Evidence for strong electron-phonon coupling from the specific heat of $YBa_2Cu_3O_{7-\delta}$

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We report precise measurements of the relative enthalpy of polycrystalline $YBa_2Cu_3O_{7-\delta}$ at high temperatures ($273\ K < T < 700\ K$). From these data, we determine the lattice and electronic contributions to the specific heat. We find that the specific heat of the charge carriers follows the temperature dependence of a Fermi liquid with a Sommerfeld constant of 25 ± 3 mJ/mole K^2. By comparing our data to measurements made at low temperatures, we determine that the electron-phonon coupling is strong in $YBa_2Cu_3O_{7-\delta}$ and adequate to account for the high transition temperature.

This paper describes measurements of the electronic specific heat of $YBa_2Cu_3O_{7-\delta}$ at high temperatures. This problem is of definite interest (see, e.g., Refs. 1 and 2) because once the value of the temperature coefficient of the electronic specific heat, γ_B (also referred to below as the Sommerfeld constant), is known, then one can obtain important information about the normal-state properties. Then, by examining the specific heat at low temperatures, the strength of the electron-phonon interaction can be determined.

We report measurements of the specific heat between 300 and 700 K. In this temperature range, the lattice specific heat approaches the classical limit, while the electronic contribution continues to increase linearly. Thus, while the accuracy of the modeled lattice contribution to the total specific heat improves, the electronic contribution grows into a larger fraction of the total. Determining γ_B from measurements (See Refs. 1–3) made below 300 K, on the other hand, is difficult, both because the electrons contribute only 1% to the specific heat and sufficiently accurate calculations of the lattice contribution are difficult to attain in this lower temperature range.

The data we describe were measured by the method of phase-change calorimetry. The data obtained are accurate enough that the electronic contribution can be determined by subtracting the lattice specific heat (c_v^l) calculated from the phonon density of states. Another common technique for measuring the specific heat in this temperature range[4] is by differential scanning calorimetry. This technique does not have sufficient accuracy to determine the electronic specific heat.

The structure of $YBa_2Cu_3O_{7-\delta}$ forms two subsystems: CuO_2 planes that extend in the a and b directions and CuO chains that follow the b axis.[5] The oxygen on the chain sites is much more volatile than on the plane sites, so the oxygen deficiency δ is mostly due to vacancies in the chains. The electronic properties are observed to be extremely sensitive to the oxygen stoichiometry. Hence, we have been careful to prepare samples with a small value of δ and to measure the specific heat under such conditions that oxygen is not lost during the course of the experiment.

Polycrystalline $YBa_2Cu_3O_{7-\delta}$ was prepared by solid-state reaction in air of stoichiometric quantities of Y_2O_3, BaO_2, and CuO to yield approximately 40 g of product. Reactants were mixed before each heating by grinding for 50 min in an agate mortar and pestle. Two heating cycles were carried out in an alumina combustion boat: (1) heat to 880 °C in 3 h, anneal for 24 h, furnace cool; (2) heat to 950 °C in 3 h, anneal for 15 h, cool in 8 h to 650 °C, cool further in 8 h to 450 °C, anneal for 12 h, cool again in 8 h to ambient temperature. The fully reacted powder was then annealed at 450 °C for 24 h in flowing oxygen. The product was a pure phase according to x-ray powder diffraction, all observed reflections matching those of the reported powder pattern.[6] Least squares refinement of the powder data yielded the following lattice parameters: $a=3.8838(8)$, $b=3.8164(4)$, and $c=11.664(1)$ Å. Bromo-iodimetric titration[7] of the powder indicated an oxygen content of 6.98 per mole compound (i.e., $\delta=0.02$). dc magnetic susceptibility measurements showed the onset of superconductivity at 92 K with a

10–90 % transition width of 6 K. We observed that 45% of the flux was expelled when the sample was cooled from 100 to 4.2 K in a 0.002-T field.

The method for measuring specific heat by means of phase-change calorimetry is described fully in Refs. 8. The sample (mass: 4.7 g) is encapsulated with exchange gas in a Pt-10% Rh vial. (We chose $\frac{1}{3}$ atm of O_2 at 300 K so that the oxygen content of the sample would not change when the sample was heated.) The encapsulated sample is heated to thermal equilibrium in a furnace and then dropped into a calorimeter immersed in a high-purity ice bath. The enthalpy released by cooling the sample from T to 273.15 K melts a proportional volume of ice. The relative enthalpy is then calculated from the change in volume of the water-ice system employing an independent electrical calibration. The measured values of the relative enthalpy of $YBa_2Cu_3O_{7-\delta}$ $[H_p(T)-H_p(273.15\ \mathrm{K})]$ are plotted vs temperature in Fig. 1.

