Evidence in the Elastic Properties for a Stress-Related Phase Transition in the High-T_c Material: $Bi_2Sr_2CaCu_2O_x$

T. M. Tritt,[1] M. Marone,[2] A. C. Ehrlich,[1] M. J. Skove,[2] D. J. Gillespie,[1] R. L. Jacobsen,[1] G. X. Tessema,[2] J. P. Franck,[3] and J. Jung[3]

[1]*Materials Physics Branch, Naval Research Laboratory, Washington, D.C. 20375*
[2]*Department of Physics, Clemson University, Clemson, South Carolina 29634*
[3]*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G 2IJ*
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We have measured the stress-strain properties of whiskerlike samples of the high-T_c material $Bi_2Sr_2CaCu_2O_x$. We observe an anomalous temperature dependence of Young's modulus (Y) around 300 K. The magnitude of Y falls by a factor of 3–4 between 270 and 330 K. We also observe hysteresis in the stress-strain curves in this same temperature range. The stress and strain relax toward the middle of the hysteresis loop with a characteristic time of approximately 20 sec. All these phenomena are reproducible as either the stress or temperature is cycled.

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Anomalous elastic properties and high-temperature superconductivity (HTSC) have a long history of association. For example, an early A-15 HTSC, V_3Si, displayed a martensitic, ferroelastic phase transition associated with a structural phase transition from cubic to tetragonal [1]. The superconducting transition temperature T_c and the martensitic temperature T_m are close: $T_c=17$ K and $T_m=27$ K. Ferroelasticity and ferroelectricity have been known to exist in the perovskites such as $BaTiO_3$ since the 1940s [2] and ferroelasticlike behavior has been recently reported in polycrystalline samples of the more recent HTSC materials [3,4]. Most recently Bussman-Holder *et al.* [5] and Semenovskaya and Khachaturyan [6] have reported theoretical calculations of structural instabilities in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$, respectively. The former focuses on a soft-mode-induced structural instability whereas the latter deals with transformations due to strain accommodations. In this paper we report a particularly dramatic manifestation of the structural instabilities that often characterize the HTSC materials [5]. We have measured for the first time in a single-crystal HTSC whisker the temperature dependence of the tensile elastic properties and have observed a thermoelastic phase transformation and its temperature dependence, specifically in $Bi_2Sr_2CaCu_2O_x$.

The new HTSC perovskite materials include the Bi-based system [7]. This system consists of many superconducting phases, the best known of which are $Bi_2Sr_2Ca_0Cu_1O_x$ (2:2:0:1), $Bi_2Sr_2Ca_1Cu_2O_x$ (2:2:1:2), and $Bi_2Sr_2Ca_2Cu_3O_x$ (2:2:2:3), with $T_c=10$, 85, and 110 K, respectively [8,9]. The large complicated unit cell and crystal structure have been described for each of these phases [10–13]. Adding to the complexity of these materials is an incommensurate superlattice (in 2:2:1:2) which has been attributed to compositional or displacive fluctuations of the Bi atoms. Buckling of the CuO_2 and Bi crystal planes has been associated with the superlattice and the buckling is a result of a large intrinsic strain in the crystal [13–15].

Whiskers of three of the superconducting phases of the Bi materials have been grown. Jung *et al.* have grown whiskers of the 2:2:1:2 and 2:2:0:1 compounds from a ceramic pellet [16]. Others have added a small amount of Pb and grown whiskers of the 2:2:1:2 and 2:2:2:3 compounds [17,18]. To the best of our knowledge, no whiskers of any other high-T_c compound have been grown. Our HTSC whiskers have been shown to exhibit elastic properties similar to those observed in high-quality whiskers of other materials [19]. We have reported on the magnitude of Young's modulus Y for whiskers of the 2:2:1:2 and 2:2:2:3 phases [20]. We found these materials to have relatively low values of Y: $Y=20$ and 30 GPa for the 2:2:1:2 and 2:2:2:3 materials, respectively, a Y comparable to that of Pb ($Y_{Pb}=15$ GPa). We also found that both materials, 2:2:1:2 and 2:2:2:3, could withstand large uniaxial stress reversibly. Other types of elastic measurements that have been performed in the high-T_c materials include ultrasonic measurements of the sound velocity and measurements of Young's modulus and internal friction using a vibrating-reed technique [4,21–24].

In this paper we report on the anomalous elastic properties and subsequent temperature dependence that we observe in single-crystal whiskers of the 2:2:1:2 material around $T=300$ K. The magnitude of Y decreases by a factor of 3–4 between 270 and 330 K (from a maximum of $Y=20$ GPa at 270 K). In addition, we observe hysteresis in the stress-strain curves at temperatures above $T\approx 275$ K. This large decrease in Y and its overall temperature dependence along with the presence of hysteresis demonstrates the existence of a phase transition. This transition is manifesting itself by a reversible deformation mechanism induced by stress. Hysteresis in the stress-strain relation is of similar form to that for a ferroelastic transition [2].

