Reentrant softening in perovskitelike superconductors

T. Datta
Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina 29208

H. M. Ledbetter
Institute for Materials Science and Engineering, National Bureau of Standards, Boulder, Colorado 80303

C. E. Violet
Lawrence Livermore National Laboratory, Livermore, California 94550

C. Almasan and J. Estrada
Department of Physics and Astronomy, University of South Carolina, Columbia, South Carolina 29208
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We suggest a model—reentrant elastic softening—that achieves three useful results. First, and principally, it reconciles existing sound-velocity–elastic-constant measurements with thermodynamics. Second, it leads to Debye characteristic temperatures that agree with those from specific-heat and phonon density-of-states determinations. Third, it links elastic-constant–temperature behavior in Y-Ba-Cu-O and La-Sr-Cu-O. The model predicts a superconducting-state elastic stiffness lower than the normal state.

Recently, several authors[1-8] reported either sound-velocity or elastic-constant changes during the normal-superconducting phase transition in Y-Ba-Cu-O. These results appear to differ from those reported for La-Sr-Cu-O and La-Ba-Cu-O.[9-13] Moreover, because these results appear to show an elastic stiffening below the critical temperature T_c, they appear to violate thermodynamic requirements. (Notably, Mathias *et al.*[5] found a large elastic-stiffness softening.)

Thermodynamics of superconductors requires that cooling through the normal-superconducting transition causes an increase in specific heat:[14,15]

$$\Delta C = C_s - C_n = \frac{V_s T_c}{4\pi}\left[H_c\left(\frac{d^2H_c}{dT^2}\right)+\left(\frac{dH_c}{dT}\right)^2\right]. \quad (1)$$

Here V denotes volume, T temperature, and H_c critical magnetic-field intensity. For Y-Ba-Cu-O, several authors[16-18] reported a positive ΔC. This means that d^2H_c/dT^2 is not large and negative.

We can extend the thermodynamics to the bulk-modulus change ΔB by invoking the Ehrenfest relationship:[19]

$$\Delta B = B_s - B_n = -TV(\Delta\beta)^2 B^2/\Delta C. \quad (2)$$

Here β denotes volume thermal expansivity $(1/V)\times(\partial V/\partial T)_P$. Thus, ΔB differs in sign from ΔC; with the above proviso about d^2H_c/dT^2, thermodynamics requires that the bulk modulus decreases upon cooling through T_c.

Pippard[20] extended the thermodynamics to the shear-modulus change:

$$\Delta G = G_s - G_n = -\frac{G^2H_0}{4\pi}\left(\frac{d^2H_0}{d\tau^2}\right)\left(1-\frac{T^4}{T_c^4}\right). \quad (3)$$

Here H_0 denotes critical magnetic-field intensity at zero temperature and τ shear stress. Equation (3) follows from two assumptions: H_c varies parabolically with T; shearing produces no change in electronic specific heat. Pippard emphasized that the shear modulus "cannot increase when a metal becomes superconducting." Pippard's relationship provided a theoretical thermodynamic basis for preexisting experimental results of Landauer[21] and Olsen[22] for tin:

$$\Delta G/G = -3.5[1-(T/T_c)^4]\times 10^{-6}. \quad (4)$$

Thus, from both observation and theory, we expect ΔG to have the same (negative) sign as ΔB and to be small.

[We note that the Landau-Lifshitz[23] theory of second-order-phase-transition thermodynamics predicts the same results as in Eqs. (1)–(3). Their theory contains an order parameter and a transition (on cooling) from a symmetrical to a nonsymmetrical state. Superconductivity represents a special type of second-order phase transition, a condensation without symmetry change, where the order parameter is the energy gap Δ.]

As an example of our model, consider previously reported[4] shear-modulus measurements shown in Fig. 1. Curves a and b in Fig. 1 represent the Varshni function:[24]

$$G(T) = G(0) - s/[\exp(t/T)-1]. \quad (5)$$

Here G denotes shear modulus, T denotes absolute temperature, s relates to zero-point vibrations, and t denotes Einstein temperature. This relationship follows from two principal assumptions. First, the material is described by an Einstein-oscillator model, where the average energy is

$$\langle E\rangle = \tfrac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/k_Bt}-1}. \quad (6)$$

Here h denotes Planck's constant and ν oscillator frequency. Second, following Leibfried and Ludwig,[25] we can represent the adiabatic-elastic-constant temperature de-

