Elastic properties of few unit cell thick superconducting crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$

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We present systematic measurements of the mechanical properties of few unit cell (UC) thick exfoliated crystals of a high-T$_c$ cuprate superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$. We determine the elastic properties of these crystals by deformation using an atomic force microscope (AFM) at room temperature. With the spatial measurements of local compliance and their detailed modeling, we independently determine the Young’s modulus of rigidity and the pre-stress. The Young’s modulus of rigidity is found to be in the range of 22 GPa to 30 GPa for flakes with thickness from ~5 UC to 18 UC. The pre-stress spreads over the range of 5 MPa - 46 MPa, indicating a run-to-run variation during the exfoliation process. The determination of Young’s modulus of rigidity for thin flakes is further verified from recently reported buckling technique.

There has been a keen interest towards the use of two-dimensional (2D) thin materials for device applications. While the electrical properties of these materials cover a wide spectrum ranging from insulating, semiconducting, metallic to superconducting behavior, their mechanical properties such as modulus of rigidity, fracture-strain, and thermal expansion are equally intriguing. This remarkable combination of characteristics make these materials accessible to novel applications such as flexible electronics and hybrid nanoelectromechanical systems for sensing applications.

For nanoelectromechanical devices, materials with high electrical conductivity, and low mass are often preferred, as these properties tend to minimize the losses and improve the displacement transduction. The mechanical properties of few unit cells (UC) thick exfoliated crystals could be significantly different from its bulk counterpart, resulting in interesting effects such as nonlinear damping and Duffing phenomena. In addition, measurements of the elastic response could be a sensitive probe to the electronic or structural phase transitions in these materials. This has led to a considerable investigation into the nanomechanical properties of materials such as graphene, MoS$_2$, NbSe$_2$, etc.

Recently, few UC thick crystals of high-transition temperature superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO) have attracted attention due to their unique superconducting phase diagram, and applications towards cavity-optomechanical devices. While the elastic coefficients of the bulk crystals of BSCCO have been observed with large variations, there is no investigation into the elastic properties of few UC thick nanoscale samples. Here we report the measurement of Young’s modulus of rigidity (E) and pre-stress (σ) on few UC thick superconducting crystals of BSCCO. These properties are helpful in engineering the resonant frequency of mechanical resonators for composite devices. In addition, determination of the Young’s modulus of rigidity by two different methods, on the crystals grown in the same run, brings clarity to the previously reported results from bulk-crystals.

We have primarily used elastic deformation by an AFM tip to measure the Young’s modulus of rigidity and the pre-stress in exfoliated flakes of BSCCO. In total, we have studied 7 mesoscopic samples having thickness in the range of 16 nm to 55 nm, corresponding to ~5 UC to 18 UC thick crystals. We have performed measurements of the local compliance of the suspended flakes of BSCCO. Detailed finite-element modeling is then carried out to extract the Young’s modulus and the pre-stress from compliance measurements. In addition, we employ a recently reported buckling technique to independently measure the Young’s modulus for thin flakes. We find that the results from the buckling technique are consistent with the AFM technique.

High-quality single-crystals of BSCCO were prepared by annealing melt-quenched shards in oxygen atmosphere. The BSCCO shards were prepared by heating the BSCCO powder (Sigma Aldrich - 365106) in a high-quality recrystallized alumina crucible. After the annealing step, these crystals are stored in liquid nitrogen and are only taken out at the time of mechanical exfoliation. To prepare the samples for AFM measurements, we first use photolithography to pattern circular trenches in photoresist (S1813) on a 285 nm thick SiO$_2$ coated silicon substrate. It is followed by a step of reactive ion etching of SiO$_2$ using a low-pressure fluorine plasma. This results in circular trenches having diameter from 1.8 to 6 μm on the substrate. Thin flakes of BSCCO are exfoliated by a Scotch tape and transferred on top of the patterned substrate using a polydimethylsiloxane (PDMS) based dry exfoliation technique.

Fig. 1(a) shows an optical image of a transferred BSCCO flake on the patterned substrate. Different optical contrast for suspended and collapsed micro-drums can be seen in the image. Fig. 1(b) shows the topography of BSCCO flake alongside a height profile measured by AFM. Drums with an uneven topographic profile are not considered for measurements. The white dotted line indicates the location of the measured height profile. Transfer of flakes thinner than 16 nm (~5 UC)
FIG. 1. (a) An optical microscope image of BSCCO flake on top of a patterned Si substrate coated with 285 nm of SiO$_2$. Difference in the contrast for suspended and collapsed drums can be seen. The scale bar corresponds to 50 µm. (b) AFM image showing the topography of the flake. A height profile taken at the position marked by a dashed line is overlaid on the AFM image, showing a thickness of ∼16 nm. The scale bar corresponds to 8 µm.

