TEMPERATURE WAVES IN $YBa_2Cu_3O_{7-\delta}$

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We have studied the thermal properties of a dense sintered $YBa_2Cu_3O_{7-\delta}$ ceramic in the temperature interval between liquid neon and room temperature. By means of the temperature wave method we have measured the thermal diffusivity D. The thermal conductivity λ of the same material was directly measured using a steady state longitudinal method. The specific heat C_p was calculated utilizing the data for λ, D and the density ρ of the samples. The results are discussed according to the theory of Debye and the total relaxation time τ.

Key words: YBCO superconductor, temperature wave, thermal conductivity, thermal diffusivity, specific heat.

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I. INTRODUCTION

It is well known that the properties of $YBa_2Cu_3O_{7-\delta}$ depend very sensitively on the O_2 content, and thus on the technique for preparation [1–3]. Different research groups have used various techniques for the preparation of $YBa_2Cu_3O_{7-\delta}$ superconducting polycrystals: solid state reaction [4, 5], citrate pyrolysis [6], coprecipitation method [7], nitrate synthesis [8], mineralization process [9].

In order to study the properties of high–temperature superconductors developed after nitrate synthesis, we investigated the thermal conductivity λ and the thermal diffusivity D of $YBa_2Cu_3O_{7-\delta}$ polycrystal samples in the temperature interval 25–300 K. The specific heat C_p was determined indirectly according to the following formula:

$$C_p = \frac{\lambda}{D\rho}, \tag{1}$$

where ρ is the density of the sample.

It is well known, that the analysis of the thermal properties allows the acquisition of data concerning the energetic spectrum of the excitements in solid. The most definitive conclusions about the character of the spectrum can be made on the basis of the analysis of the specific heat in a wide temperature interval reaching low temperatures. This fact is a consequence of the theory itself, that can be applied only for phenomena at temperatures near the absolute zero.

II. SAMPLES AND EXPERIMENTAL METHOD

The samples were prepared by nitrate technology described by us in detail earlier [8]. The superconducting transition temperature T_c was determined to be 90.12 K as defined by the maximum of specific heat at the transition (see Fig. 6). This result was consistent with the one measured by the magnetic susceptibility. The width of the transition was 0.8 K. Thermal diffusivity was measured under unsteady–state conditions by the temperature waves method proposed by Angstrem [10], while the thermal conductivity was determined under steady–state conditions. The one–dimensional partial differential equation for heat flow, giving the temperature distribution as a function of position x and the time with heat losses included, can be written as

$$D\frac{\partial^2 T(x,t)}{\partial x^2} = \frac{\partial T(x,t)}{\partial t} + \nu T(x,t), \tag{2}$$

where $T(x,t)$ is the transient temperature change in the sample, and D is the thermal diffusivity. The heat losses are considered to be proportional to $T(x,t)$ with a proportionality constant ν. Sidles and Danielson [11] have shown, that if the heat source located at one end of a semi–infinite rod varies harmonically with time, the thermal diffusivity can be found from the following expression:

$$D = Lv/2\ln q, \tag{3}$$

where L is the distance between the two points of the sample where the temperature is measured, q is the heat amplitude decrement between the above two points, and v is the velocity of the heat pulse.

The experimental arrangement is shown on Fig. 1 T_1 and T_2 are platinum “Lake Shore” thermometers model PT–103. Their resistance was determined according to the four–points method. The temperature of the heat sink was measured by a Carbon Glass Resistor. The power supply of the thermometers was 120 Current Source, “Lake Shore Cryotronics”. The voltage was measured with an Autocal Digital Multimeter — Datron Instruments. Temperature waves were recorded by a XY–recorder SE–780 — Gearz Metrawatt. One end of the sample was attached to the heat sink of the cryostat, while a heater, H, made of constantan wire with a resistance of 185Ω was attached to the other end. The distance $H - T_1$, $T_1 - T_2$ and T_2–heat sink were 0.8, 2.5 and 1 cm respectively. The heater voltage supply (Pulse/Function Generator Model 175, Wavetek) varied harmonically, and the sample was allowed to reach equilibrium, which was established after several thermal cycles. The amplitude of the current was 3 mA, and the period $\tau = 5$ min. The velocity of the thermal pulse $v = L/\Delta t$, where Δt is the time difference between the maximum of temperature recording. The heat amplitude decrement is $q = Ta_1/Ta_2$ (Fig. 1).

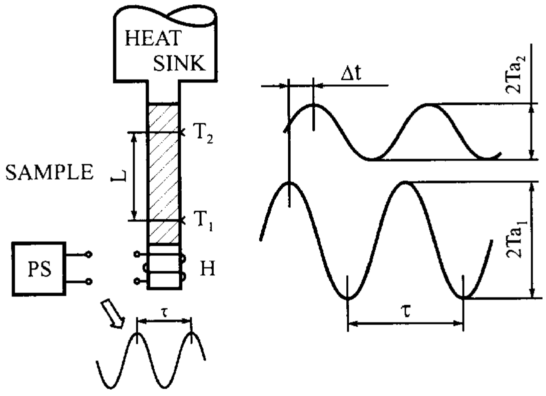

Fig. 1. The experimental arrangement around the sample.

