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Thermal Properties of High-Temperature Superconductors[1]

I. K. Kamilov,[2,3] Sh. B. Abdulvagidov,[2] G. M. Shakhshaev,[4] Kh. K. Aliev,[4] and A. B. Batdalov[2]

The specific heat and thermal conductivity measurements of $YBa_2Cu_3O_{7-\delta}$ high-T_c superconductors were performed by an a.c. calorimetry method. Investigations of the specific heat of $YBa_2Cu_3O_{7-\delta}$ ceramics in magnetic fields show that an increase in the magnetic field reduces the jump in the specific heat, broadens the transition region, and shifts the transition temperature downward by about 0.5 K. Temperature dependence of the specific heat of a $YBa_2Cu_3O_{7-\delta}$ high-T_c superconducting ceramic reveals that fluctuation affect the specific heat near the superconducting transition. Critical exponents $\alpha = \alpha' = 0.5$, the critical amplitudes $C^+ = C^- = 0.5\ J \cdot mol^{-1} \cdot K^{-1}$, the space dimensionality $d = 3$, and the number of components in the order parameter $n = 3$ is calculated. The specific heat and the along-c-axis thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ single crystal were simultaneously measured.

KEY WORDS: a.c. calorimetry; fluctuation effects; specific heat; superconductors; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

Experimental data on specific heat is of importance in the determination of the nature of superconductivity. Knowledge of the behavior of the thermal conductivity makes it possible to estimate the role of different mechanisms of heat transfer and the scattering of heat carriers.

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[2] Institute of Physics, Daghestan Science Center, Russian Academy of Sciences, 94 Bakinskikh Komissarov Street, Makhachkala, Republic of Daghestan 367003, Russia.

[3] To whom correspondence should be addressed.

[4] Department of Physics, Daghestan State University, 8 Sovetskaya Street, Makhachkala, Republic of Daghestan 367025, Russia.

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In this paper we present the experimental results of the specific heat and the thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ high-T_c superconductors.

2. MEASUREMENTS

2.1. Specimens

High-temperature superconducting $YBa_2Cu_3O_{7-\delta}$ ceramic samples were prepared by solid-state reaction from the appropriate starting components. The density of the samples was $\rho = 5.36\ g \cdot cm^{-3}$.

Single-crystal $YBa_2Cu_3O_{7-\delta}$ samples were grown in an alumina crucible using excess BaO and CuO as solvent [1]. The crucible was heated in a vertical furnace with temperature gradient of $3°C \cdot cm^{-1}$, which was decreased during the cooling. The optimum growth parameters were chosen as follows: Initial compositions were heated to 1050°C at $50°C \cdot h^{-1}$, held for 2–4 h, cooled at $2°C \cdot h^{-1}$ to 980°C, maintained at 980°C for 24 h, then cooled at $0.2–1°C \cdot h^{-1}$ from 980 to 920°C. After this process the crucible was turned up to get crystals free of the melt. Typical size was $1.3 \times 1.0 \times 0.25\ mm^3$; weight, 2.45 mg; and density, $6.4\ g \cdot cm^{-3}$.

2.2. Procedure

The a.c.-calorimetry method [2] was modernized to measure specific heat, thermal diffusivity, and thermal conductivity.

A disk-shaped sample with thickness h is uniformly heated on one side by the chopped light. The junction of the chromel–constantan thermocouple is glued to the other side of the sample using a small amount of varnish.

Sullivan and Seidel [2] showed that the amplitude of the temperature oscillations is expressed by

$$\Delta T = \frac{\Delta P_A}{\omega C_A}\left(1 + \frac{1}{(\omega\tau_1)^2} + (\omega\tau_2)^2 + 2\sqrt{10}\,\frac{\tau_2}{\tau_1}\right)^{-1/2} \tag{1}$$

where ΔP_A is the heat power absorbed by the sample, ω is the cycle frequency of the temperature oscillations, C_A is the specific heat per unit surface $(J \cdot cm^{-2} \cdot K)$, τ_1 is the external relaxation time, and τ_2 is the internal relaxation time of the sample. If $\tau_2/\tau_1 \ll 1$ and $\omega\tau_1 \gg 1 \gg \omega\tau_2$, Eq. (1) is used to determine the specific heat.

