10G$ for the polycrystal. Elastic hysteresis is probably driven by the relative motion of crystallites undergoing lattice distortions, with resulting anisotropic thermal expansion. As for $YBa_2Cu_3O_7$,[14] there are large, anomalous changes in the shear modulus at and below T_c.

Acknowledgement-This work was funded in part by the National Science foundation--Solid State Physics, Grants #DMR-8615463 and #DMR-8400041.

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