Superconductivity and lattice distortions in high-T_c superconductors

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A thermodynamic analysis of the behavior of the lattice parameters and elastic properties at T_c in the orthorhombic high-T_c superconductors $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ is presented. Expressions for the singularities in the specific heat, lattice parameters, and sound velocities are derived using a mean-field expression for the superconducting free energy, and Gaussian fluctuation corrections and critical behavior are discussed. The mean-field expressions are used to interpret presently available data on the thermal, structural, and elastic properties of polycrystalline samples, and additional measurements necessary to complete the determination of the theoretical parameters are suggested. The usefulness of the theory in providing quantitative consistency checks among different types of experimental measurements and in understanding the coupling between crystal structure and superconductivity is emphasized. It is found that although the first strain derivatives of T_c are comparable in magnitude to those in conventional superconductors, some second strain derivatives of T_c are anomalously large.

I. INTRODUCTION

There have been a number of reports in the high-T_c oxide superconductors of unusual behavior of the structural and elastic properties at the superconducting transition temperature T_c, most notably of anomalous temperature dependence of the lattice parameters and of large discontinuities in the temperature derivative of the sound velocities. While this behavior indicates a significant coupling between superconductivity and the lattice, the precise interpretation and significance of individual measurements has, up to now, not been systematically examined. In this paper, we present a thermodynamic analysis of the singular behavior of the structural and elastic properties of $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ at T_c. In addition to mean-field behavior, we consider Gaussian fluctuation corrections and behavior in the critical region. From the most general free energy allowed by symmetry for the coupled superconducting-lattice system, we derive expressions for the singularities in the behavior of the lattice parameters and sound velocities near T_c. With a relatively small number of parameters— T_c, the specific-heat jump at T_c, the elastic moduli and the strain derivatives of T_c —these expressions provide a coherent and systematic framework for analyzing and interrelating a wide variety of thermal, mechanical, and structural measurements. This approach has been successfully applied to the $A15$ superconductors,[1] yielding an understanding of the interplay between superconductivity and structural instabilities in those materials. For the oxide superconductors, this analysis has the advantage of being based on purely thermodynamic arguments, thus being independent of the details of the microscopic mechanism for superconductivity while yielding strain derivatives of T_c, which are relevant to the construction of realistic microscopic models. Using this approach, we examine the presently available experimental data for $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$. Since at this writing the only published sound velocity data are on polycrystalline samples, we use an effective medium formalism to derive appropriate theoretical expressions. We find strong indications that in both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ some second strain derivative of T_c is unusually large, $(1/T_c)d^2T_c/d\epsilon^2 \sim 10^3$, although the first strain derivatives are relatively small. Thus, further measurements to determine these derivatives more precisely are likely to yield important information on the nature of high-T_c superconductivity.

The outline of this paper is as follows. In Sec. II, we give the mean-field expression for the free energy and derive from it expressions for various measurable quantities. Where possible we give the BCS values for parameters in our equations. In Sec. III we show how these expressions would be modified were the transition not mean-field, we give estimates of the size of the critical region within which mean-field theory breaks down and we give formulas for the Gaussian fluctuation contributions to quantities of interest. In Sec. IV we give the effective medium equations for ceramic samples, use the framework to analyze presently available data, compare various experiments, and suggest further measurements. Section V is a summary of the results derived in the previous sections and a discussion of their physical interpretation.

II. MEAN-FIELD ANALYSIS

In this section, we write the mean-field free energy as the sum of a normal-state contribution and a superconducting contribution which explicitly contains the coupling to the lattice. From this free energy, we obtain expressions for three types of singularities at T_c: (1) a discontinuity in the temperature derivatives of the lattice parameters; (2) a discontinuity in some of the elastic moduli, and hence a discontinuity in the magnitudes of the corresponding sound velocities; (3) a discontinuity in the temperature derivatives of the elastic moduli and hence a discontinuity in the temperature derivatives of the corresponding sound velocities.

The normal-state contribution to the free energy can be written as an expansion in symmetry-invariant combinations of the strain ϵ_{ij}, referred to the equilibrium structure at T_c. At temperatures near T_c the high-T_c superconductors are orthorhombic ($a \approx b \neq c$), with a structural transition to a tetragonal phase ($a = b \neq c$) at higher temperatures. In $La_{2-x}Sr_xCuO_4$, the orthorhombic phase is related to the tetragonal phase through the buckling of the a-b CuO_2 planes, with the corrugations running along $(\bar{1}10)$.[2] In $YBa_2Cu_3O_7$, a pair of a-b CuO_2 planes sandwiches an a-b CuO plane.[3] In the orthorhombic phase, the oxygens in this plane order to form CuO chains along the b direction. In writing the normal-state contribution to the free energy, we can ignore the (smooth) temperature dependence of the expansion coefficients without loss of generality, since we are focusing on singular changes at T_c. Thus, we get

$$F_n(\vec{\epsilon}) = \tfrac{1}{2}\epsilon_i c_{ij}\epsilon_j + \tfrac{1}{2}\tilde{c}_i\tilde{\epsilon}_i^2 + \Gamma_{ijk}\epsilon_i\epsilon_j\epsilon_k + \Lambda_{ij}\epsilon_i\tilde{\epsilon}_j^2 + \sigma_i\epsilon_i + \cdots \quad (i,j,k=1,2,3). \tag{2.1}$$

Here ϵ_i represents the diagonal strain $\epsilon_{xx},\epsilon_{yy},\epsilon_{zz}$, $\tilde{\epsilon}_i$ stands for the off-diagonal strains $\epsilon_{xy},\epsilon_{xz},\epsilon_{yz}$. c_{ij} and $\tilde{c}_i$ are the orthorhombic elastic moduli, Γ_{ijk} and Λ_{ij} are anharmonic coefficients, and σ_i are the applied stresses. Unless otherwise specified, we assume the applied stress $\sigma_i = 0$. Combinations of elastic moduli are related to the various sound velocities. For example, v_i, the velocity of longitudinal sound propagating along $\hat{i}$, is given by

$$v_i^2 = c_{ii}/\rho ,$$

where ρ is the mass density of the crystal.

By setting $\sigma_i = P$, we can examine the effects of pressure for $T = T_c^+$:

$$\epsilon_i(P) = -P\sum_j c_{ij}^{-1} - 3P^2\Gamma_{jkl}\left(\sum_m c_{jm}^{-1}\right)\left(\sum_n c_{kn}^{-1}\right)c_{li}^{-1} . \tag{2.2}$$

We now consider the superconducting contribution to the free energy. In mean-field theory the difference in free energy between normal and superconducting states is, for $T \leq T_c$,

$$F_S = -\tfrac{1}{2}N(T-T_c)^2\left[1 - A\left(1-\frac{T}{T_c}\right) + \cdots\right] . \tag{2.3}$$

Here N has units of states per unit energy and volume, while A is dimensionless. Coupling of superconductivity to the lattice is a consequence of the dependence of T_c and N on strain, which we write as

$$T_c = T_{c0}(1 + \alpha_i\epsilon_i + \tfrac{1}{2}\epsilon_i\Delta_{ij}\epsilon_j + \tfrac{1}{2}\tilde{\Delta}_i\tilde{\epsilon}_i^2 + \cdots) , \tag{2.4a}$$

$$N = N_0(1 + \beta_i\epsilon_i + \cdots) , \tag{2.4b}$$

where we define

$$\alpha_i \equiv \frac{d\ln T_c}{d\epsilon_i}, \quad \Delta_{ij} \equiv \frac{1}{T_{c0}}\frac{d^2T_c}{d\epsilon_i d\epsilon_j} ,$$

$$\tilde{\Delta}_i \equiv \frac{1}{T_{c0}}\frac{d^2T_c}{d\tilde{\epsilon}_i^2}, \quad \beta_i \equiv \frac{d\ln N}{d\epsilon_i} .$$

The superconducting contribution to the specific heat at constant strain, $C_v = NT[1+3A(T-T_c)/T_c]$, can be obtained directly from (2.3). We will see below that the difference between the specific heat at constant strain and at constant stress is a small correction which will be neglected. Thus we obtain for the specific-heat jump at T_c

$$\Delta C \equiv C(T_c^-) - C(T_c^+) = N_0T_{c0} \tag{2.5}$$

and for the discontinuity in the temperature derivative at T_c we have

$$\left.\frac{dC}{dT}\right|_{T_c^+} - \left.\frac{dC}{dT}\right|_{T_c^-} = -3N_0A . \tag{2.6}$$