The thermal diffusivity of the sample was determined by the equation [2]

$$\eta = h^2/3\sqrt{10}\,\tau_2 \tag{2}$$

The value τ_2 is obtained from a phase shift between oscillations of radiation impinging on the sample and the temperature of the sample [3]:

$$\tau_2 = \varphi/2\pi f_n \tag{3}$$

where φ is a phase shift in radian, and f_n is the frequency (Hz) used in the measurements.

Thus, the ΔT and φ measurements permit the calculation of specific heat, thermal diffusivity, and thermal conductivity simultaneously.

The amplitude of oscillations of the temperature of a sample was 5–10 mK. The rate of change of the temperature of a sample during measurements did not exceed 0.1 K · min^{-1}.

3. RESULTS

3.1. Specific Heat of Ceramic $YBa_2Cu_3O_{7-\delta}$ in the Region of the Superconducting Transition in Magnetic Fields

Figure 1 shows the temperature dependence of the specific heat of the $YBa_2Cu_3O_{7-\delta}$ ceramics in the superconducting transition region both in zero magnetic field and in fields 350, 900, and 1500 Oe. It can be seen that there was a strong anomaly in the transition region. This behavior of the

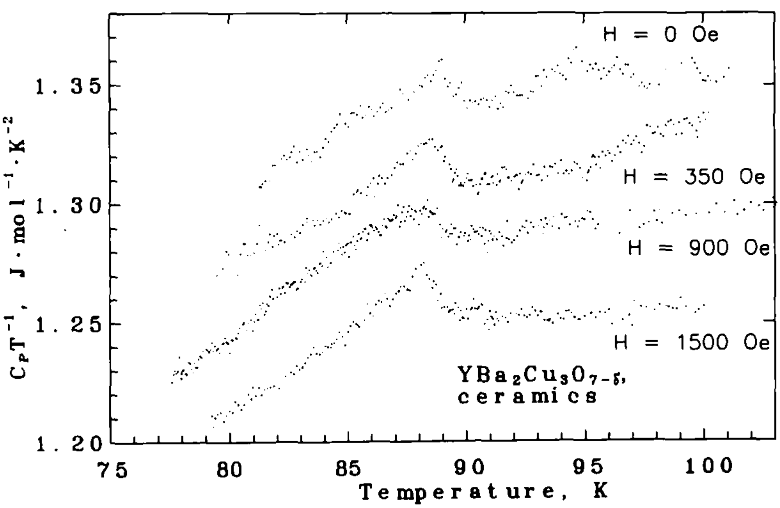

Fig. 1. Temperature dependence of C_pT^{-1} of $YBa_2Cu_3O_{7-\delta}$ in the region of the superconducting transition in zero magnetic field and in magnetic fields.

specific heat in the transition region was clearly due to the influence of fluctuations. The width of the transition from the normal to the superconducting state was about 2 K. The jump in the specific heat in the region of this transition, calculated by extrapolation of the experimental values before and above the transition, amounted to $\Delta C_p \approx 2.31\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. The presence of the jump at the transition and its magnitude indicated that the superconducting transition was a bulk phenomenon. The jump at the transition temperature T_c and the ratio $\Delta C_p/\gamma T_c = 1.43$ known from the Bardeen, Cooper, and Schrieffer (BCS) theory were used to calculate the coefficient of the electronic specific heat $\gamma = 18\ \mathrm{mJ \cdot mol^{-1} \cdot K^{-2}}$. The curves in Fig. 1 show that application of a magnetic field lowers the transition temperature, broadens the transition region, and reduces the anomalous part of the specific heat, which was readily seen by examination of the slopes of the temperature dependence of the specific heat at $T > T_c$. The value of the electronic specific heat in the region of the transition was used to calculate, employing the expression $N(E_F) = 3C_e/\pi^2 k_B^2 T_c$, the density of the electronic states near the Fermi surface per one spin of a copper atom $N(E_F) = 1.3$ states $\cdot\,\mathrm{eV^{-1}} \cdot (\mathrm{Cu\ atom})^{-1}$.