Single-crystal whiskers of the 2:2:1:2 material were grown by Jung and Franck [16]. They investigated several samples in an electron microscope. They determined the unit cell dimensions to within 1% and the results essentially agreed with the more precise results of Sunshine *et al.* [10] who found $a=5.414$ Å, $b=5.418$ Å, and $c=30.89$ Å. Furthermore, Jung and Franck clearly observed the incommensurate modulation along the b axis and also found that the b axis along several places on an individual whisker was always perpendicular to the a axis (the growth direction of the whiskers) [25]. The same result was found for each whisker and for several selected areas of individual whiskers. The a axis (unmodulated) is the growth direction of the whiskers and the b axis (modulated) lies in the flat plane with the c axis perpendicular to this. Thus, there is no evidence of the common 90° twist observed in the ceramic 2:2:1:2 materials [26]. These results show that these whiskers are single-domain crystals and that they are crystallographically identical. These whiskers have typical dimensions of 0.4–1.0 mm $\times$2–15 μm$\times$1–4 μm. Jung *et al.* [16] and Gygax [27] mounted similar 2:2:1:2 whiskers in a SQUID magnetometer with the c axis perpendicular to the magnetic field (B parallel to the a-b plane) and were able to detect the superconducting transition, $T_c \approx 75$ K.

We utilized a stress-strain probe which allows us to measure Y of whiskerlike materials; $Y=\Delta\sigma_{11}/\Delta\varepsilon_{11}$, where σ_{11} is the uniaxial stress and ε_{11} is the strain. This device, calibrations, and measuring techniques are described in detail elsewhere [28]. Summarizing, the stress-strain probe allows static, nearly uniform stress to be applied in a smooth, reversible manner while the elongation of the sample is measured. One end of the sample is attached to a movable rod suspended by leaf springs and the other end is held fixed. Force is applied to the sample by a coaxial electromagnet acting on permanent magnets attached to the movable rod and displacements are measured capacitively. This device fits into a Dewar allowing temperature variation: 20 K $< T <$ 360 K. The data are taken by performing the stress-strain measurement at various selected temperatures constant to within ± 30 mK.

A plot of the total applied force versus displacement ($F_{\rm tot}$ vs Δd) for a 2:2:1:2 whisker at $T=255$ and 300 K is shown in Figs. 1(a) and 1(b), respectively. The sample starts out in a bowed configuration and as force is applied, the rod moves, unbowing the sample. To find the force on the sample the contribution of the leaf springs is then subtracted as discussed in the figure caption. A stress-strain (σ-ε) plot extracted from the data in Fig. 1(a) ($T=255$ K) would be linear and elastic up to $\varepsilon \approx 0.7\%$ with no sign of hysteresis. However, a much different behavior is observed above 275 K. As seen in Fig. 1(b), hysteresis is quite evident in the $F_{\rm tot}$ vs Δd plot at $T=300$ K. The total force $F_{\rm tot}$ is increased to its maximum value, as indicated by the asterisk (in a time of 15–60 sec, with no significant difference seen), and then held constant. With $F_{\rm tot}$ held constant, the sample then undergoes a relaxation, in a characteristic time of 20 sec, which results in a lengthening of the sample. Our device

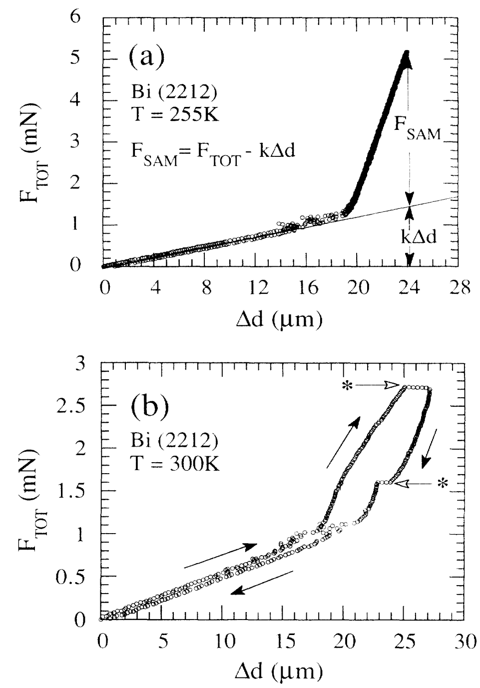

FIG. 1. (a) The total applied force ($F_{\rm tot}$) vs the displacement of the rod (Δd) at $T=255$ K. A large change in slope occurs when the sample gets tight. The smaller slope is due to the leaf springs (with the sample bowed) and is the spring constant of the apparatus ($k=0.065$ mN/μm). The force on the sample then is given by $F_{\rm sam}=F_{\rm tot}-k\Delta d$. (b) $F_{\rm tot}$ vs Δd at a temperature of $T=300$ K. $F_{\rm tot}$ was held constant at the points indicated by an asterisk and open arrows. The solid arrows indicate the direction of the applied force. Hysteresis is very much evident in this plot and the sample length or strain exhibits some type of relaxation.