To obtain the behavior of the elastic properties and lattice parameters at T_c, we expand F_S in powers of $T - T_{c0}$ and ϵ. The total free energy then is $F = F_n + F_s$, where

$$F_S = -\tfrac{1}{2}N_0(T-T_{c0})^2\left[1 - A\left(1-\frac{T}{T_{c0}}\right)\right] - \tfrac{1}{2}N_0T_{c0}^2\left[-2\frac{T-T_{c0}}{T_{c0}}\alpha_i\epsilon_i + \left(\alpha_i\alpha_j + \frac{T-T_{c0}}{T_{c0}}(3A\alpha_i\alpha_j - 2\alpha_i\beta_j - \Delta_{ij})\right)\epsilon_i\epsilon_j - \frac{T-T_{c0}}{T_{c0}}\tilde{\Delta}_j\tilde{\epsilon}_j^2\right] - \cdots . \tag{2.7}$$

From the term of order $(T-T_{c0})^0\epsilon^2$, we derive a jump in c_{ij} at T_c:

$$\frac{\Delta c_{ij}}{c_{ij}} \equiv \frac{1}{c_{ij}}[c_{ij}(T_c^+) - c_{ij}(T_c^-)] = \frac{\Delta C T_{c0}}{c_{ij}}\alpha_i\alpha_j . \tag{2.8}$$

Discontinuities also occur in the corresponding sound velocities. For example,

$$\frac{\Delta v_i}{v_i} = \frac{\Delta C T_{c0}\alpha_i^2}{2c_{ii}} . \tag{2.9}$$

Because of the restrictions of orthorhombic symmetry, there is no term of order $(T-T_{c0})^0\tilde{\epsilon}^2$ and the $\tilde{c}_i$ do not have a discontinuity at T_c.

The dimensionless parameter $\Delta C T_{c0}/c_{ij}$, which appears in Eqs. (2.8) and (2.9), is the ratio of the superconducting condensation energy to an elastic energy and sets the scale of effects of superconductivity on the lattice. It turns out to be extremely small ($\sim 10^{-5}$) and thus we work only to leading nontrivial order in this parameter.

The equilibrium strains for $T < T_c$ are obtained by minimizing F with respect to ϵ_i and $\tilde{\epsilon}_i$:

$$\tilde{\epsilon}_i(T) = 0 ,$$

$$\epsilon_i(T) = -N_0T_{c0}(T-T_{c0})c_{ij}^{-1}\alpha_j .$$

The discontinuity in the logarithmic temperature derivative of the lattice parameters is thus

$$\Delta_1\epsilon_i \equiv T_{c0}\left(\left.\frac{d\epsilon_i}{dT}\right|_{T_c^+} - \left.\frac{d\epsilon_i}{dT}\right|_{T_c^-}\right)$$

$$= -\Delta C T_{c0} c_{ij}^{-1} a_j \,. \tag{2.10}$$

The difference between the superconducting contribution to the specific heat at $T < T_c$ at constant (zero) strain and at constant (zero) pressure arises from changes in the free energy due to the temperature variation of the strains. From Eq. (2.10) it can be seen to be of order $\Delta C T_{c0}/c_{ij}$ so its neglect in (2.5) and (2.6) is justified.

Finally, we examine the discontinuities at T_c in the temperature derivatives of the elastic moduli, which give rise to discontinuities of the slopes of the corresponding sound velocities. For $T < T_c$, replacing ϵ_i by $\epsilon_i' + \epsilon_i(T)$ in F yields the temperature derivative of c_{ij} from the term of order $(T - T_{c0})(\epsilon')^2$:

$$\Delta_1 c_{ij} \equiv T_{c0}\left.\frac{d}{dT}\right|_{T_{c0}^+} c_{ij} - T_{c0}\left.\frac{d}{dT}\right|_{T_{c0}^-} c_{ij}$$

$$= \Delta C T_{c0}[3A a_i a_j - 2a_i\beta_j - \Delta_{ij} + 6\Gamma_{ijk} c_{kl}^{-1} a_l] \,. \tag{2.11}$$

For computing the temperature dependent part of $\tilde{c}_i$, we replace ϵ_i by $c_{ij}^{-1}[-N_0 T_{c0}(T - T_{c0})a_j + \Lambda_{jk}\tilde{\epsilon}_k^2]$, obtained by minimizing F at fixed $\tilde{\epsilon}_i^2$, yielding

$$\Delta_1\tilde{c}_i = -\Delta C T_{c0}(\tilde{\Delta}_i + 2c_{jk}^{-1} a_k \Lambda_{ji}) \,. \tag{2.12}$$

These slope discontinuities involve the parameters β_i, Δ_{ij}, $\tilde{\Delta}_i$, and various combinations of Γ_{ijk} and Λ_{ij} which do not appear in the previous expressions.

III. FLUCTUATION EFFECTS

The results in the previous section were derived from a mean-field expression for the superconducting free energy. It is easy to see that in each of these cases the nonanalytic behavior derives from and is identical to the nonanalyticity in the specific heat. We define $\phi(T,\epsilon)$ as the free-energy difference between normal and superconducting states at temperature T and strain ϵ. Sufficiently close to the superconducting T_c we may approximate ϕ by its most singular part:[4]

$$\phi(T,\epsilon) = \frac{A\pm}{\alpha}\left(\frac{|T - T_c(\epsilon)|}{T_c(\epsilon)}\right)^{2-\alpha} + \cdots \,. \tag{3.1}$$

Here α is the specific-heat exponent and $A+$ and $A-$ are dimensional factors, presumably of order $N_0 T_c^2$, which refer to $T > T_c$ and $T < T_c$, respectively. The ellipsis refers to terms involving higher powers of $T - T_c$. By expanding (3.1) in powers of ϵ and combining the result with the lattice free energy, Eq. (2.1), one may obtain singular contributions to the longitudinal sound velocities and the lattice parameters. For, e.g., $T > T_c$ one finds

$$\epsilon_i(T) = -(2-\alpha)\frac{A+}{\alpha} c_{ij}^{-1} t^{1-\alpha} a_i \,, \tag{3.2a}$$

$$\rho v_i^2(T) = c_{ii} - A_+ \frac{(2-\alpha)(1-\alpha)}{\alpha} t^{-\alpha} a_i^2 \,. \tag{3.2b}$$

Here the reduced temperature $t = (T - T_{c0})/T_{c0}$.

According to (3.2) the lattice parameters do not diverge near T_c if $\alpha < 1$, while the sound velocity diverges negatively if $1 > \alpha > 0$. A nonpositive sound velocity is unphysical; other terms not included in the arguments leading to (3.2b) become important for T sufficiently close to T_c, modifying the critical behavior in that region. The lower bound of the range of reduced temperatures for which (3.2b) is valid may be estimated from the condition

$$c_{ii} > A_+ \frac{(2-\alpha)(1-\alpha)}{\alpha} \,. \tag{3.3}$$

Now the superconducting transition for conventional superconductors is in the x-y universality class. If the transition has three-dimensional (3D) x-y exponents, α is very small, so that $(1/\alpha)t^{-\alpha} \sim -\ln(t)$. Thus in this case (3.2a) and (3.2b) would give approximately logarithmic divergences for the sound velocity and the temperature derivatives of the lattice parameters over some range of temperatures sufficiently far from T_c. Using (3.3), the smallness of α, the estimate $A_+ \sim \Delta C T_{c0}$, and Table I we find that Eqs. (3.2) are valid for

$$t > \exp\left(\frac{-\Delta C T_{c0} a_i^2}{c_{ii}}\right) \sim \exp(-10^4) \,.$$

The upper bound of the region over which (3.3) applies is determined by the requirement that the term written in (3.1) dominate the less singular parts of the free energy. In the absence of a detailed theory of the less singular terms a quantitative bound cannot be given. A rough estimate may be obtained from the Ginzburg criterion,[5] which determines the temperature scale t_g at which a simple perturbation expansion about mean-field theory breaks down. True critical behavior will be observable only for $t \ll t_g$. For the x-y model in $d < 4$ dimensions one has

$$t_g \sim \gamma_d^{2/(4-d)} \tag{3.4}$$

with

$$\gamma_3^{-1} = 8\pi\Delta C \xi_0^3 \,, \tag{3.5a}$$

$$\gamma_2^{-1} = 4\pi\Delta C \xi_0^2 a \,. \tag{3.5b}$$

Here ΔC is the mean-field specific-heat jump per unit volume and ξ_0 is the bare coherence length of the mean-field theory. Equation (3.5b) is written for a three-dimensional material consisting of uncoupled layers; ΔC is the bulk specific heat and a is the distance between layers.