We note that this method accurately measures the difference between the enthalpy between any given temperature and the enthalpy at 273.15 K. The sample temperature is known to within 10 mK and enthalpy changes are measured with an imprecision of 0.5 J. The enthalpy of the empty vial (half of the total enthalpy for the measurements reported here) is measured in a second experiment. The accuracy of the measurement has been verified by an independent measurement of the enthalpy of NIST Standard Reference Material 720 (α-Al_2O_3).[9] The estimated overall inaccuracy of an individual enthalpy datum is 0.5%. Specific-heat data derived from the enthalpy are estimated to have an inaccuracy not exceeding 1%.

The Sommerfeld constant is calculated from the measured enthalpy data by two methods. In each method the model lattice contribution is determined from the phonon density of states $F(\omega)$, which is, in turn, deduced from the measured neutron density of states, $G_{\mathrm{meas}}(\omega)$.[10,11]

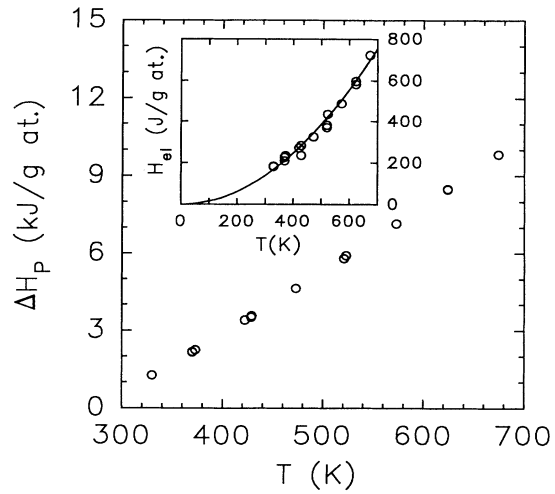

FIG. 1. Relative enthalpy of $YBa_2Cu_3O_{7-\delta}$. The inset shows the quadratic contribution remaining after the lattice contribution is subtracted.

We calculate the harmonic contribution to the enthalpy by directly integrating the contribution of each mode in the phonon spectrum according to the formula

$$H_v^1=\hbar^2\int_0^\infty d\omega F(\omega)\omega f_b(\omega,T)\ , \tag{1}$$

where $f_B(\omega,T)$ is the Bose-Einstein distribution. The harmonic contribution to the specific heat (c_v^1) is the derivative with respect to temperature of the above expression.

In the first method, the electronic specific-heat coefficient is determined directly from the enthalpy data. The difference between the measured enthalpy and the lattice enthalpy (see inset of Fig. 1) is fit with the function $a+bT+cT^2$, where a is varied, subject to the constraint that $b=0$.[12] We find that $a=3450$ J/g-at. and $c=1.54$ mJ/g-at. K^2. (We measure and fit the enthalpy relative to the value at the ice point. Thus, a corresponds to H (273.15, which is 3415 J/g-at. from the fit parameters and the calculated lattice specific heat.) When the dilatation correction[14] is subtracted, we find that $\gamma_B=2.0\pm0.1$ mJ/g-at. $K^2=26.5\pm1$ mJ/mole K^2. Details of the fitting procedure will be given in a later paper.[17]

Alternatively, we calculate the specific heat in a way similar to that described by Douglas and King.[8] First, the average specific heat ($\bar{c}_p\equiv\Delta H_p/t$) is determined for each datum of Fig. 1 and these values are fit with a function, $a+bt^\alpha$ ($t=T-273.15$ K). The true specific-heat values are then calculated from the relation

$$c_p\equiv\bar{c}_p+t(d\bar{c}_p/dt)=d\Delta H_p/dt=\Delta H_p/t+\alpha bt^\alpha\ . \tag{2}$$

In the fitting process, we iteratively, vary α, to satisfy the constraint that the difference between c_p and the lattice contribution extrapolate to zero. This is identical to the above constraint that there be no linear contribution to the enthalpy (i.e., anharmonic effects are small). In this way, we find that α is 0.442. Finally, we calculate the specific heat at constant volume (c_v) by subtracting the dilatation correction[14] and a contribution due to the motion of oxygen defects.[18] The resulting values for the specific heat at constant volume are plotted in Fig. 2. Note that the specific-heat data measured below 300 K (Ref. 21) (smaller circles) are in good agreement with the higher temperature data.