Under steady–state conditions the coefficient of thermal conductivity λ can be calculated from the relation

$$\frac{dQ}{dT}\frac{1}{S} = -\lambda \cdot \mathrm{grad}T, \qquad (4)$$

where dQ/dT is the power consumed by the heater H, S is the sample's cross–section, $\mathrm{grad}T = (T_2 - T_1)/L$. The geometrical factor L/S for this experimental arrangement is 29.07 cm^{-1}.

The error for the determination of D was not more than $\pm 4\%$. The absolute accuracy of the λ measurements is limited by the uncertainty in the specimen geometry and estimated to be $\pm 15\%$. The error for λ due to combined heat losses via conduction through the leads and via radiation was estimated to be less than 2%.

III. RESULTS AND DISCUSSION

The results from the measurements of the thermal diffusivity D in the interval between liquid neon and room temperatures are shown on Fig. 2. It can be observed that D increases with the decreasing of temperature. This is due to the growth in the velocity of the temperature waves, and the decreasing of the heat amplitude decrement with the fall of the temperature. The average velocity of the heat wave at $T = 25$ K and $T = 300$ K was 1.68 cm/s and 0.028 cm/s respectively, while the average amplitude decrement q at these temperatures was 2.4 and 4.3 respectively.

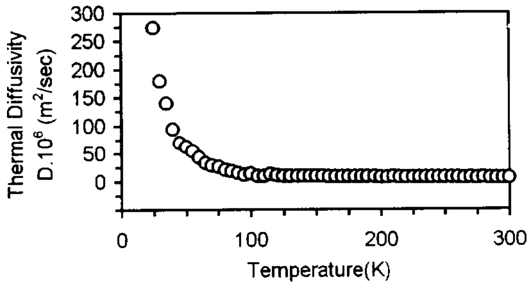

Fig. 2. Thermal diffusivity D versus T for polycrystalline $YBa_2Cu_3O_{7-\delta}$.

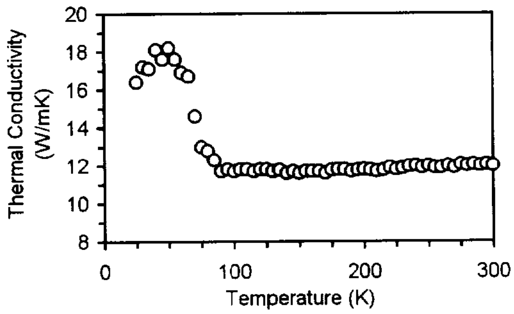

Fig. 3. Thermal conductivity λ versus T for polycrystalline $YBa_2Cu_3O_{7-\delta}$.

Fig. 3 shows typical experimental data for λ as a function of T. The displayed relation is concordant with the data presented by other researchers [12–16]. The figure shows a weak dependence of λ on the temperature when $T > T_c$.This behavior is characteristic of the electron thermal conductivity λ_e of normal metals in the temperature interval $T \sim \Theta_D$. If we apply the standard expression $\lambda_e = L_0 T \sigma$, where L_0 is the Lorenz number and σ — the electrical conductivity, for a polycrystal $YBa_2Cu_3O_{7-\delta}$ λ_e is nearly 30% of the total thermal conductivity. Besides, the increase of $\lambda(T)$ with the decrease of the temperature beneath T_c, is a proof for the electron–phonon scattering. This is due to the condensation of the normal electrons.

Keeping in mind the evaluated value for λ_e and the low electron concentration when $T > T_c$, as well as the presence of a big number of scatterers for the electrons (oxygen vacancies, grain boundaries), we suppose that: (i) the phonons had the biggest contribution for the thermal conductivity; (ii) the increase of the thermal conductivity when $T < T_c$ was due to the decrease in the electron–phonon scattering because of the condensation of the electrons in Cooper's couples; (iii) the decrease of thermal conductivity for $T < T_c/2$ after the maximum had been reached, was due to the decrease in the number of the phonons when the temperature decreased.

The lattice thermal conductivity can be written [17, 18]

$$\lambda_p = T^3 \int\limits_0^{\Theta_D/T} \frac{\tau(x,T)x^4 e^x\,dx}{(e^x-1)^2}, \tag{5}$$

where Θ_D is the Debye temperature, $x = \hbar\omega/k_BT$, and the total relaxation time τ is given by

$$\tau^{-1} = A + BT^4x^4 + CTxg(x,y) + DT^3x^2\exp(-\Theta_D/\alpha T). \tag{6}$$

All numerical prefactors have been included in Eq. (6), in which the four terms describe scattering by boundaries, defects, electrons (holes), and phonons respectively; g is a function describing the ratio of electron–phonon scattering in the normal and superconducting states, and α is a numerical constant. The phonon–phonon term, given above differs from that given by Uher [17] and co–workers [19-22]. The standard approximation [23] is DT^3x^2 giving $\lambda_p \sim 1/T$ at high T. In Refs. [19, 20, 22], a term DT^4x^2 is used because this is found to give the best fit close to T_c, but this form gives $\lambda_p \sim 1/T^2$ at high T. On the other hand the standard expression leads to the constant λ_p as $T \to 0$, in contrast to the exponential increase actually observed [24]. The exponential factor is often introduced to solve this problems. For insulators the exponential factor α is usually around the value 2.2 [24].