For temperatures $|t| > t_g$ one may observe Gaussian fluctuation corrections to mean-field expressions. It is straightforward to derive an expression for the specific heat including both mean-field and Gaussian fluctuations. For x-y critical behavior one finds[6]

$$C = \Delta C \gamma_d t^{(d-4)/2} \quad (t > t_g) \,, \tag{3.6a}$$

$$C = \Delta C\left(1 + \frac{\gamma_d |t|^{(d-4)/2}}{2^{(d-2)/2}}\right) \quad (-t > t_g) \,. \tag{3.6b}$$

Fluctuation behavior in the specific heat implies fluctuation behavior in the elastic properties considered in the previous section. Applying the previous arguments to the term in the superconducting free energy yielding Eq. (3.4) gives a mean-field plus fluctuation expression for the sound velocity

$$\frac{\Delta v_i}{v_i} = \frac{-\Delta C T_c \alpha_i^2}{c_{ii}} \gamma_d t^{(d-4)/2} \quad (t > t_g), \tag{3.7a}$$

$$\frac{\Delta v_i}{v_i} = \frac{-\Delta C T_c \alpha_i^2}{c_{ii}} \left[1 + \frac{\gamma_d |t|^{(d-4)/2}}{2^{(d-2)/2}} \right] \quad (-t > t_g), \tag{3.7b}$$

and for the lattice parameter

$$T_c \frac{d\epsilon_{ii}}{dT} = -\Delta C T_c c_{ij}^{-1} \alpha_j \gamma_d t^{(d-4)/2} \quad (t > t_g), \tag{3.8a}$$

$$T_c \frac{d\epsilon_{ii}}{dT} = -\Delta C T_c c_{ij}^{-1} \alpha_j \left[1 + \frac{\gamma_d |t|^{(d-4)/2}}{2^{(d-2)/2}} \right] \quad (-t > t_g). \tag{3.8b}$$

The behavior near T_c of the lattice parameter and longitudinal sound velocity is shown schematically in Fig. 1.

We now give estimates of the size of the critical region and of the magnitude of the Gaussian fluctuation contributions to elastic properties in the high-T_c superconductors. The high-T_c materials seem to consist of weakly coupled layers. If the interlayer coupling is weak enough, then for sufficiently large t the fluctuations will be of low dimension, while as t decreases the system will cross over to three-dimensional critical behavior. The scale for crossover to 3D behavior, t_x, may in principle be either larger or smaller than the scale t_g which determines the boundary of the critical region. The parameters t_x and t_g are not accurately known for the high-T_c materials. At this writing preliminary data are available for $YBa_2Cu_3O_7$, but no data for $La_{2-x}Sr_xCuO_4$. A recent analysis[7] of upper critical fields and fluctuation conductivity has yielded values ~8 Å for the geometric mean of the a-, b-, and c-axis coherence lengths and a value of $t_x \sim 0.05$–0.1 for a 2D-3D crossover. Using this value for the coherence length, Eq. (3.5) and Table I, we find $\gamma \sim 0.02$ (i.e., $t_g \sim 4\times10^{-4}$), so that for $\gamma^2 \ll t \ll t_x$ (i.e., $0.04\ \mathrm{K} \ll |T-T_c| < 10\ \mathrm{K}$) three-dimensional Gaussian fluctuation behavior should be observable, while true critical behavior should be observable only for $|T-T_c| \ll 0.04$ K. Direct measurements of the fluctuation contribution to the specific heat consistent with these estimates have been reported.[8]

The values quoted for t_g and t_x should be regarded as rough estimates. For example, mean coherence lengths of ~15 Å have been reported by other workers.[9] However, it seems likely that although true critical behavior would occur only in an unobservably small temperature window about T_c, Gaussian fluctuation contributions to the longitudinal sound velocity may be observable in samples with sufficiently sharp transitions for temperatures within a few degrees of T_c. Fluctuation behavior in the lattice parameter should also be observable in principle, but as we shall see in Sec. IV, even the mean-field behavior of the lattice parameters is very difficult to resolve with presently available techniques.

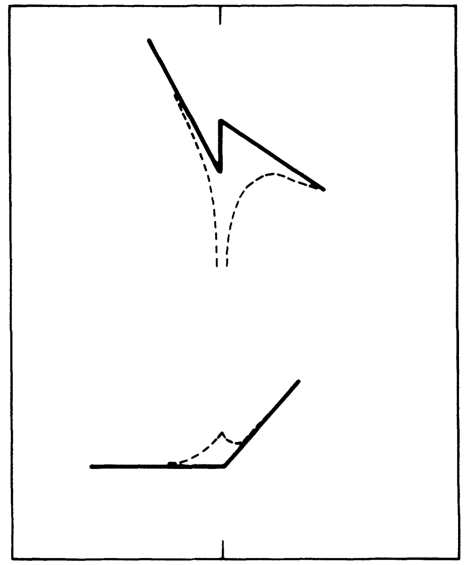

FIG. 1. Sketch of temperature dependence of lattice parameter (lower curve) and longitudinal sound velocity (upper curve) for temperatures near the superconducting transition. The solid lines represent mean-field behavior, the dashed lines represent the Gaussian fluctuation and critical behavior. For the lattice parameter, the change in slope of the mean-field lines and the deviation of critical from mean-field curves may be positive or negative according to the sign of the strain derivative of T_c.

TABLE I. Parameters determining the order of magnitude of the effect of superconductivity upon elastic properties of the $A15$ superconductor V_3Si and the oxide superconductors $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_7$. T_c is the superconducting transition temperature, ΔC the specific-heat jump at the transition, and B is the bulk modulus. The data on V_3Si are taken from Ref. 1. The data on the oxide superconductors are taken from the references indicated in the text.

	T_c (K)	$\Delta C \left[\frac{\mathrm{mJ}}{\mathrm{cm^3\,K}}\right]$	$B(10^3$ kbar)	c_e/B	$\frac{\Delta C T_c}{B}$ (ppm)	$B\frac{d\ln T_c}{dP}$
V_3Si	17	61	1.7	0.04	6	4
$La_{1.85}Sr_{0.15}CuO_4$	36	11	1.7	...	2	14
$YBa_2Cu_3O_7$	92	50	1.7	...	27	1.3

IV. ANALYSIS OF EXPERIMENTAL DATA

We apply the results of the mean-field theory to a variety of experimental data. We obtain, when possible, estimates for the parameters which appear in the theory; we discuss the consistency of the various measurements and suggest further measurements.

Before considering the more problematic situation in the high-T_c materials, it is instructive to review the application of the theory to the $A15$ superconductor V_3Si, which has been thoroughly studied and for which the effects of superconductivity on the lattice are relatively large. V_3Si has a superconducting transition temperature $T_c = 17$ K. Depending on sample preparation, it either undergoes a second-order cubic-tetragonal structural transition at a temperature T_d between 18 and 25 K ($T_d > T_c$) or remains cubic to low temperatures ($T_d = 0$ K). The expression for the mean-field free energy of a cubic sample is particularly simple because of the cubic symmetry. From measurements of the specific-heat anomaly ΔC, various sound velocities, and the pressure derivative of T_c,[10] the two elastic moduli $B = (c_{11}+2c_{12})/3$ and $c_e = (c_{11}-c_{12})/2$ and the first- and second-order coefficients in $T_c(\epsilon)$ can be readily determined. Values of various parameters for V_3Si are given in Table I. While the sound velocities show no elastic constant discontinuities at T_c within experimental resolution, the discontinuities at T_c in their temperature derivatives are very large. This fact is reflected in the values of the theoretical parameters, with the first-order coefficients in $T_c(\vec{\epsilon})$, $\alpha_1^{(c)} = \alpha_2^{(c)} = \alpha_3^{(c)} = 4$, being much smaller than the second-order coefficients $\Delta_{11}^{(c)} = -1.4\times 10^4$, $\Delta_{12}^{(c)} = -2.9\times 10^3$, and $\Delta_{44}^{(c)} = -5.9\times 10^2$. From Table I we find $(\Delta C T_c/B)\alpha_i^{(c)} \sim 24\times 10^{-6}$. The resulting effect on lattice parameters in cubic V_3Si at T_c is small.

For samples with $T_c < T_d$, below T_d a tetragonal strain

$$\vec{\epsilon} = \left(\frac{2\delta_t}{3}, \frac{-\delta_t}{3}, -\frac{\delta_t}{3}, 0,0,0\right)$$

develops. The distortion from cubic symmetry at T_c is small, a representative value being[11] $\delta_t \sim 2.5\times 10^{-3}$. In a noncubic material the α_i need not all be equal. The α_i in the tetragonal phase may be estimated from the cubic values of the Δ_{ij} and the distortion δ_t. One finds the anisotropic (and relatively large) values $\alpha_2^{(t)} = \alpha_3^{(t)} = 10$, $\alpha_1^{(t)} = -17$. At T_c a sharp break in the temperature dependence of δ_t is observed, a typical value being $\Delta_1\delta_t = 5\times 10^{-3}$. As a result, δ_t becomes virtually temperature independent below T_c. This large break in slope follows from the small value of c_e and the large anisotropy in the α_i. Using the previously quoted α_i, the value of c_e from Table I and Eq. (2.10), we find

$$\Delta_1\delta_t = \left.\frac{d\delta_t}{d\ln T}\right|_{T=T_c^+} - \left.\frac{d\delta_t}{d\ln T_c}\right|_{T=T_c^-} = \frac{\Delta C T_c}{c_e}\frac{\alpha_1^{(t)}-\alpha_3^{(t)}}{2} = 3\times 10^{-3}$$

in rough agreement with the experimental value.