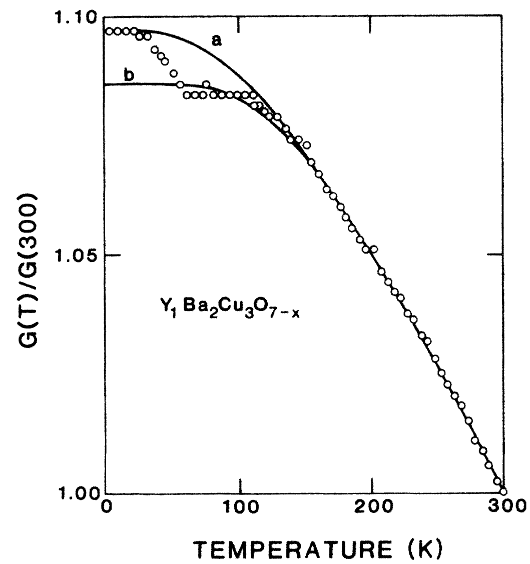

FIG. 1. Relative shear modulus of $YBa_2Cu_3O_{7-x}$ normalized to $T=300$ K. Curves a and b represent the Varshni relationship, Eq. (5). Curve a represents elastic softening followed by rehardening below T_c; curve b represents no softening and anomalous hardening below T_c.

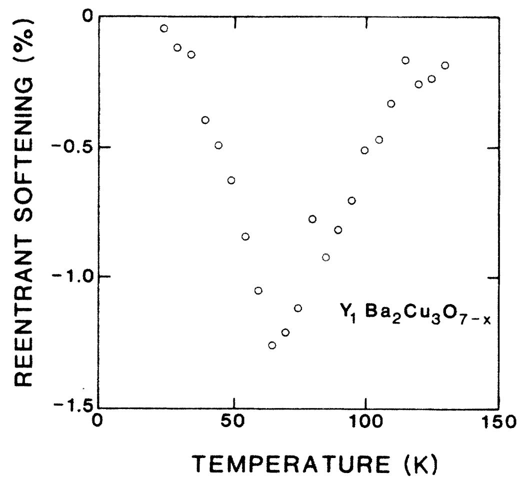

FIG. 2. Reentrant softening, $[G(T)/G(300)](\text{meas}) - [G(T)/G(300)]$ (curve a), based on the measurements and on curve a of Fig. 1.

pendence by

$$C_{ij} = C_{ij}(0)(1 - D\langle E\rangle) . \tag{7}$$

Here C_{ij} denotes a second-order elastic-stiffness constant, and the D parameter depends on the type of crystal and the model.

Varshni's relationship describes well the regular temperature variation of the elastic-stiffness constants. It applies to many elastic constants: the monocrystal C_{ij} and the quasi-isotropic polycrystalline Young, bulk, and shear moduli. It also applies to squares of resonance frequencies and to squares of velocities: extensional, longitudinal, shear, and torsional. The parameters of curves a and b in Fig. 1 are, respectively, $G(0)=1.081$ and 1.070; $s=0.187$ and 0.363; $t=330$ and 498 K. The large difference in the two Einstein temperatures arises from the high value of t required to fit the extended flat region of curve b. Curve a connects the higher-temperature and lower-temperature measurements, ignoring those between 110 and 30 K. Curve b ignores measurements below 65 K and reflects the viewpoint of previous investigators:[1–4,6,7] cooling below the superconducting-transition temperature results in an anomalous increase in elastic stiffness.

If curve a is taken as the correct representation of the normal-state temperature variation of $G(T)$, the behavior near T_c can be termed "reentrant softening." To quantify this behavior, we define reentrant softening as the difference between the observed and normal-state behaviors. Thus, for the measurements shown in Fig. 1, the reentrant softening is $[G(T)/G(300)](\text{meas}) - [G(T)/G(300)]$ (curve a). Figure 2 shows the results. The minimum occurs, as it must, at 65 K, the temperature of the discontinuity in the $G(T)/G(300)$ measurements. This agrees with the estimated transition temperature of this sample determined by magnetization measurements: $T_c=62$ K.[26] The elastic-constant behavior shown in Fig. 2 indicates increasing softness as the temperature decreases above T_c. Below T_c, we observe rehardening as the softening is offset by the increasing elastic stiffness associated with the developing superconducting state. The stiffening approaches, without exceeding, normal-state stiffness as T approaches absolute zero. Therefore, based on our analysis, this rehardening is neither anomalous nor inconsistent with thermodynamic requirements.

