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ELASTIC PROPERTIES OF SINGLE CRYSTAL $Bi_2Sr_2CaCu_2O_8$

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We have measured the (in-plane) Young's and (out-of-plane) shear moduli of superconducting crystals of $Bi_2Sr_2CaCu_2O_8$ (T_c = 88K) as functions of temperature using "vibrating reed" techniques. No anomalous behavior is observed at any temperature (below room temperature), consistent with conventional thermodynamic behavior at T_c and the absence of other structural phase transitions.

1. Introduction

Since the discovery of "high temperature superconductivity" in the layered cuprates[1], there have been many reports of measurements of their elastic properties[2-11]. The motivation for these experiments has been both to illuminate the thermodynamics of the superconducting transition[12,13], and to search for additional (structural) phase transitions. Regarding the latter, most experimenters agree on the presence of one or more structural transitions in both the "214" (e.g. $La_{2-x}Sr_xCuO_4$)[2,3,4] and "123" (e.g. $YBa_2Cu_3O_y$)[3,6,8] families of materials, although the relationships of these transitions to superconductivity is not clear.

On the other hand, the results of measurements, mostly on sintered pellets, at T_c vary. For the 214 compounds, minima of ~0.1% have been observed for the Young's, bulk, and shear moduli, with the moduli increasing anomalously below T_c[2,3,4]. For the 123 compounds, no minima in the bulk or Young's moduli are observed; estimates of anomalous stiffening below T_c vary from zero to 0.8%[3,6,7,8]. For the shear modulus, both increases[3] and decreases[5] of up to 1% at T_c have been reported.

This variation in results presumably reflects differences in sample compaction and texturing (crystallite alignment) in sintered samples. Nonetheless, it appears that the polycrystalline elastic properties are dominated by changes in the single crystal shear moduli[3,4]. Since general thermodynamic arguments[12] predict no discontinuities or large anomalies in high symmetry shear moduli, the variety of large anomalies observed at T_c is therefore quite surprising. However, for polycrystalline samples, such moduli (e.g. c_{44}) must be averaged with the "off-axis" shear moduli [e.g. $1/2(c_{11}-c_{13})$];[4] the latter can be discontinuous[13], e.g. if the strain derivatives at T_c are anisotropic ($\partial T_c/d\varepsilon_1 \neq \partial T_c/d\varepsilon_3$). In general, the difficulty in correctly averaging the crystallite anisotropies, and accounting for sample voids and texturing, have prevented a quantitative understanding of the polycrystalline elastic properties[4,13].

Recently, results of elastic measurements on 123 single crystals have been reported[9,10,11]; surprisingly, results still vary. Ultrasonic measurements[9] revealed no anomalous behavior at T_c (i.e. $\Delta c/c < 5\times10^{-5}$) for c_{11}, c_{33}, and c_{44}. On the other hand, vibrating reed measurements indicated small dips in the (in-plane) Young's modulus[10,11] of $1\text{-}4\times10^{-4}$, and a region of increased slope below T_c for both the Young's and shear moduli[11] (e.g. $\Delta d\ln c_{44}/dT \sim 1.5\times10^{-4}K^{-1}$).

In this paper, we report on measurements of the Young's and shear moduli of single crystals of superconducting $Bi_2Sr_2CaCu_2O_8$ ("BSCCO").[14] No anomalies are observed in either modulus at any temperature; i.e. there is no indication of any structural phase transition (below room temperature) nor of unusual elastic behavior at the superconducting transition.

2. Sample Preparation and Experimental Techniques

The crystals of BSCCO were grown at the University of California at Berkeley from a mixture of Bi_2O_3, CuO, $SrCO_3$ and $CaCO_3$ with molar percentages of respectively 22.4%, 32%, 26.9%, and 18.7%. The powders were mixed in a ball mill with acetone, then placed in a gold crucible and heated at 920°C for 5 hours and cooled to 820°C at a rate of 3°C/hr. in flowing oxygen. The result was a black, glasy mass

that cleaved into micaceous sheets. Small "foil" shaped crystals were removed from the mass for characterization and measurement. X-Ray analysis showed that the $\hat{c}$-axis was perpendicular to the cleavage plane and had a spacing of 3.0 nm, in agreement with the $Bi_2Sr_2CaCu_2O_8$ compound identified by others[14,15], but we did not determine the orientation of the $\hat{a}$ and $\hat{b}$ axes in the crystals used in the elastic measurements. The stoichiometry was confirmed by SEM elemental analysis of single crystals.