In the case of the high-T_c materials, it is more difficult to apply the theory of Sec. II for several reasons. The lower orthorhombic symmetry means there are more than twice as many parameters as in the cubic $A15$ case. Data on the lattice properties near T_c are available only for polycrystalline samples, and such measurements can be interpreted in terms of averages of intrinsic properties of the material only approximately. Also, the superconducting transition can be broad enough partially to obscure the associated singularities. Lastly, if the relevant elastic modulus is not small, the scale of the effect of superconductivity on the lattice is likely to be such that only very high precision measurements can detect it. So, pending accurate measurements on single crystals, the extraction of the theoretical parameters is a difficult task which cannot be fully completed. However, our partial analysis will prove to contain some useful information.

We start by considering measurements of the elastic moduli. Though a complete determination has not yet been made, information is available from the dependence of the lattice parameters on pressure $d\epsilon_i/dP = -\sum_j c_{ij}^{-1}$, measured using x-ray diffraction. A bulk modulus $B = (\sum_{ij} c_{ij}^{-1})^{-1}$ of 1700 ± 160 kbar and c/a constant up to 220 kbar was measured at 15 K for $La_{1.8}Sr_{0.2}CuO_4$, which is tetragonal at that temperature.[12] For $YBa_2Cu_3O_7$, the identification of peaks associated with different lattice constants is complicated by $b \approx c/3$, with either[13]

$$B\frac{d\epsilon_1}{dP} = B\frac{d\epsilon_2}{dP} = -0.30, \quad B\frac{d\epsilon_3}{dP} = -0.40\,,$$

or

$$B\frac{d\epsilon_1}{dP} = B\frac{d\epsilon_3}{dP} = -0.29, \quad B\frac{d\epsilon_2}{dP} = -0.42\,.$$

In either case, $B = 1700$ kbar, as has been confirmed by several other measurements.[14] In $La_{1.8}Sr_{0.2}CuO_4$, the deviation from linearity of volume as a function of P is approximately $\Delta V/V_0 = 0.01$ at 200 kbar.[12] With (2.2), this permits an estimate of the average third-order elastic constant

$$\Gamma \equiv \sum_{jkl}\left(B\sum_m c_{jm}^{-1}\right)\left(B\sum_n c_{kn}^{-1}\right)\left(B\sum_i c_{li}^{-1}\right)\Gamma_{jkl}$$

of

$$\frac{\Gamma}{B} = -\frac{\Delta V}{3V_0}\Bigg/\left(\frac{P}{B}\right)^2 \approx -0.2\,.$$

In $YBa_2Cu_3O_7$, no significant deviation from linearity with P is observed up to 150 kbar,[13] at a resolution $\Delta V/V_0 < 0.01$. The same type of estimate yields $|\Gamma/B| < 0.4$. We can obtain an independent order of magnitude estimate of Γ and the shear anharmonicity Λ from the measured average Grüneisen parameter[15] γ, which is defined as the average over all phonon modes of $d\ln\omega/d\ln V$. In our elastic continuum model, γ is roughly a third-order elastic constant (Γ or Λ), divided by some average elastic constant ($\sim B$). Thus, with a measured value of $\gamma = 3$ in $YBa_2Cu_3O_7$, we find Γ/B and Λ/B to be of order unity.

In both materials, there have been a number of measurements of $C(T)$ near T_c and determinations of ΔC, the specific-heat jump at the transition. Of the latter,[16] we select the largest, given in Table I, as probably reflecting the highest superconducting fraction in the sample. Even so, the parameter $\Delta C T_c/B$, which sets the scale of superconductivity effects on the lattice, is 2×10^{-6} in $La_{1.85}Sr_{0.15}CuO_4$ and 27×10^{-6} in $YBa_2Cu_3O_7$ and is in both cases very much smaller than the relevant ratio $\Delta C T_c/c_e = 210\times10^{-6}$ in V_3Si. From the measured change in slope of the specific heat at the transition [Eq. (2.6)] we estimate $4\le A\le 6$ in $La_{1.85}Sr_{0.15}CuO_4$ and $2\le A\le 5$ in $YBa_2Cu_3O_7$. These values are substantially larger than in conventional superconductors ($A_{BCS}=0.67$, $A_{Pb}\cong 2$).

Next, we examine measurements which give information about $T_c(\overleftrightarrow{\epsilon})$. The hydrostatic pressure derivative of T_c determines the average of the stress derivatives, i.e.,

$$B\frac{d\ln T_c}{dP} = B\sum_i \frac{d\ln T_c}{d\sigma_i} = \sum_i \left[B\sum_j c_{ij}^{-1}\right]\alpha_i\,.$$

For $La_{1.85}Sr_{0.15}CuO_4$, $B(d\ln T_c/dP)$ is unusually large and positive, with a value of 14.[17] In $YBa_2Cu_3O_7$, the value 1.3 is significantly smaller.[18] The $B\sum_j c_{ij}^{-1}$ are obtained from the pressure dependence of the lattice constants, as discussed above. Thus, for $La_{1.85}Sr_{0.15}CuO_4$ we obtain $\frac{1}{3}\sum \alpha_i = 14$, while for $YBa_2Cu_3O_7$ we have either $0.30(\alpha_1+\alpha_2)+0.40\alpha_3=1.3$ or $0.29(\alpha_1+\alpha_3)+0.42\alpha_2 = 1.3$, the ambiguity arising from the previously discussed difficulty in the assignment of peaks in the x-ray pressure measurement because $b\approx c/3$. In both materials, no significant deviation from linearity of T_c as a function of P is observed up to 8 kbar. In $La_{1.85}Sr_{0.15}CuO_4$, with a resolution of $\Delta T_c = 0.1$ K, this gives a bound

$$\frac{B^2}{T_{c0}}\left|\frac{d^2T_c}{dP^2}\right| < 240\,,$$

and in $YBa_2Cu_3O_7$, with a resolution $\Delta T_c = 0.05$ K, we find

$$\frac{B^2}{T_{c0}}\left|\frac{d^2T_c}{dP^2}\right| < 60\,.$$

This provides a constraint on the parameters $\overleftrightarrow{\Delta}$ and Γ_{ijk}, since

$$\frac{B^2}{T_{c0}}\frac{d^2T_c}{dP^2} = \sum_{ij}\left[\Delta_{ij} + 6\sum_k\left[\frac{\Gamma_{ijk}}{B}\frac{B\,d\ln T_c}{d\sigma_k}\right]\right] \times\left[B\sum_l c_{il}^{-1}\right]\left[B\sum_m c_{jm}^{-1}\right].$$

This expression shows that while d^2T_c/dP^2 has a contribution from the second strain derivatives of T_c, the contribution from the first derivatives of T_c can also be significant if the anharmonicity is large. From the previous estimate of Γ, we find that anharmonicity contributes to $(B^2/T_{c0})(d^2T_c/dP^2)$ roughly

$$6\left[\frac{B\,d\ln T_c}{dP}\right]\left[\frac{\Gamma}{B}\right] \sim \begin{cases} -20 \text{ for } La_{1.85}Sr_{0.15}CuO_4 \\ 3 \text{ for } YBa_2Cu_3O_7 \end{cases}$$

and thus is much less important than the second derivative.

We now consider measurements of the variation of the lattice parameters with temperature near T_c. From Eq. (2.6), we see that discontinuities in the temperature derivatives at T_c yield $c_{ij}^{-1}\alpha_j = -d\ln T_c/d\sigma_i$, and that the scale of lattice effects is extremely small, set by

$$\frac{\Delta C T_c}{B}\left[\frac{B\,d\ln T_c}{dP}\right] = \begin{cases} 2.8\times10^{-5} \text{ for } La_{1.85}Sr_{0.15}CuO_4 \\ 3.3\times10^{-5} \text{ for } YBa_2Cu_3O_7 \end{cases}$$

However, it is possible that the effects on individual lattice parameters could be larger if an elastic constant were small compared to B, or if T_c depended sensitively on some volume preserving deformation.