3.2. Fluctuation Effects in the Specific Heat of $YBa_2Cu_3O_{7-\delta}$ High-Temperature Ceramics

The width of the fluctuation region is estimated from

$$\varepsilon = (1/32)(k_B/\Delta C \xi_0^3)^2 \tag{4}$$

where $\varepsilon = |T/T_c - 1|$ is the reduced temperature, and ξ_0 is the coherence length [4, 5].

For high-T_c superconductors, the coherence length is very short, of the order of interatomic distances. Nevertheless, Eq. (4) yields a value of $\varepsilon \approx 0.001$ for the width of the fluctuation region. This width is much smaller than that found experimentally [6]: $\varepsilon \approx 0.02$–0.04. Equation (4) thus does not hold for the high-T_c superconductors. Values of ε which agree with the experiment can be found by a modification of the Ginzburg–Landau theory to incorporate the anisotropy of the properties of the high-T_c superconductors [7]. It is also necessary to allow for the anisotropic nature of the coherence length itself [8] and the effects of structural defects and impurities [9].

It was shown in Ref. 10 that in the range of applicability of the mean field theory, the Gaussian component of the specific heat is given above and below T_c by

$$\Delta C_p = C^{\pm}(\pm\varepsilon)^{-(2-d/2)} \tag{5}$$

where $C^{+} = k_B/8\pi\xi^3_{GL}(0)$ is the Ginzburg–Landau coherence length at $T = 0$. It also follows from the mean-field theory in the $O(n)$ model, in the case of quadratic fluctuations, that the ratio of critical amplitudes is

$$C^{+}/C^{-} = n/2^{d/2} \tag{6}$$

where n is the number of components in the order parameter, and d is the space dimensionality.

To analyze fluctuation effects near T_c, we single out the anomalous part of the specific heat, ΔC_p, subtracting from the experimental values of the specific heat C_p the background part C_B, written as a polynomial

$$C_B = aT + bT^2 + cT^3 \tag{7}$$

where T is in K and $a = -0.130813\ \mathrm{J \cdot mol^{-1} \cdot K^{-2}}$, $b = 0.0287022\ \mathrm{J \cdot mol^{-1} \cdot K^{-3}}$, $c = -0.130813 \times 10^{-3}\ \mathrm{J \cdot mol^{-1} \cdot K^{-4}}$.

Figure 2 shows the temperature dependence of the anomalous part of the specific heat, $\Delta C_p = C_p - C_B$. We see that the transition from the superconducting state to the normal state occurs continuously, not with discontinuity at T_c, as in conventional superconductors. That thermodynamic fluctuations play an important role is obvious from the anomaly in the specific heat at the transition.

Figure 3 shows the results of $\log \Delta C_p$ plotted versus $\log[(T - T_c)/T_c]$ at $T > T_c = T_M$. The results in Fig. 3 show that the dependence is linear in the interval from -1.7 to -2.3. These results yield a critical exponent $\alpha = 0.7$ for specific heat, with the specific heat reaching a maximum at the temperature $T_c = T_M = 89.2$ K. At $T < T_c = T_M$, we do not see a linear region; the implication is that the power law in Eq. (5) does not hold.

The value of the critical exponent α at $T > T_c = T_M$ agrees well with the results reported in Ref. 11, but not with the results given in Ref. 12. We believe that this discrepancy is due to the choice of T_c. If we use a scaling theory, then we must take T_c to be the temperature at which the critical exponents above and below T_c are equal: $\alpha = \alpha'$. Furthermore, at $T < T_c$ there is the standard BCS component of the specific heat:

$$C_{BCS} = 1.43\gamma(1 + 1.83\varepsilon)\,T \tag{8}$$

where ε is in the interval from -0.1 to 0.