The low T_c in the present material probably results from a too-low oxygen content. X-ray diffraction confirms this, giving the following unit-cell dimensions: $a=3.8403$, $b=3.9036$, $c=11.7128$ Å. This b/a axial ratio, 1.0165, is too low for a maximum T_c. A T_c near 90 K corresponds to a b/a axial ratio near 1.0175. We studied another Y-Ba-Cu-O material with a T_c near 90 K and found similar $G(T)$ results with two differences: a smaller softening near T_c and a second, higher-temperature softening near 180 K.

Crystals having the perovskite crystal structure often undergo crystal-structure transformations where phonon softening plays an important role.[27] Elastic softening as the temperature approaches T_c from above strongly suggests lattice instability associated with phonon softening. Such premonitory behavior occurs with martensitic or displacive structural transformations in various materials, including $A15$ superconductors.[28] For example, V_3Si, which can undergo a displacive structural transformation at $T=20.5$ K, shows, above T_c, increased softening with decreasing temperature. The onset of superconductivity at 17 K quenches this growing instability.[28] This behavior resembles that shown in Fig. 1.

If we invoke an electron-phonon mechanism, then the large increase in elastic stiffness or phonon frequency, $\omega(q)$, shown at temperatures below T_c, could be caused by decrease in the static polarization, $\Pi^r(\mathbf{q},T)$, as shown by the relationship[29] ($|q| \to 0$)

$$\omega^2(\mathbf{q}) = \omega_0^2(\mathbf{q})^2 - \frac{g^2}{\rho}\sum_{r=1}^{3}(\hat{e}_r q_r)^2 \Pi^r(\mathbf{q},T) . \tag{8}$$

Here $\mathbf{q}$ denotes the propagation vector, $\hat{\mathbf{e}}$ the unit polarization vector, ω_0 a temperature-independent frequency, g an electron-phonon coupling parameter, and ρ the mass density. In the long-wavelength limit,

$$\Pi^r(\mathbf{q},T) = -\int n(E)\left[\frac{\partial f}{\partial E}\right] dE . \tag{9}$$

Here $n(E)$ denotes the electronic density of states, f the Fermi function, and E the electron energy. Thus, as electrons condense into pairs, the polarization may decrease, increasing the phonon frequency. We expect a larger polarization in these low-carrier-density superconductors than in metals. The reduction in electron and phonon densities, thermal fluctuation, and the increasing superconducting gaps at lower temperatures would encourage this stiffening. Of course, other mechanisms, nonphononic,[30,31] may affect the elastic constants.

We turn our attention now to the elastic Debye temperature, Θ_D, which we can estimate from the $G(T)$ results and the Varshni relationship by recognizing that[32]

$$\Theta_D = \tfrac{4}{3} t . \tag{10}$$

For curve b we obtain $\Theta_D = 664$ K. This result seems too high. For cubic $BaTiO_3$ the building-block perovskite crystal structure for Y-Ba-Cu-O, Ledbetter, Austin, Kim, and Lei[33] calculated that $\Theta_D = 500$ K. This represents an upper bound for Y-Ba-Cu-O because of the oxygen vacancies (especially along the c axis), which create weak interionic bonds, which dominate the effective Debye temperature. From curve a, corresponding to reentrant softening, we obtain $\Theta_D = 440$ K. This agrees with a specific-heat value:[18] $\Theta_D = 440$ K. Also, it agrees with a value calculated from the phonon density of states:[34] $\Theta_D = 452$ K. To obtain the latter value for the phonon spectrum we took three cutoff energies: 26, 45, and 77 meV; and we used the usual $\Theta_D^{-1.5}$ averaging method. Thus, we find agreement among Debye temperatures estimated three ways: by the specific heat, the phonon density of states, and the reentrant-model shear-modulus versus temperature.

The reentrant-elastic-softening model achieves another result: it links the elastic-constant–temperature behavior of Y-Ba-Cu-O and La-Sr-Cu-O. Without our model, the two appear qualitatively different. The La-Sr-Cu-O materials soften elastically well above T_c, at near-ambient temperatures. Although it predicts softening at lower temperatures, our model does predict softening in Y-Ba-Cu-O. For both materials our model emphasizes softening above T_c and stiffening below T_c. The onset of stiffening varies with material. Microscopic softening mechanisms may include a change in Cu's magnetic state, a change in oxygen-atom order, or a subtle crystal-structure change. For La-Ba-Cu-O, Fossheim *et al.*[11] suggested that softening arises from interactions between acoustical and optical phonons driving an instability through a Kohn anomaly.

We encourage experimentalists to test our model, which predicts a lower elastic stiffness in the superconducting state. One experiment would be to measure sound-velocity change caused by turning on a high magnetic field at a temperature just below T_c. A second experiment would be to measure accurately the thermal expansivity β and use Eq. (2) to predict ΔB.

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