Dilatometric measurements of the linear thermal expansion along the ith symmetry axis, $\alpha_{\text{th},i} = d\epsilon_i/dT$, can be sufficiently sensitive to detect these discontinuities. From the information in Table I we calculate that the discontinuity at T_c in the average thermal expansion $\Delta\alpha_{\text{th}} = \frac{1}{3}\sum_i \alpha_{\text{th},i}$ is 2.5×10^{-7} K^{-1} for $La_{2-x}Sr_xCuO_4$ and 1.2×10^{-7} K^{-1} for $YBa_2Cu_3O_7$. The only available data, on polycrystalline samples, give substantially smaller values of $\Delta\alpha_{\text{th}} = (0.6\pm0.15)\times10^{-7}$ K^{-1} in $La_{1.85}Sr_{0.15}CuO_4$ (Ref. 19) and $\Delta\alpha_{\text{th}}$ below resolution of 0.5×10^{-7} K^{-1} in $YBa_2Cu_3O_7$.[20] These low values can partly be attributed to small superconducting fractions in these samples and partly to the approximate nature of the average over the individual crystallites. Additional thermal expansion data, particularly on single crystals, would be extremely useful.

Direct measurements have been made of the lattice parameters at a variety of temperatures near T_c with both x-ray and neutron diffraction in each material. Slope discontinuities can be extracted or bounded by choosing an appropriate temperature window about T_c and fitting separate straight lines to the data above and below T_c. However, as will be discussed in more detail below, the expected effects are at the limit of resolution of currently available measurements of this type.

In x-ray measurements in $La_{2-x}Sr_xCuO_4$ no singularities in the lattice parameters are observed. Upper bounds for the singularities can be obtained from bounds on slopes in the window $T_c\pm30$ K. For $x=0.15$,[21] with a structural transition temperature T_d of 200 K, $\Delta_1\delta\lesssim5\times10^{-4}$, where the orthorhombicity $\delta\equiv2(b-a)/(b+a)$. For $x=0.2(T_d<10$ K),[22] $\Delta_1\epsilon_1\lesssim1.1\times10^{-4}$ and $\Delta_1\epsilon_3\lesssim0.8\times10^{-4}$. A potentially interesting measurement would be for $x\approx0.18$–0.19, for which $T_c\approx T_d$, so that the corresponding small elastic constant might lead to a sufficient enhancement of the effect.

At present, there have been three measurements in $YBa_2Cu_3O_7$ which show behavior which might be interpreted as discontinuities in the temperature derivatives of the lattice parameters at T_c.

The first two, high-resolution x-ray powder diffraction measurements[23,24] show an apparent change in temperature dependence of the orthorhombicity $\delta=2(b-a)/(b+a)$ at T_c. In both, a rapid rollover in the temperature dependence of δ was observed. In Ref. 23, an additional anomalous enhancement of δ near T_c was observed. Because this enhancement has not been observed in other samples[24,25] we shall not discuss it here. Attempts to interpret the rollover in the temperature dependence of δ in terms of a break in slope by drawing various straight lines through the data above and below T_c yield $\Delta_1\delta$, given in Table II. Upper bounds for the singularities in individual lattice parameters can be obtained from bounds on slopes in the window $T_c \pm 30$ K; these bounds were used in Eq. (2.10) to derive the bounds on $d\ln T_c/d\sigma_i$ given in Table II. These give a bound $B(d\ln T_c/dP) \leq 24$ consistent with the directly measured value in Table I.

In the third measurement,[25] Rietveld analysis of the neutron powder pattern yields $\Delta_1\epsilon_1=(2\pm 7)\times 10^{-5}$, $\Delta_1\epsilon_2=(-7\pm 10)\times 10^{-5}$, $\Delta_1\epsilon_3=(13\pm 10)\times 10^{-5}$, within the bounds established above by x rays. These values were used to obtain values for $d\ln T_c/d\sigma_i$ given in Table II. However, calculation of $\delta(T)$ directly from a and b shows no anomalous enhancement near T_c and a break in the slope of the orthorhombicity $\Delta_1\delta=(-10\pm 12)\times 10^{-5}$ smaller than that suggested by x rays. The only significant break appears to be in the c parameter. The resulting value

$$B\frac{d\ln T_c}{dP}=\left[\frac{\Delta C T_c}{B}\right]^{-1}\Delta_1 V=2.4\pm 3.4$$

is, as in the case of the x-ray measurements, consistent with the directly measured value given in Table I.

We now consider sound propagation. It was shown in Sec. II that at T_c sound velocities are expected to have discontinuities in magnitude and temperature derivative, from which one may extract the first and second strain derivatives of T_c. From Eq. (2.8) and Table I we see that the order of magnitude of the relative discontinuity in the sound velocity at T_c is $\lesssim 100$ ppm. There are by now many published studies of sound velocities in high-T_c materials, but only a few measure changes in the sound velocity to the requisite accuracy. Also, as of this writing, data have been published only for ceramic samples. In what follows we present a method for analyzing data on ceramic samples, and we then discuss the results of various experiments.

A ceramic sample can be regarded as an isotropic elastic medium characterized by a bulk modulus B and a shear modulus G. There are two corresponding sound velocities, longitudinal (l) and transverse (s), given by

$$v_l^2=(B+4/3G)/\rho\,, \tag{4.1}$$

$$v_s^2=G/\rho\,. \tag{4.2}$$

Estimates of the elastic moduli B and G can be obtained from the elastic moduli of the individual crystallites through a variational effective-medium procedure which provides rigorous upper and lower bounds.[26] The simplest such expression which provides an upper bound, due to Voigt, assumes constant strain in the crystallites:

$$B\leq B_v=\tfrac{1}{9}\left[\sum_i c_{ii}+\sum_{i\neq j} c_{ij}\right], \tag{4.3a}$$

$$G\leq G_v=\tfrac{1}{15}\left[\sum_i c_{ii}-\tfrac{1}{2}\sum_{i\neq j} c_{ij}+3\sum_i \tilde{c}_i\right]. \tag{4.3b}$$

The assumption of constant stress in the crystallites leads to an equally simple lower bound, due to Reuss:

$$B\geq B_R=\left[\sum_i c_{ii}^{-1}+\tfrac{1}{2}\sum_{i\neq j} c_{ij}^{-1}\right]^{-1}, \tag{4.4a}$$

$$G\geq G_R=15\left[4\sum_i c_{ii}^{-1}-2\sum_{i\neq j} c_{ij}^{-1}+3\sum_i \tilde{c}_i^{-1}\right]^{-1}. \tag{4.4b}$$

Even at the cost of considerable additional complication,[27,28] these bounds cannot typically be improved beyond a level where they differ by $\sim 1\%$, depending on the degree of anisotropy. Thus Eqs. (4.3) or (4.4) or their generalizations cannot provide useful bounds on the small (<100 ppm) expected changes in elastic moduli at T_c. However, it seems physically reasonable that calculations of changes at T_c of the Voigt or Reuss estimates can be used to provide estimates of the true changes in elastic moduli, if the elastic anisotropy is not too large. Thus, for the discontinuities at T_c, we have either

$$\Delta B_v=\frac{\Delta C T_c}{9}\left[\sum_i \alpha_i\right]^2, \tag{4.5a}$$

$$\Delta G_v=\frac{\Delta C T_c}{30}\left[3\sum_i \alpha_i^2-\left[\sum_i \alpha_i\right]^2\right], \tag{4.5b}$$

or

$$\Delta B_R=\Delta C T_c (B_R d\ln T_c/dP)^2\,, \tag{4.5c}$$

$$\Delta G_R=\frac{2\Delta C T_c}{15}\frac{G_R^2}{B_R^2}\left[3\sum_i\left[B_R\frac{d\ln T_c}{d\sigma_i}\right]^2-\left[B_R\frac{d\ln T_c}{dP}\right]^2\right]. \tag{4.5d}$$

Note that both B and G acquire discontinuities at the transition, in contrast to the case of a purely isotropic medium where, by symmetry, only a discontinuity in B is permitted. The discontinuity in G_R (or G_V) vanishes when all the stress (or strain) derivatives of T_c are equal. In what follows, we will use the Reuss estimates as ap-

TABLE II. Stress derivatives of T_c and discontinuity in logarithmic temperature derivative of orthorhombic distortion δ for $YBa_2Cu_3O_7$, as deduced from x-ray and neutron scattering measurements.