When the lattice component [see discussion following Eq. (1)] is subtracted, we are left with the electronic contribution to the specific heat seen in the inset of Fig. 2. The temperature dependence of the specific heat is linear, with a slope of 25 ± 3 mJ/mole K^2. This agrees with the value (26.5 ± 1 mJ/mole K^2) determined directly from the enthalpy data. This consistency indicates that the function, αt^α, is a reasonable choice to represent $\bar{c}_p$.

We note that if the charge carriers pair to form a simple Bose gas of bipolarons in the normal state, (see, e.g., Ref. 22), we would expect a different temperature dependence for the specific heat. That is, the specific heat should peak at the condensation temperature ($T_c=92$ K in the case of $YBa_2Cu_3O_{7-\delta}$) and then decrease monotonically to the equipartition value.[23] Our data are inconsistent with this model.

The measured Sommerfeld constant is higher than the

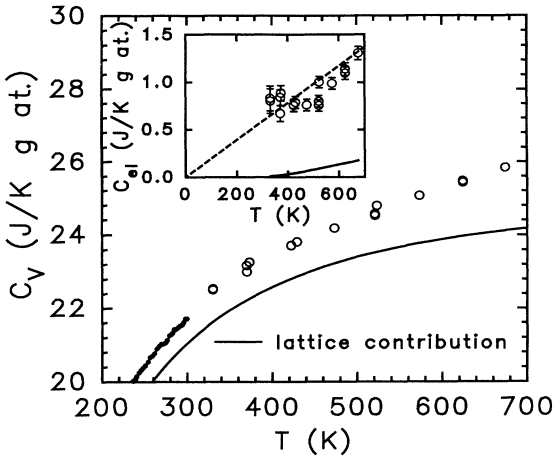

FIG. 2. Specific heat vs temperature for $YBa_2Cu_3O_{7-\delta}$ (open circles). The small circles are the data measured by Junod *et al.* (Ref. 21). The solid line is the model-lattice specific heat. [See Eq. (2) and discussion following.] The inset shows the electronic specific heat vs temperature for $YBa_2Cu_3O_{7-\delta}$. The solid line is the estimated contribution from oxygen defects (Ref. 18).

value of 13 mJ/mole K^2 obtained from band-structure calculations.[24] This discrepancy could be due to the complicated band structure in $YBa_2Cu_3O_{7-\delta}$. The Fermi energy lies near the foot of a peak in the calculated electronic density of states.[24] Hence, sample stoichiometry, defects, or inaccuracies in the calculation could shift the electronic structure enough to raise $D(\varepsilon_F)$ to a value more consistent with our measurements.

The electronic properties of $YBa_2Cu_3O_{7-\delta}$ are best understood in terms of a two-band model.[25] A number of experiments, including the resistivity measurements of untwinned single crystals,[26] show the existence of two conducting bands: one attributed to the chains and the other to the planes. Thus, separating the plane and chain contributions is vitally important.

An independent estimate of the plane density of states can be obtained from measurements of the electric-field modulation of the penetration depth. These show that the unrenormalized effective mass for the plane carriers is five times the free-electron mass.[27] For a quasi-two-dimensional metal, the electronic density of states is proportional to the effective mass, or $\gamma_{pl}^{HT}=(p\pi/3)(k_B/\hbar)^2(m_{pl}^*/d)$ (Ref. 25) (d is the unit-cell spacing, 11.6 Å, γ_{pl}^{HT} is the plane-Sommerfeld constant at high temperatures, and p is the number of planes per unit cell). We find that $\gamma_{pl}^{HT}=14.7$ mJ/mole K^2 and $\gamma_{ch}^{HT}=10.3$ mJ/mole K^2.

At low temperatures ($T<T_0\approx 0.25\bar{\Omega}$, $\bar{\Omega}$ is the characteristic phonon frequency), the electronic specific heat is renormalized by the electron-phonon interaction.[28] The temperature dependence of the renormalized electronic specific-heat coefficient can be written[28,29] $\gamma^{LT}=(1+\lambda)\gamma_B$ (λ is strength of the interaction and $\gamma_B=\gamma^{HT}$ is the unrenormalized value of the Sommerfeld constant).