The samples were characterized by both 4-probe dc resistance and dc magnetic susceptibility mesurements, which indicated a bulk transition temperature of approximately 88K. Full transition widths were of order 2-3K.

Crystalline samples were mounted as cantilevered reeds by glueing one end to a copper rod with silver paint. Typically, the samples were 3-20 μm thick (i.e. along $\hat{c}$), 30-300 μm wide, and 1-2 mm long. Flexural and torsional vibrations were driven and detected with electrostatically coupled electrodes[4,16]. To allow us to couple to torsional modes, a stiff wire "flag" was attached to the free end of the sample with vacuum grease and silver paint[4]; the flag also lowered the resonant frequency of the flexural modes of thicker samples to convenient values (e.g. <10kHz).

Changes in resonant frequencies, and hence elastic moduli, of several crystals as functions of temperature were precisely measured at the University of Kentucky, as described elsewhere[16]. For the fundamental shear mode, the resonant frequency $f_G \propto G^{1/2}$, while for the fundamental flexural mode, $f_E \propto E^{1/2}$, where E and G are the appropriate Young's and shear moduli, respectively[4]. Due to irregularities in sample dimensions, however, we could not meaningfully estimate the absolute magnitudes of the moduli. Also, because we did not determine the orientation of the $\hat{a}$ and $\hat{b}$ axes of our samples, the measured Young's modulus may be E_1 ($=1/s_{11}$), E_2 ($=1/s_{22}$), or some average, and G may very between c_{44} and c_{55} (or, in fact, include off-diagonal shear moduli). From the crystalline structure[15], large anisotropy is not expected in the $\hat{a}\hat{b}$ plane, the major anisotropic feature being the superlattice modulation along $\hat{b}$. The (very interesting) in-plane shear modulus, c_{66} could not be measured.

The temperature dependence of the quality factor (Q) for each mode was also measured. Changes in internal friction are given by $\Delta 1/Q$.

3. Results and Discussion

The temperature dependence of E and G for two samples is shown in Figure 1. The solid curves show the "uncorrected" results; i.e. $\Delta G/G = 2\Delta f_G/f_G$ and $\Delta E/E = 2\Delta f_E/f_E$. A large hysteretic jump occurred (for samples with "flags") between 190 and 240K, and a smaller anomaly was observed at ~150K. The hysteretic behavior was subsequently shown, using differential scanning calorimetry, to be due to a first order transition in the vacuum grease used to attach the flags. A 150K anomaly was also observed for a "dummy" metal sample "glued" with the same conducting paint as used for the BSCCO samples,

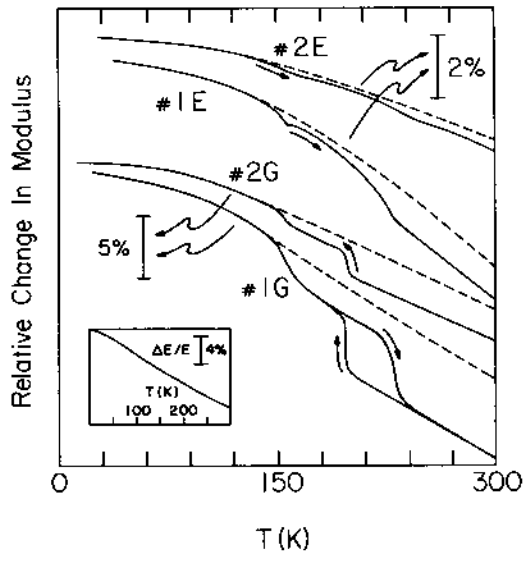

Figure 1: Relative changes in Young's (E) and shear (G) moduli of two crystals of BSCCO vs. temperature, measured at the University of Kentucky. The solid curves are experimental values (i.e. propertional to frequency shifts); the dashed lines show values corrected for anomalies in the clamping materials (see text). The vertical offsets are arbitrary. Inset: Relative change in Young's modulus of a sample measured at the University of California, as previously reported[10b].

and is therefore believed to be due to this paint. In fact, results for the Young's modulus of a sample previously measured at Berkeley[10b] are shown in the inset; no anomalies at these temperatures are observed. The dashed curves in Figure 1 show the "intrinsic" behavior of the cyrstals, i.e. they are (visually) corrected for the changes due to the vacuum grease and silver paint.