	$B\frac{d\ln T_c}{d\sigma_a}$	$B\frac{d\ln T_c}{d\sigma_b}$	$B\frac{d\ln T_c}{d\sigma_c}$	$\left[\frac{\Delta C T_c}{B}\right]^{-1}\Delta_1\delta$
X-ray (Ref. 23)	<12	<4	<32	-15 ± 8
X-ray (Ref. 24)	<10	<7	<10	-10 ± 4
Neutron (Ref. 25)	1 ± 3	-3 ± 4	5 ± 4	2 ± 3

proximations for the elastic moduli, since our previous analysis gives direct information about $d\ln T_c/d\sigma_i$. The resulting expressions for the discontinuities at T_c in the longitudinal and transverse sound velocities are

$$\left[\frac{\Delta v_l}{v_l}\right]=\frac{1}{2}\frac{\Delta C T_c}{B}\left[1+\frac{4}{3}\frac{G}{B}\right]^{-1}\left\{\left[B\frac{d\ln T_c}{dP}\right]^2+\frac{8}{45}\frac{G^2}{B^2}\left[3\sum_i\left[\frac{Bd\ln T_c}{d\sigma_i}\right]^2-\left[B\frac{d\ln T_c}{dP}\right]^2\right]\right\}, \tag{4.6a}$$

$$\left[\frac{\Delta v_s}{v_s}\right]=\frac{1}{15}\frac{\Delta C T_c}{B}\frac{G}{B}\left[3\sum_i\left[B\frac{d\ln T_c}{d\sigma_i}\right]^2-\left[B\frac{d\ln T_c}{dP}\right]^2\right]. \tag{4.6b}$$

We now apply these results to experiments on polycrystalline $YBa_2Cu_3O_7$ and $La_{2-x}Sr_xCuO_4$. G and B have been measured by propagating longitudinal and transverse sound through these materials.[29–31] The values obtained for B are only about 60% of the values obtained by x-ray measurements of the variation of lattice parameter with pressure. The difference is possibly due to voids in the polycrystalline samples, which were not taken into account in our averaging procedure but which can have significant effects on the measured values of various properties. In our analysis, we use the x-ray value for B and estimate a void-corrected value for G by using the measured ratio G/B which we assume to be relatively insensitive to the density of voids, and is given by $G/B=0.75$ ($YBa_2Cu_3O_7$) and $G/B=0.4$ ($La_{1.8}Sr_{0.2}CuO_4$).[29]

As discussed above, the x-ray and neutron measurements of lattice parameter changes at T_c are, by virtue of their relatively large uncertainties, consistent with each other, with the hydrostatically measured $Bd\ln T_c/dP$, and indeed with isotropy of the stress derivatives of T_c ($dT_c/d\sigma_i=\frac{1}{3}dT_c/dP$). However, the mean values of the $Bd\ln T_c/d\sigma_i$ are larger and anisotropic; thus it is of interest to inquire whether they are consistent with the sound velocity experiments. Using the values of G/B given above, data from Tables I and II and Eqs. (4.4), we can compute the discontinuities in sound velocities predicted for $YBa_2Cu_3O_7$ by the neutron lattice parameter measurements, finding

$$\left[\frac{\Delta v_l}{v_l}\right]_R=-130\text{ ppm}, \tag{4.7a}$$

$$\left[\frac{\Delta v_s}{v_s}\right]_R=-130\text{ ppm}. \tag{4.7b}$$

The analysis of the x-ray lattice parameter data to obtain these discontinuities is more difficult, since the values for $d\ln T_c/d\sigma_i$ given in Table II are only upper bounds. However, these enter only through the combination

$$3\sum_i\left[B\frac{d\ln T_c}{d\sigma_i}\right]^2-\left[B\frac{d\ln T_c}{dP}\right]^2,$$

which is proportional to the anisotropy. Thus we can obtain lower bounds on the predicted sound-velocity jumps by using the measured $\Delta_1\delta$ which provides a constraint on the anisotropy, as follows:

$$\sum_i\left[B\frac{d\ln T_c}{d\sigma_i}\right]^2\geq\frac{1}{3}\left[B\frac{d\ln T_c}{dP}\right]^2+\frac{1}{2}\left[\left[\frac{\Delta C T_c}{B}\right]^{-1}\Delta_1\delta\right]^2.$$

Thus, using for definiteness the smaller of the two x-ray values, $(\Delta C T_c/B)^{-1}\Delta_1\delta=-10$, we find

$$\frac{\Delta v_l}{v_l}\geq\frac{1}{2}\left[\frac{\Delta C T_{c0}}{B}\right]\left[1+\frac{4}{3}\frac{G}{B}\right]^{-1}\left\{\left[B\frac{d\ln T_c}{dP}\right]^2+\frac{4}{15}\frac{G^2}{B^2}\left[\left[\frac{\Delta C T_c}{B}\right]^{-1}\Delta_1\delta\right]^2\right\}=160\text{ ppm},$$

$$\frac{\Delta v_s}{v_s}\geq\frac{\Delta C T_{c0}}{B}\frac{G}{B}\frac{1}{10}\left[\left[\frac{\Delta C T_{c0}}{B}\right]^{-1}\Delta_1\delta\right]^2=200\text{ ppm}.$$

For both longitudinal and transverse sound velocities, no jump has been observed within experimental resolution; thus $\Delta v_l/v_l$ is $\lesssim 20$ ppm and $\Delta v_s/v_s\lesssim 100$ ppm.[29,31] Therefore, the mean values of the $d\ln T_c/d\sigma_i$ inferred from neutron measurements and the upper bounds inferred from x-ray measurements are inconsistent with the sound velocity data. There are two possibilities for resolving this inconsistency. One, a reasonable possibility in view of the large experimental uncertainties, is that the true values of the $d\ln T_c/d\sigma_i$ are considerably smaller than the mean values or upper bounds, perhaps because the observed behavior of the lattice parameters near T_c cannot be primarily attributed to breaks in slope. This conclusion has been independently reached in Ref. 24, where the observed thermal expansion was analyzed using an anharmonic lattice model which does not involve superconductivity. Alternatively, the Reuss estimates for the sound velocity jumps could be inaccurate due to a large elastic anisotropy. In this case the anisotropy in $d\ln T_c/d\sigma_i$ could be large, but this would not necessarily imply a large anisotropy in α_i.

In $La_{2-x}Sr_xCuO_4$, no definite information about the anisotropy in $B(d\ln T_c/d\sigma_i)$ can be extracted from the available lattice parameter measurements. Therefore we assume

$$B\frac{d\ln T_c}{d\sigma_i}=\frac{1}{3}B\frac{d\ln T_c}{dP},$$

and from Eq. (4.6), Table I, and the value $G/B=0.4$ we find

$$\frac{\Delta v_l}{v_l}=130\text{ ppm}.$$

This is consistent with observations of a jump of 150 ppm in $La_{1.8}Sr_{0.2}CuO_4$ (Ref. 30) and 130 ppm in $La_{1.8}Sr_{0.2}CuO_4$.[29] The predicted jump in $\Delta v_s/v_s$ is identically zero because of the assumption of isotropy.

In both materials, further accurate measurements of the sound velocity jumps near T_c would be of interest, especially of the transverse velocity, which is directly sensitive to the anisotropy in $B(d\ln T_c/d\sigma_i)$. Ultimately, questions of anisotropy will best be addressed by measurements in single crystals.

To end this section we discuss the discontinuity in the temperature derivative of the sound velocity at T_c. This discontinuity is large, and has been observed in many experiments on oxide superconductors. However, it is more difficult to interpret than the measurements previously discussed, because [as Eqs. (2.11) and (2.12) show] it depends on many more parameters. We shall argue that the changes are much too large to be explained by the values of the a_i discussed, and estimate the other terms in Eqs. (2.11) and (2.12), concluding that some combination of the Δ_{ij} and $\tilde{\Delta}_i$ must be large.