To find the value of the transition temperature which satisfies the scaling law, we studied α and α' as functions of T. We took T_c to be the temperature at which the equality $\alpha = \alpha'$ holds. The T_c calculated in this manner turns out to be 89.7 K. Figure 4 shows the results of $\log \Delta C_p$ plotted versus $\log[(T - T_c)/T_c]$ at $T > T_c = 89.7$ K. The calculated values

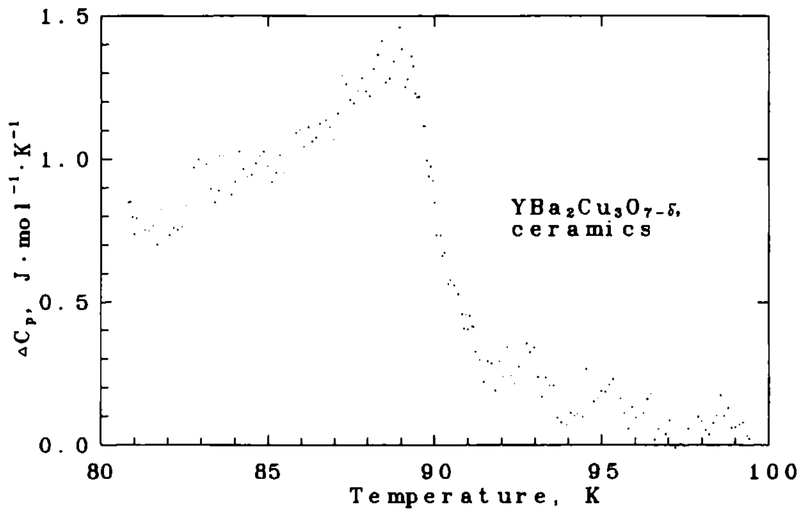

Fig. 2. Anomalous part of the specific heat, $\Delta C_p(C_p - C_B)$ obtained by subtracting the background part C_B from the measured values C_p.

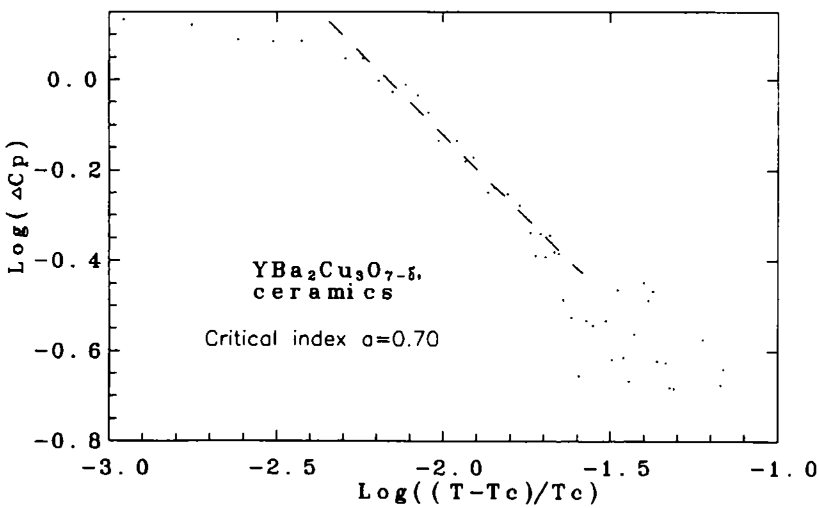

Fig. 3. Logarithmic plot of the anomalous part of the specific heat, ΔC_p, versus the reduced temperature $(T - T_c)/T_c$ at $T > T_c = T_M = 89.2$ K.