As seen, there is considerable sample dependence of the overall temperature dependence. This variation presumably reflects excitation of "impure" modes, especially probable for the torsional oscillations of wide samples, as well as different orientations in the $\hat{a}\hat{b}$ plane. (Sample #2 had the most "ideal" geometry, width comparable to thickness, for a "pure" torsional oscillation.) The observed variation for the Young's modulus (i.e. [E(0K)-E(300K)]/E varies from 3% to 11%), suggests that the $\hat{a}\hat{b}$ plane has considerable elastic anisotropy, contrary to expectations.

Details of results near T_c are shown in Figure 2. No anomalies are observed in either modulus or their internal friction; $\Delta 1/Q < 10^{-5}$ for both modes, in marked contrast to large anomalies observed in the internal friction for the 123 compounds[10,11]. Upper limits on the anomalies in the moduli are $\Delta E/E < 5\times10^{-5}$ (sample #3), $\Delta d\ln E/dT < 4\times10^{-6}K^{-1}$ (#1), $\Delta G/G < 10^{-4}$ (#2), and $\Delta d\ln G/dT < 4\times10^{-5}K^{-1}$ (#2). These upper limits are generally less than the anomalies observed in the 214 and 123 compounds[2-11].

These generalized Ehrenfest equations for

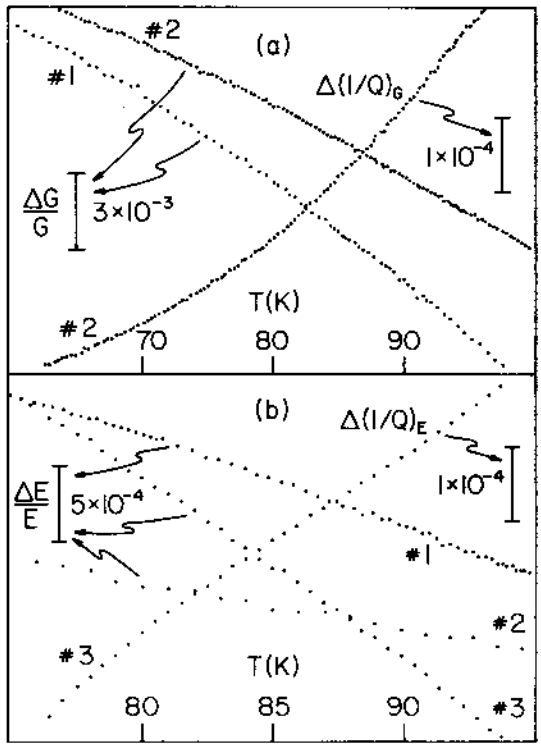

Figure 2: a) Relative changes in the shear modulus, and related internal friction, for two crystals near T_c (88K). b) Relative changes in Young's modulus, and related internal friction, for three crystals near T_c.

a second order phase transition give:[12,13]

$$\Delta c_{\beta\beta} = 0$$

$$\Delta E_\alpha/E_\alpha = -\frac{E_\alpha \Delta C}{T_c} (\partial T_c/\partial\sigma_\alpha)^2 \qquad (1)$$

$$\Delta d\ln E_\alpha/dT = -\frac{E_\alpha \Delta C}{T_c} [\partial^2 T_c/\partial\sigma_\alpha^2 + \frac{2z}{T_c} (\partial T_c/\partial\sigma_\alpha)^2] \qquad (2)$$

$$\Delta d\ln c_{\beta\beta}/dT = -\frac{c_{\beta\beta}\Delta C}{c_{\beta\beta}} \partial^2 T_c/\partial\sigma_\beta^2 \qquad (3)$$