Several groups have obtained data on the temperature dependence near T_c of sound velocity in ceramic samples. From measurements of longitudinal and transverse sound, the discontinuities in the logarithmic temperature derivatives at T_c of the elastic moduli B and G can be obtained by using

$$\begin{aligned}\Delta_1\ln B&=2\left[\left(1+\frac{4}{3}\frac{G}{B}\right)\Delta_1\ln v_l-\frac{4}{3}\frac{G}{B}\Delta_1\ln v_s\right],\\ \Delta_1\ln G&=2\Delta_1\ln v_s\,.\end{aligned}\tag{4.8}$$

For $La_{2-x}Sr_xCuO_4$, there are two measurements of $\Delta_1\ln v_l$: $\Delta_1\ln v_l=9.4\times10^{-4}$ (Ref. 29) and $\Delta_1\ln v_l=6.1\times10^{-4}$ (Ref. 30). The observed value for $\Delta_1\ln v_s$ is 2.1×10^{-3} (Ref. 29). Thus

$$\Delta_1\ln B=0.6\times10^{-3}\text{ or }0.4\times10^{-3},$$

$$\Delta_1\ln G=4.2\times10^{-3}.$$

For $YBa_2Cu_3O_7$, we find $\Delta_1\ln v_l=5.8\times10^{-3}$ (Ref. 29) or $\Delta_1\ln v_l=4.2\times10^{-3}$ (Ref. 31) and $\Delta_1\ln v_s=5.9\times10^{-3}$ (Ref. 29), yielding

$$\Delta_1\ln B=1.1\times10^{-2}\text{ or }0.5\times10^{-2},$$

$$\Delta_1\ln G=1.2\times10^{-2}.$$

$\Delta_1\ln G$ is obtained directly from the measured transverse sound velocity. To obtain $\Delta_1\ln B$ requires knowledge of G/B and also the subtraction of two roughly equal quantities; thus we believe the values of $\Delta_1\ln B$ to be much less reliable than those of $\Delta_1\ln G$. However, it seems likely that in $La_{2-x}Sr_xCuO_4$, $\Delta_1\ln G\gg\Delta_1\ln B$, and that as first pointed out by Bhattacharya[29] it is the large value of $\Delta_1\ln G$ that accounts for the observed change in temperature derivative of both longitudinal and transverse sound velocities in $La_{2-x}Sr_xCuO_4$. In contrast, in $YBa_2Cu_3O_7$, $\Delta_1\ln B$ is comparable in magnitude to, but perhaps somewhat smaller than, $\Delta_1\ln G$. Both contribute significantly to the observed $\Delta_1\ln v_l$.

We turn now to an analysis of these results. By combining Eqs. (2.11), (2.12), and (4.4) we obtain Reuss estimates for these quantities. For the change in B we find

$$(\Delta_1\ln B)_R\Big/\frac{\Delta CT_c}{B}=\left[3A\left(B\frac{d\ln T_c}{dP}\right)^2-2\left(B\frac{d\ln N_0}{dP}\right)\left(B\frac{d\ln T_c}{dP}\right)-\frac{B^2}{T_c}\frac{d^2T_c}{dP^2}\right].\tag{4.9}$$

For the change in G

$$\begin{aligned}(\Delta_1\ln G)_R\Big/\frac{\Delta CT_c}{B}=\frac{1}{15}\frac{G}{B}\Bigg\{&6A\left[3\sum_i\left(B\frac{d\ln T_c}{d\sigma_i}\right)^2-\left(B\frac{d\ln T_c}{dP}\right)^2\right]\\&+4\left[\left(B\frac{d\ln T_c}{dP}\right)\left(B\frac{d\ln N_0}{dP}\right)-3\sum_i\left(B\frac{d\ln T_c}{d\sigma_i}\right)\left(B\frac{d\ln N_0}{d\sigma_i}\right)\right]\\&+\frac{2B^2}{T_{c0}}\left(\frac{d^2T_c}{dP^2}-3\sum_i\frac{d^2T_c}{d\sigma_i^2}\right)-3\sum_i B^2\tilde{c}_i^{-2}\left(\tilde{\Delta}_i-2B\frac{d\ln T_c}{d\sigma_k}\frac{\Lambda_{ki}}{B}\right)\Bigg\}.\end{aligned}\tag{4.10}$$

First, we compare the expression for $\Delta_1\ln B$ with the experimentally measured value. In $La_{1.85}Sr_{0.15}CuO_4$, the first term in (4.9) is, for the experimentally measured values of $A=4$–6, 4.8–7.2×10^{-3}, an order of magnitude larger than the observed $\Delta_1\ln B$. Thus the contribution from the second and third terms must be comparable to the first and opposite in sign. Our estimate of

$$\frac{B^2}{T_c}\left|\frac{d^2T_c}{dP^2}\right|\lesssim240$$

shows that the third term is about an order of magnitude too small to be significant, while for the second term to be important one would have to have $80<Bd\ln N_0/dP<130$. Such extreme values seem unlikely on physical grounds, if N_0 is essentially an electronic density of states, and are inconsistent with the estimate $Bd\ln N_0/dP\sim1$ extracted[32] from measurements of the pressure dependence of the magnetic susceptibility by assuming this arises from the pressure dependence of the Pauli contribution.

In $YBa_2Cu_3O_7$, the first term in (4.9) is 10–25 for

$2 \leq A \leq 5$, which leads to a contribution to $\Delta_1 \ln B_R$ an order of magnitude too small to explain the observed $\Delta_1 \ln B$. Similarly, the bound

$$\frac{B^2}{T_c}\left|\frac{d^2T_c}{dP^2}\right| \leq 60$$

shows that the third term is at least a factor of 4 too small to explain the observed $\Delta_1 \ln B$, while for the second term to contribute one would have to postulate the unphysically large value $B d\ln N_0/dP \sim -100$.

Next, we consider the various contributions to $\Delta_1 \ln G$ for $La_{1.85}Sr_{0.15}CuO_4$. The first term in (4.10), which involves the anisotropy of the first stress derivatives of T_c, can be rewritten as

$$\left[\frac{\Delta C T_c}{B}\right]^{-1} 6A\frac{\Delta v_s}{v_s} \lesssim 300A\ .$$

Clearly, for reasonable values of A, this term alone cannot account for the observed $\Delta_1 \ln G$. The scale of the second term is set by our estimate of $B(d\ln N_0/dP)$ from $\Delta_1 \ln B$ and the limits on the anisotropy of the first stress derivatives of T_c as $\lesssim 25$. The last term in (4.10), which involves the shear anharmonicity Λ_{ij}, can be estimated as

$$(0.16)\left[B\frac{d\ln T_c}{dP}\right]\left[\frac{\Lambda}{B}\right] \approx 2.5$$

if we use the order of magnitude estimate from the Grüneisen parameter $\Lambda/B \sim 1$. Thus, to account for the observed $\Delta_1 \ln G$, there must be a large contribution from the second derivative terms: either

$$\frac{B^2}{T_c}\frac{d^2T_c}{d\sigma_i^2} \sim \frac{-B^2}{T_c}\frac{d^2T_c}{d\sigma_i d\sigma_j} \sim -5\times 10^3\ ,$$

or

$$\frac{B^2}{\tilde{c}_i^2}\tilde{\Delta}_i \sim -1\times 10^4\ .$$

An analogous series of arguments using the Voigt estimates (4.3) leads to either $\Delta_{ii} \approx -\Delta_{ij} \approx -2000$ or $\tilde{\Delta}_i \approx -1400$.

The analysis of $\Delta_1 \ln G$ for $YBa_2Cu_3O_7$ is very similar. The first term in (4.9) is $\lesssim 22A$. The second term and the shear anharmonicity term are similarly too small. Thus, in this case too there must be a large contribution from the second derivative terms to account for $\Delta_1 \ln G$: either

$$\frac{B^2}{T_c}\frac{d^2T_c}{d\sigma_i^2} \sim \frac{-B^2}{T_c}\frac{d^2T_c}{d\sigma_i d\sigma_j} \sim -5\times 10^2$$

or

$$\frac{B^2}{\tilde{c}_i^2}\tilde{\Delta}_i \sim -1\times 10^3\ .$$

An analogous series of arguments using the Voigt estimates (4.3) leads to either $\Delta_{ii} \approx -\Delta_{ij} \approx -800$ or $\tilde{\Delta}_i \approx -600$.

In summary, the large observed discontinuities in the temperature derivatives of the effective shear modulus G and the transverse sound velocity in both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ indicate that a second derivative of T_c with respect to some volume preserving strain is very large, even though none of the first derivatives are large. However, within the approximations we have used, the discontinuity in the derivative of the effective bulk modulus B is unexplained, the experimental value being an order of magnitude larger than the theoretical estimate in $YBa_2Cu_3O_7$ and an order of magnitude smaller in $La_{2-x}Sr_xCuO_4$. There are several possible explanations; as previously mentioned, the experimental values for $\Delta_1 \ln B$ are in our view considerably less reliable than those for $\Delta_1 \ln G$; alternatively, it is possible that the bounds we have quoted for d^2T_c/dP^2 are too small; also, the theoretical values depend quadratically on $d\ln T_c/dP$, so that a factor of 3 error there could resolve the discrepancy. Finally, in the Reuss averaging procedure, the expression for $\Delta_1 \ln B$ involves only isotropic pressure derivatives. It is possible that in the present case, in which the $\Delta_1 \ln G$ results indicate that some second derivative of T_c is very large compared to $(B^2/T_c)d^2T_c/dP^2$, the Reuss approximation is inaccurate and the large derivative contributes also to $\Delta_1 \ln B$.