Elastic deformation by an AFM tip is a well-established method to characterize the elastic properties of nanoscale materials. An AFM cantilever with a known spring constant is used to apply a force on top of the suspended structure. This force deflects the flake depending on the elastic properties of the material and boundary conditions. In this study, we used an AFM tip with a spring constant of $k_{\text{tip}} = 5.6$ N m$^{-1}$, measured using thermo-mechanical noise calibration. The spring constant of the tip relates the applied force $F$ to the tip deflection $\Delta z_{\text{tip}}$, given by $F = k_{\text{tip}} \Delta z_{\text{tip}}$. The elastic deformation of the flake $\delta$ then can be expressed in terms of the net displacement of the AFM piezo $\Delta z_p$ as: $\delta = \Delta z_p - \Delta z_{\text{tip}}$.

Fig. 2(a) shows traces of loading-curve for flakes of different thicknesses while indenting at the center of the circularly-shaped suspended part. We do not observe any hysteresis between loading and unloading curves, suggesting no slippage at the flake boundary. The loading curve is quite linear for the thick flake (31 nm). A nonlinear behavior can be easily observed for the thin flake (16 nm). Within continuum mechanics for an isotropic solid, the elastic deformation of the flake $\delta$ is related to the applied force $F$ as:

$$ F = \frac{4\pi E}{3(1-\nu^2)} \left( \frac{t^3}{a^2} \right) \delta + (\sigma \pi t) \delta + \left( q^3 E t^3 \right) \delta^3, \quad (1) $$

where $q = 1/(1.049 - 0.15\nu - 0.16\nu^2)$ is a dimensionless constant, $a$ and $t$ are the radius and thickness of the suspended BSCCO flake, respectively. By using a Poisson's ratio of $\nu = 0.2$ for BSCCO, and other geometrical quantities obtained from the AFM measurements, we fit the loading curves using Eq. 1 shown by the solid lines in Fig. 2(a).

In the membrane-limit, the contribution from bending rigidity (first term in Eq. 1) can be neglected and the nonlinear relation between force and deformation can be used to extract the pre-stress and Young’s modulus independently. In the plate-limit however, due to the comparable contributions from bending rigidity and tensile stress to the total elastic energy, it is impossible to separate out $\sigma$ and $E$ from the deformation measurement at the center of the flake alone. Therefore, we resort to the spatial measurement of local compliance, defined...
as \( k^{-1}(r_0, \theta_0) = (d\delta/dF)|_{r_0, \theta_0} \), over the suspended part of the flake.\(^{27}\) Spatial map of the measured local compliance over a grid of 64x64 points for a suspended flake of \( \approx 3 \mu m \) diameter is shown in the inset of Fig. 2 (b). As the compliance profile is radially symmetric, Fig. 3(b) shows the variation of \( k^{-1} \) with the distance from the center of the flake \( r_0 \).

To extract the elastic properties of the BSCCO flakes from the spatial compliance maps, we perform finite element simulations using COMSOL (see Supplementary Material (SM) for details). For a linear elastic solid, the deformation under a point load can be well described by the Euler-Lagrange differential equation.\(^{28}\) However, when the contribution of bending rigidity and pre-stress to the elastic energy are comparable, it is difficult to find a closed-form solution of the elastic deformation \( \delta(r, \theta) \) and hence compliance \( k^{-1} = \partial \delta / \partial F \). To model the system, we consider the deformation of a linear elastic material under a load applied by an AFM tip of 40 nm radius. A rigid boundary condition is applied at the edge of the elastic material under a load applied by an AFM tip of 40 nm radius.

The radial shape of the compliance, however, depends on the ratio of pre-stress and bending rigidity \( D = \frac{E\delta}{12(1-\nu^2)} \). Fig. 3(b) shows the plots of the simulated radial profile of normalized compliance \( k^{-1} / k^{-1}(r_0 = 0) \) for three different values of \( \lambda \), defined as \( \lambda = \sqrt{\frac{\sigma o^2}{D}} \). To fit the simulated results with the experimental data, we choose the contour of \( k^{-1}(r_0 = 0) \) that matches with the AFM data. Along this contour, radial compliance profiles are computed for various combinations of \( (E, \sigma) \) to fit the experimentally obtained data. A result of this procedure is shown in Fig. 2(b) by a black continuous line.

A plot summarizing the Young’s modulus and the pre-stress for 7 different exfoliated flakes of varying thickness is shown in Fig. 3(c, d). Detailed characterization of these flakes is provided in the SM. It is important to highlight that the pre-stress in these flakes results from the dry transfer process and is independent of material properties. Therefore, it spreads over significantly from 5 MPa to 46 MPa. However, the Young’s modulus of rigidity is found to be in the range of 22 GPa to 30 GPa. Typically, elastic coefficients of ultra-thin samples, where the surface elastic energy is non-negligible to the bulk elastic energy, show a thickness-dependent \(^{12,13,29}\). We do not observe any prominent thickness dependence in the Young’s modulus of rigidity as the samples studied here are at least 16 nm thick.