goes from a uniformly increasing or decreasing force to a constant force in much less than a second (and probably on the order of milliseconds). After approximately 1 min, $F_{\rm tot}$ is then decreased to the point indicated by the other asterisk and held constant again. On this cycle of the hysteresis loop the relaxation results in a shortening of the sample, which does work against the device, with essentially the same characteristic relaxation time as before. If the force on the sample is reduced to zero and the experiment repeated, the same curve is traced out although the hysteresis loop is (10–20)% smaller than it was originally. Subsequent σ-ε cycles are essentially reproducible.

Resulting σ-ε curves from data such as in Fig. 1 are shown in Figs. 2(a)–2(f), with temperature as a parameter. As seen in Figs. 2(a) and 2(b), below $T=270$ K, the σ-ε relationship is linear and reversible up to elastic strains greater than 0.5%. There is some small curvature at small ε which is due primarily to uncertainty in the determination of zero strain. In Figs. 2(c)–2(f), hysteresis is apparent in the σ-ε curves above 275 K and grows as the temperature is increased from 275 to 300 K,

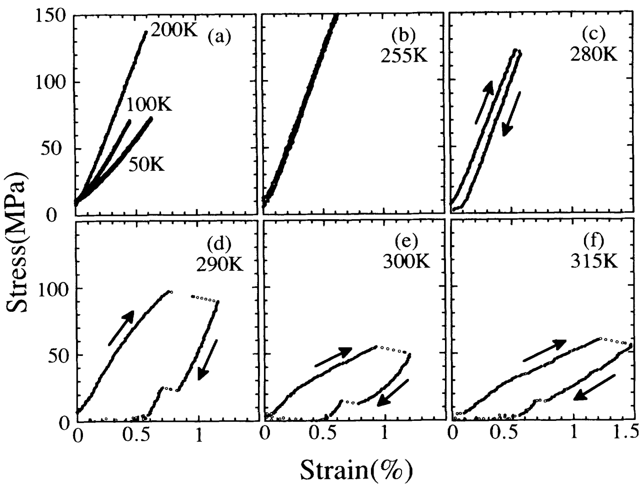

FIG. 2. Stress vs strain at various temperatures for a 2:2:1:2 whisker: (a) 50, 100, and 200 K; (b) 255 K; (c) 280 K; (d) 290 K; (e) 300 K; (f) 315 K. Hysteresis appears in the stress-strain relationship above 270 K. The direction of the hysteresis loop is indicated by the arrows. The slope of the stress-strain curve at $T=270$ K gives a value for Young's modulus of 20 GPa. The sample has the following dimensions: $L=0.65$ mm, $A=12$ μm^2.

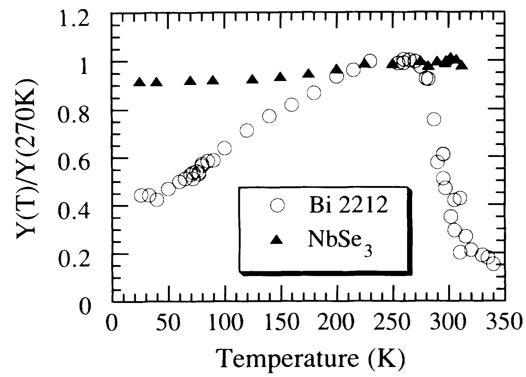

FIG. 3. The normalized modulus, $Y(T)/Y(270$ K), as a function of temperature for a sample of the 2:2:1:2 material (o) and a $NbSe_3$ sample (▲). The values of Y at $T=270$ K for the 2:2:1:2 and $NbSe_3$ samples are $Y=20$ and 91 GPa, respectively.

after which it seems to have saturated. A relaxation process is associated with the hysteresis, in which the stress and strain relax toward the center of the σ-ε hysteresis loop. Below 270 K, there is not any hysteresis down to the lowest temperature we investigated, 25 K.

The existence of hysteresis causes some ambiguity in the determination of Y. At a given temperature, we have used the initial linear region of the σ-ε slope to arrive at a value of Y for that temperature. This yields a larger value for Y than most other regions but is less apt to be associated with a phase change. The temperature dependence of Y normalized to its maximum value, $Y(T)/Y(270$ K), is shown in Fig. 3 for the 2:2:1:2 material. This curve shows a sharp decrease in Y, by a factor of 3–4, between 270 and 330 K.