where σ is the stress, C_p is the specific heat, and (in our case) $\alpha = 1,2$ and $\beta = 4,5$. z is a number (of order unity) that depends in detail on the temperature dependence of the free energy near T_c. (There are also corrections to Eqtns. 2 and 3 due to anharmonicity, strain dependent band structure, etc.[12,13]). If we assume that E_α~220 GPa, $C_{\beta\beta}$~130 GPa, and ΔC_p~4J/mole K, as for the 123 superconductors[3,14,17], we find from Eqtn. 1 that $|dT_c/d\sigma_\alpha| < 0.08$ K/kbar. This value is comparable to the measured pressure dependence, dT_c/dP=0.17 K/kbar,[18] so the stress dependence need not be very anisotropic in this material. The normalized derivative $|(E_\alpha/T_c)dT_c/d\sigma_\alpha| < 2$, comparable to the lowest estimates (from neutron diffraction)[13,19] for 123. However, in the present case, unlike for 123,[13] the change in slope of E is sufficiently small that one need not assume an anomalously large second derivative of T_c with uniaxial strain; i.e. the second term on the right of Equation 2 ($< 10^{-6}zK^{-1}$) can be comparable to the left hand side. For the shear modulus, with an order of magnitude poorer resolution, we have (from Equation 3) $d^2T_c/d\sigma_\beta^2 < 9\times10^{-3}$K/kbar^2; i.e. $(c_\beta^2/T_c)d^2T_c/d\sigma_\beta^2 < 170$. This latter value is an order of magnitude less than that estimated for the other cuprate superconductors (from polycrystalline elastic measurements);[13] from the large second derivatives needed for these, it was speculated that the order parameter was strongly coupled (quadratically) to shear strains, perhaps due to an inhibited structural distortion.[13] Our results suggest that this is not so for BSCCO. However, it should be reemphasized that we are not sensitive to the in-plane shear modulus (c_{66}).

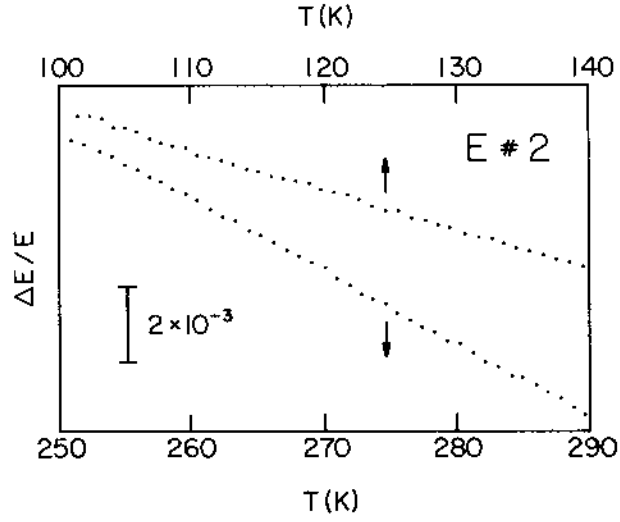

Figure 3: Relative change in Young's modulus for sample #2 in two temperature intervals above T_c.

No anomalies (not attributable to the clamping materials) in either modulus ($\Delta E/E$, $\Delta G/G < 10^{-4}$) or internal friction are observed at any other temperature as well. For example, details of the Young's modulus of sample #2 in two temperature regions are shown in Figure 3. The absence of a phase transition between 120K and room temperature was confirmed by differential scanning calorimetry on a sample consisting of two large flakes of total mass 32mg. As shown in Figure 4, the DSC heating curve, (roughly proportional to the change in specific heat) is remarkably featureless, in contrast to the curve observed for 123.[8] As mentioned above, there have been speculations that various structural changes in the 214 and 123 compounds are related to their high-temperature superconductivity[2,6,8]; we find this not to be the case for BSCCO, for which any structural transition (e.g. formation of the superlattice) must occur above room temperature.

In conclusion, no anomalies are observed in the (in-plane) Young's modulus and (out-of-plane) shear modulus of $Bi_2Sr_2CaCu_2O_8$,

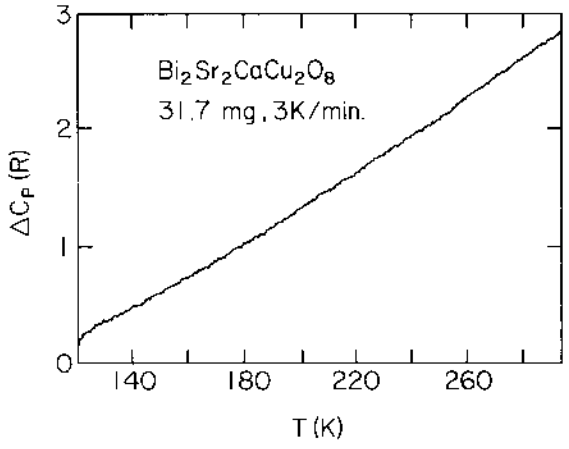

Figure 4: Differential scanning calorimetry trace (heating curve) for a sample consisting of two small flakes of BSCCO.

implying both no unusual thermodynamics at the superconducting transition (e.g. due to an incipient soft-mode) and the absence of additional phase transitions.

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