The Young’s modulus of rigidity can also be determined by a simple buckling technique.\(^{21}\) We use this technique to independently verify the AFM results. A schematic representation of the steps used for buckling of BSCCO is shown in Fig. 4(a).

In this process, flake is transferred directly on a pre-stressed substrate. We use a PDMS substrate (PF-X4 6.5 mil from Gel-Pak), which has Young’s modulus of \( E_s = 492 \) kPa and Poisson’s ratio of \( \nu = 0.49 \). PDMS is elongated up to 30-40% of its original length in a direction perpendicular to its surface to generate the pre-stress. After releasing the stress from PDMS, BSCCO flake buckles with a particular wavelength.

Fig. 4 (b) shows an optical microscope image of buckled BSCCO flake over PDMS substrate. Different buckling wavelengths for different thickness are evidently visible. The wavelength of induced ripples (\( \lambda_b \)) is independent of initial stress and depends on the elastic properties of both flake and substrate, given by \(^{21}\)

\[
\lambda_b = 2\pi t \left( \frac{1 - \nu_s^2}{3(1 - \nu^2)E_s} \right)^{\frac{1}{2}}.
\] (2)

The wavelength is estimated by analyzing the optical microscope image of the buckled structure. For calibration of length, micron/pixel is calculated using a pre-patterned sample with known dimensions. The thickness of the flake was measured to be 7 UC using AFM. The average value of \( \lambda_b \) is \( \sim 2.11 \mu m \), calculated from four different data points. Using Eq. 2, we estimated the Young’s modulus of rigidity to be 24.5 GPa, which is similar to values obtained from the AFM measurement.

It is interesting to contrast our results on few UC samples to the observations made on the bulk crystals of BSCCO and other high-\( T_c \) layered superconductors. The Young’s modulus of rigidity for bulk crystals of BSCCO has been reported over a range of values (see Table I). Crystalline quality dependent variations in the Young’s modulus of rigidity has been observed for other layered high-\( T_c \) superconductors such as \( \text{YBa}_2\text{Cu}_3\text{O}_y \).\(^{19,20}\) The reduction in modulus of rigidity and breaking strength can be attributed to defects formed during the crystal growth process.\(^{13,32}\) Under a normal applied load, the material tends to yield at the defect sites first, before stretching of the atomic bond.\(^{33}\) Importance of the defect density in determining elastic coefficients and the breaking strength has been reported for mesoscopic samples of different materials.\(^{14,15,19}\) Layered superconductors having several weakly interacting layers with defects are therefore expected to show reduced material stiffness.

For application towards the composite nanoelectromechanical devices, the resonant frequency of the mechanical resonator is an important design parameter. From the variation in the Young’s modulus and pre-stress reported in this study, we expect the mechanical resonance frequency to be in the range of 6 MHz to 18 MHz for 5 UC thick crystals of 6 \( \mu m \) diameter, as also observed experimentally.\(^{36}\) We further note that for few UC thick mechanical resonators, the resonant frequency is primarily dominated by the pre-stress induced by the exfoliation process. The expected high frequency of BSCCO mechanical resonators and typical linewidhts of superconducting microwave resonators (< 500 kHz) place these devices in the sideband-resolved limit, an important criterion for experiments in the quantum limit.\(^{13}\)
FIG. 3. (a) Contour plot showing local compliance $k^{-1}$ at the center of the drum with a variation of the Young’s modulus and pre-stress, simulated by finite element method. (b) The simulated radial profile of compliance for different values of $\lambda$ given by 1 (blue), 10 (orange) and 100 (green), respectively. Panels (c) and (d) show the extracted value of the Young’s modulus and pre-stress of BSCCO flakes of different thicknesses. The error bars are calculated from the spread in the radial compliance data.

TABLE I. Summary of Young’s modulus of rigidity for high-$T_c$ superconductors

| Material | Structure | Technique | Technique                  | $E$ [GPa] |
|----------|-----------|-----------|----------------------------|-----------|
| BSCCO    | bulk polycrystalline | ultrasonic velocity $^{[19]}$ | 38.8 |
|          | bulk single crystal | vibrating reed $^{[20]}$ | 70 |
|          | few unit cells thick | AFM and buckling methods $^{[22]}$ | [This work] |
| YBa$_2$Cu$_3$O$_7$ | bulk single crystal | ultrasonic velocity $^{[31]}$ | 46.4 |

To summarize, we have studied the mechanical properties of exfoliated thin BSCCO crystals using deformation caused by an AFM tip. Finite element simulations are used for the numerical analysis of spatial compliance maps, and to extract the Young’s modulus and pre-stress. The reported mechanical properties could potentially be useful in engineering nanoelectromechanical resonators of BSCCO for various applications.

SUPPLEMENTARY MATERIAL

See supplementary material for the characterization of additional flakes and details of simulations.

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FIG. 4. (a) A schematic representation of the steps used to obtained buckled flake on top of PDMS. (b) An optical microscope image of buckled BSCCO flake. The scale bar corresponds to 12 \( \mu \text{m} \).

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