For comparison, we also show in Fig. 3 the temperature dependence of $Y(T)/Y(270$ K) for a $NbSe_3$ whisker we measured with this σ-ε device. The $NbSe_3$ sample had a value of $Y=91$ GPa at $T=270$ K: a factor of 4–5 times larger than that of the 2:2:1:2 material. We chose $NbSe_3$ to act as a standard for a number of reasons: It too is a whiskerlike material and has interesting behavior over the desired temperature range; i.e., it has two charge-density-wave phase transitions which occur below 300 K ($T_{c1}=145$ K and $T_{c2}=59$ K) [29]. As seen in Fig. 3, there is, at most, a weak dependence of Y on temperature for the $NbSe_3$ sample, quite unlike that of the 2:2:1:2 samples. There was also no hysteretic behavior for the $NbSe_3$ sample. In addition, we have measured the stress-strain properties of the 2:2:2:3 material at 300 K with no indication of the hysteretic behavior we have observed in the 2:2:1:2 material. The techniques used for measuring all these samples were identical.

We have also measured the elastic properties of the 2:2:1:2 whiskers with the vibrating-reed (VR) technique. The characteristic relaxation time we report here (20 sec) is 4–5 orders of magnitude longer than the period employed in the VR (kHz) experiments. The anomalous temperature dependence of Y that we observe is not evident with the VR technique, as seen in Fig. 3. This suggests that some type of relaxation phenomena may exist. It could be very elucidating to determine whether the frequency or the stress level (both of which are orders of magnitude different with the two techniques) is more important in giving the differences. Nes *et al.* [24] and Xiang *et al.* [21] have also measured the temperature dependence of Y in single-crystal cleaved platelets of the 2:2:1:2 material using the VR technique. They observe a monotonically increasing modulus (only a few percent change in the range $20\ K < T < 300\ K$) with decreasing temperature which agrees with our VR results. They also observe three peaks in the internal friction at $T=145$, 225, and 285 K.

The data above $T=275$ K, on our single crystals, is characteristic of a first-order displacive phase transformation and in particular a ferroelastic transformation. For example, they bear a striking similarity to certain stress-induced transformations considered by Otsuka and Shimizu when discussing pseudoelasticity [30]. More generally, a thermoelastic martensitic phase transformation in which the pseudoelastic behavior can arise from one of two possible sources: (1) The applied stress induces the martensitic transformation at temperatures $T > T_s$, or (2) at $T < T_f$, the stress can move the intervariant interfaces, allowing certain variants to grow at the expense of others and thereby resulting in a strain. For example, two variants in the 2:2:1:2 Bi-Sr-Ca-Cu-O system might involve displacements of some atoms in the (100) and ($\bar{1}00$) directions.

The second possibility, involving a 90° twist, is not possible in our samples. The reversibility of the transformation mechanism is suggestive of a transition between different variants of some phase, but it cannot be a simple 90° twist because of both the single-domain nature of our sample and the following: If the buckling of the lattice changed from the *b* direction to the *a* direction under an *a*-direction stress, a lengthening of the sample would occur. But the difference in the best measurements [10,14] of the *a* and *b* lattice parameters is only approximately 4 parts in 5400, which is too small to account for the 0.4% change in dimension of the sample at constant stress seen in Fig. 2(d), even if *a* and *b* were interchanged over the whole sample. However, were this accompanied by even a partial unbuckling of the lattice, such a mechanism could easily account for our results.

The specific atomic rearrangement can only be speculated on here. There is a large mismatch between the actual constrained atomic spacing within the various layers and the relaxed atomic spacing within the layers [31]. This, in combination with the size and complexity of the unit cell, provides fertile grounds for a variety of displacive transformations. Indications of a number of phase transformations have been seen with ultrasonic-velocity and vibrating-reed experiments in the Bi 2:2:1:2 compounds [24] but none of these has been shown to be associated with a dimensional change of the unit cell. Whether such a transition includes diffusion is uncertain.

Studies by pair-distribution-function analysis of pulsed neutron scattering data in the crystallographically similar Tl-Ba-Ca-Cu-O system have recently been reported [31-33]. These studies show, among other things, displacements of O_3 and Tl atoms from their high-symmetry sites such as to give close to the expected spacing between these constituents and displacements of both the Cu and O in the CuO_2 plane. In both cases there is only short-range order and the average crystallographic position remains unchanged.

In summary, we have observed anomalous behavior in the temperature dependence of the elastic properties of whiskerlike samples of $Bi_2Sr_2CaCu_2O_x$. The dramatic temperature dependence of Y and the existence of hysteresis in the temperature range 270 K $< T <$ 330 K appears to indicate the presence of a new stress-induced phase transition or stress-related formation and dynamics of domain walls leading to the growth of one variant of a phase at the expense of the other. Much more investigation needs to be done to elucidate the exact origin of these results.

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