We will estimate γ^{LT} and, hence, λ from the magnetic-field dependence of the specific heat at low temperatures. To do this, we assume that the enhancement of the specific heat comes entirely from the contribution of normal electrons in the vortex cores. Then, the additional field-dependent contribution is linear both in temperature and in applied field, or $\gamma^*T=\gamma^{LT}TH/H_{c2}$.

In $YBa_2Cu_3O_{7-\delta}$, the anisotropy of H_{c2} is large enough that the vortices produced by the applied field lie in the two-dimensional (2D) planes and the measured γ^* is due to the plane band only. The model of the anisotropy of the effective-mass tensor describes the penetration of the flux into the superconductor in thermodynamic equilibrium.[30] After averaging the angular dependence for H_{c2} in this model over all directions (for polycrystalline samples), we find that $H_{c2}^{ave}=H_{c2}^{ab}(1/\sqrt{2}\pi)\ln(32\Gamma^2/3)$, where Γ^2 is the effective-mass ratio m_c/m_{ab}.[17] We use the Werthamer, Helfand, and Hohenberg (WHH) formula $H_{c2}=0.59T_c(dH_{c2}/dT_c)$,[31] and the published values $dH_{c2}^{ab}/dT_c=-2T/K$ (Ref. 32) and $\Gamma=7.7$,[33] to find $H_{c2}^{ave}=171$ T.

There is considerable disagreement over the size of the magnetic-field-induced enhancement of the low-temperature specific heat.[1,2] Nevertheless, the published values of γ^* and H_{c2} provide upper and lower bounds for γ_{LT}. That is, for the range $0.3<\gamma^*/H<0.7$ mJ/mole K^2 T, we find that $51<\gamma_{pl}^{LT}<120$ mJ/mole K^2. Writing the low-temperature specific heat of the planes as $\gamma_{pl}^{LT}=\gamma_{pl}^{HT}(1+\lambda_{pl})$, we find that $2.5<\lambda_{pl}<7$. (Here we neglect the small off-diagonal terms due to the charge exchanged between the planes and chains.[24]) Therefore $YBa_2Cu_3O_{7-\delta}$ is characterized by strong electron-phonon coupling. Note that among the conventional superconductors, lead is considered to be strongly coupled: there, $\lambda\approx 1.4$.

In conventional superconductors, the discontinuity in the specific heat at T_c provides additional information about the strength of the electron-phonon coupling. This is usually expressed as the ratio of the specific-heat jump to the specific heat of the normal electrons or $\beta=(c_s-c_n)/\gamma T_c$. For the case of $YBa_2Cu_3O_{7-\delta}$, the measured values of $\beta\gamma$ range from 50 to 80 mJ/mole K^2, depending upon sample quality and the method for analyzing the data.[1] We use the unrenormalized value $\gamma=25$ mJ/mole K^2, since the specific heat is mostly undressed by T_c ($\bar{\Omega}=300$ K, the mean energy of the phonon density of states). Then we find that $2<\beta<3.2$ ($\beta=1.43$ for weak coupling). This analysis, however, must be undertaken with caution because the presence of two gaps (from the planes and chains) complicates the theoretical description. Thus, a more complete theory of multi-gap superconductors is required for further progress in this area. We emphasize that such a complicated approach is unnecessary because we obtain the strength of the electron-phonon coupling from the normal-state specific-heat data.

An estimate of T_c can be made using the expression for T_c derived by one of the authors (V.Z.K.) (Ref. 34) which is appropriate for any strength of the coupling,

$T_c = 0.25\text{-}\bar{\Omega}/[\exp(2/\lambda)-1]^{1/2}$. (For simplicity we neglect μ^*.) We have taken the average phonon energy, $\bar{\Omega}$, to be 300 K from the phonon density of states. Thus $70 < T_c < 130$ K for $2.5 < \lambda < 7$. Clearly, phonons can account for superconductivity in $YBa_2Cu_3O_{7-\delta}$.

We conclude that the specific heat of $YBa_2Cu_3O_{7-\delta}$ is characteristic of a conventional Fermi liquid with strong electron-phonon coupling. In fact, the strength of the electron-phonon interaction is sufficient to account for the high transition temperature of $YBa_2Cu_3O_{7-\delta}$.

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