V. SUMMARY

We have outlined the theory and analyzed currently available experimental data concerning changes in lattice properties at the superconducting T_c in the high-T_c oxide superconductors. We have considered the possibility of non-mean-field critical behavior, finding that Gaussian fluctuation corrections to the mean field may be observable, but that true critical behavior will occur only in a very small (10^{-2} K) temperature window about T_c. Within mean-field theory we have written equations for the discontinuities that occur at the superconducting T_c in the magnitude and temperature derivative of elastic moduli and sound velocities for single-crystal and ceramic materials and in the temperature derivatives of the lattice parameters. The accuracy with which the discontinuities should be measured is set by $\Delta C T_c/c_{ij}$, where ΔC is the specific-heat jump and c_{ij} is an elastic modulus. We estimate this to be 10^{-5}–10^{-6} for the oxide superconductors, although it may be larger if some elastic constant is very small relative to the bulk modulus. Because much of the available data are not of the requisite accuracy and were measured on incompletely characterized samples, it is difficult to come to definite conclusions. However, we have argued that the data suggest that in both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ the first strain derivatives of T_c are roughly equal to each other and therefore to $\frac{1}{3}B(dT_c/dP)$. This conclusion is based on effective-medium analysis of ceramic sound velocity data; the effective-medium analysis applies only if the elastic anisotropy is not large. The magnitudes of the first strain derivatives of T_c are not large compared with other superconductors. The dramatic change in the temperature derivative of the sound velocity shows that some second strain derivative of T_c is large:

$$\frac{1}{T_c}\frac{d^2T_c}{d\epsilon_{ij}^2} \sim 10^3\ .$$

In principle, lattice anharmonicity and higher-order temperature terms may contribute to the slope change, but our estimates indicate these contributions are by 1–2 orders of magnitude too small to account for the observed change. Transverse sound velocity experiments in polycrystals and the relatively small value of $B^2 d^2 T_c/dP^2$ (as determined by hydrostatic pressure measurements) each indicate that the hardening is due to the extreme sensitivity of T_c to some volume-preserving shear distortion. The data available to us do not permit more than a very rough estimate of the magnitude of the second derivative, and we are of course unable to determine which of the various second derivatives are most important. Because the effect is so large, we believe that a more precise determination of the magnitudes of the various second derivatives of T_c would be very useful.

Perhaps the most straightforward determination of the various strain derivatives of T_c would involve measurements of longitudinal and transverse sound velocities and thermal expansions in single crystals. In view of the apparent importance of Cu-O planes in high-T_c superconductivity, sound modes which deform the a-b plane are of particular interest. In the absence of single-crystal data, precise ($\sim$ppm) measurements of any discontinuity in transverse sound velocities in well-characterized ceramic samples would provide useful information on the anisotropy of the first strain derivatives of T_c. In addition, measurements of elastic moduli are necessary for accurate analysis of ceramic data.

An accurate determination of the anisotropy in the first strain derivatives of T_c combined with a physically reasonable assumption about $T_c(\epsilon)$ can be used to provide information about the magnitude of some second strain derivatives of T_c. Assume that the orthorhombic structure at T_c can be regarded as a slight distortion of a tetragonal structure in which T_c as a function of strain has tetragonal symmetry (as is true for $La_{2-x}Sr_xCuO_4$ and may also be true for $YBa_2Cu_3O_7$ if the anisotropy produced by the chains is irrelevant). For tetragonal symmetry $\alpha_1^{(t)} = \alpha_2^{(t)}$. For a small orthorhombic distortion δ, the anisotropy in the α_i may be estimated from the second strain derivatives Δ_{ij}, which should be nearly independent of δ. One finds

$$\delta(\Delta_{11} - \Delta_{12}) = \alpha_1 - \alpha_2 .$$

Thus a bound on the anisotropy in the α_i may be used to obtain a bound on $\Delta_{11} - \Delta_{12}$. However, it was shown in Sec. IV that some second derivative of $T_c \sim 0.5\text{-}1 \times 10^3$ (in $La_{2-x}Sr_xCuO_4$) and $\sim 1-2\times 10^3$ (in $YBa_2Cu_3O_7$). Values of $\Delta_{11} - \Delta_{12}$ of this magnitude would lead to values $\alpha_1 - \alpha_2 \sim 16$ for $La_{2-x}Sr_xCuO_4$, where $\delta = 0.004$, and $\alpha_1 - \alpha_2 \sim 27$ in $YBa_2Cu_3O_7$, where $\delta = 0.017$. Such a large anisotropy is ruled out in both materials by the bound on the jump in the polycrystal transverse sound velocity v_s. This argument suggests that $\Delta_{11} - \Delta_{12}$ is not large. However, since $\Delta_{33} \neq \Delta_{11}$ and $\Delta_{13} \neq \Delta_{12}$, the size of $\Delta_1 \ln v_s$ may be accounted for by the Δ_{ij} alone. Alternatively, the shear derivatives $\tilde{\Delta}_i$ may be large.

In conclusion, we discuss what may be learned from the strain derivatives of T_c. The first strain derivatives provide constraints on microscopic models. According to one physical picture of $YBa_2Cu_3O_7$, the Cu-O chains are of crucial importance. We take the chains to run along the b axis. In this case one might expect $\alpha_b \gg \alpha_a, \alpha_c$. According to another picture, the Cu-O_2 planes are the important features. Then $|\alpha_b| \sim |\alpha_a| \neq \alpha_c$. Depending on the symmetry of the superconducting order parameter one may have $\alpha_a = \pm \alpha_b$. If the coupling between planes, though weak, sets T_c, one expects $\alpha_c \gg \alpha_a, \alpha_b$.

The existence in the high-T_c materials of such a large second derivative of T_c, along with the much smaller values of the first derivatives, requires explanation, since in general we expect $\Delta_{ij} \approx \alpha_i \alpha_j$. It could be that T_c depends sensitively upon a lattice distortion which, by symmetry, cannot couple to T_c at linear order. A similar situation occurs in the $A15$ superconductor V_3Si, where $\Delta_{11} \sim 10^4$ and $|\alpha_i| < 20$, because the superconductivity is strongly coupled to a charge-density-wave transition which produces a small tetragonal distortion in a cubic structure. However, there are difficulties in applying this argument to the oxide superconductors. Although structural phase transitions do occur in the oxide materials, typically the transition temperature $T_d \gg T_c$. The exception, which might be interesting to study, is $La_{2-x}Sr_xCuO_4$ for $x \cong 0.18\text{-}0.19$. Further, in the oxide superconductors the observed structural phase transitions are most probably not driven by Fermi-surface instabilities. The transition in $YBa_2Cu_3O_7$ is an order-disorder transition, while in $La_{2-x}Sr_xCuO_4$ T_d is maximum in La_2CuO_4 which is a magnetic insulator with a gap-to-charge excitations greater than 1 eV. Finally, the previously presented estimate of $\Delta_{11} - \Delta_{12}$ in terms of $\alpha_1 - \alpha_2$ is inconsistent with this model. Thus if proximity to a structural phase transition causes the sensitivity of T_c to strain, the transition is most likely not the observed orthorhombic-tetragonal transition but instead a potential transition to a still lower symmetry phase, which is inhibited by the presence of superconductivity.

Note added. We have recently received reports[33,34] of ultrasound measurements on single crystals of $YBa_2Cu_3O_7$. Longitudinal sound was propagated in the basal plane and along the c axis; transverse sound was propagated along the c axis. In one experiment,[33] the small and nearly isotropic values $\alpha_i \sim 1.5$ were found, in agreement with the estimates we have presented. Values for temperature derivative discontinuities of longitudinal sound in the a-b plane ($\Delta_1 \ln v_l \sim 2.5\times 10^{-3}$) and c axis ($\Delta_1 \ln v_l \sim 1.0\times 10^{-3}$) were also given, yielding $\Delta_1 \ln c_{ab} \sim 5\times 10^{-3}$ (c_{ab} is some effective longitudinal elastic modulus in the a-b plane) and $\Delta_1 \ln c_{33} \sim 2\times 10^{-3}$. These are somewhat smaller than the values of $\Delta_1 \ln B$ inferred from polycrystalline data. In another experiment,[34] the bounds $|\alpha_i| \lesssim 2.5$ were reported, consistent with the other results. Values for derivative discontinuities were not given; from the figures we infer (although the low density of points near T_c leads to some uncertainty in our results) $\Delta_1 \ln v_l = 1.5\times 10^{-3}$ (longitudinal, a-b plane), $\Delta_1 \ln v_l = -6\times 10^{-3}$ (longitudinal, c axis), and $\Delta_1 \ln v_s = -1.2\times 10^{-2}$ (transverse, c axis). Note that the c-axis values are opposite in sign to the other single-crystal and the polycrystal results, and are somewhat larger in magnitude as well.

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