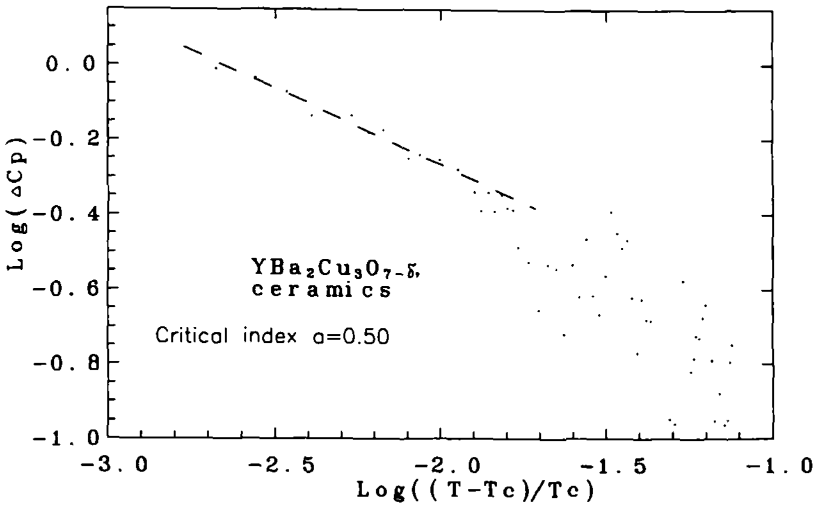

Fig. 4. Logarithmic plot of the anomalous part of the specific heat, ΔC_p, versus the reduced temperature $(T-T_c)/T_c$ at $T > T_c = 89.7$ K.

of the critical exponents and amplitudes are $\alpha = \alpha' = 0.5$ and $C^+ = C^- = 0.5\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, respectively. Using the relationship between the exponent in Eq. (6) and α $(\alpha = 2 - d/2)$, we find the space dimensionality $d = 3$. This result indicates that three-dimensional Gaussian fluctuations are realized in this superconductor. This conclusion becomes obvious from the fact that there is a weak coupling between ab planes because of the Josephson effect.

3.3. Thermal Conductivity of the $YBa_2Cu_3O_{7-\delta}$ Single Crystal Along the *c*-Axis

The thermal conductivity of $YBa_2Cu_3O_{7-\delta}$ single crystals in the *ab*-plane κ_{ab} has been discussed in a few papers [13–15]. However, we know of only one paper which presented the results of the thermal conductivity along the *c*-axis [15]. According to Ref. 15, the κ_{ab} of single crystals is similar to that of ceramic samples, which shows an upturn at T_c, but κ_c does not go through an anomalous transition at T_c and is a few times smaller than κ_{ab}.

The results on κ_c calculated from the measured values of C_p and η using $\kappa = C_p\eta$ is depicted in Fig. 5. Our results agree well with the data of Ref. 15.

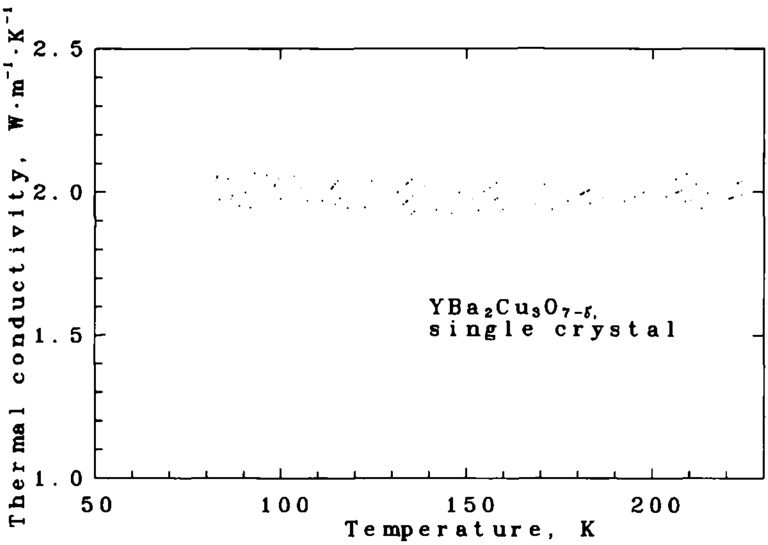

Fig. 5. The temperature dependence of the out of plane thermal conductivity κ_c in a $YBa_2Cu_3O_{7-\delta}$ single crystal.

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