To illustrate this we define an effective thermal resistivity $1/\lambda_p$, where λ_p is calculated from Eq. (5) using only single term in Eq. (6) for τ. Thus, $1/\lambda_p$, corresponds to the thermal resistivity that would be observed if phonons were only scattered by other phonons, for example $\tau^{-1} = \tau_p^{-1} = DT^3x^2$. On Fig. 4 we have shown the calculated values for $1/\lambda_p$ vs. T/Θ_D using three different expressions for τ_p: the "classical" [24] term $\tau_p^{-1} = DT^3x^2$ the modified term [19, 20, 22] DT^4x^2 and the term $DT^3x^2\exp(-\Theta_D/\alpha T)$. Calculated data are shown for $0 \le T \le \Theta_D$. The Figure shows that the phonon relaxation time can be given by the expression: $\tau_p^{-1} = DT^3x^2$.

C_p as a function of T for the interval 25–300 K is shown on Fig. 5. C_p is estimated by Eq. (1). The specific heat for the interval 1.5–120K for $YBa_2Cu_3O_{7-\delta}$ polycrystalline specimens achieved by the nitrate technology, was studied in our previous paper [25].

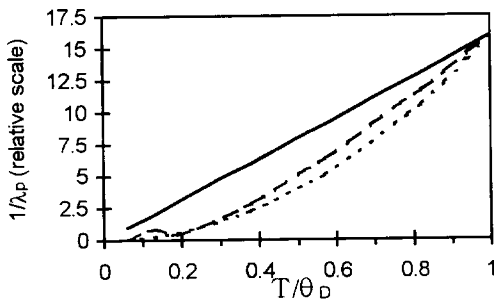

Fig. 4. Calculated phonon–phonon thermal resistivity $1/\lambda_p$ versus T/Θ_D. Curves show $1/\lambda_p$ as given by $\tau_p^{-1} = DT^3x^2$ (solid line), $\tau_p^{-1} = DT^4x^2$ (dotted line), and $\tau_p^{-1} = DT^3x^2\exp(-\Theta_D/\alpha T)$ (dashed line).

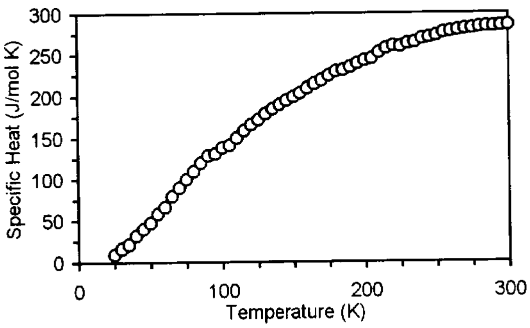

Fig. 5. Molar specific heat of polycrystalline $YBa_2Cu_3O_{7-\delta}$ as function of temperature.

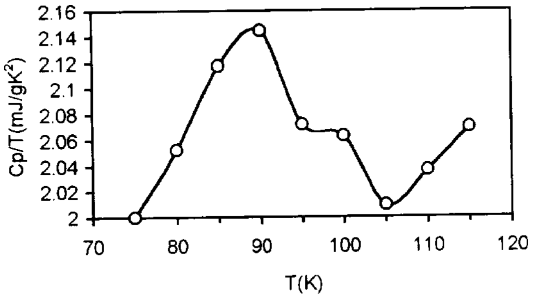

Fig. 6. C_p/T as a function of temperature in vicinity of T_c.

Different terms describe the temperature dependence of the specific heat. The number of terms needed to fit the low temperature specific heat data varies, and is somewhat arbitrary. Polynomial fits must be viewed with some caution because the terms in the fits are not naturally orthogonal. Fitting routines usually employ the least squares algorithm. It should be noted that this technique can give deceptive results when fitting a term which is small relatively to other terms in the fit. A typical result of the fitting routines is [26–28]

$$C_p = \gamma T + \beta T^3. \tag{7}$$

The T^3 term is attributed to the lattice contribution in the Debye approximation [29]. From the coefficient of T^3 the Debye temperature can be calculated [30]:

$$\Theta_D = (1943730 N_{\text{at.}}/\beta)^{1/3}. \tag{8}$$

In Eq. (8), β is the coefficient of the T^3 term in units of mJ/mol·K^4, $N_{\text{at.}}$ is the number of atoms in a unit cell (for $YBa_2Cu_3O_7$, $N_{\text{at.}} = 13$). In the Debye approximation the specific heat should be linear in C_p/T vs. T^2 up to approximately $\Theta_D/20$ (Fig. 7). We received for $\Theta_D = 398$ K — a value which is consistent with the results of other authors [26, 27, 31]. For the determination of γ, the temperature dependence of C_p should be investigated, for example, at the temperatures lower than 10 K as demonstrated by us in Ref. 25.

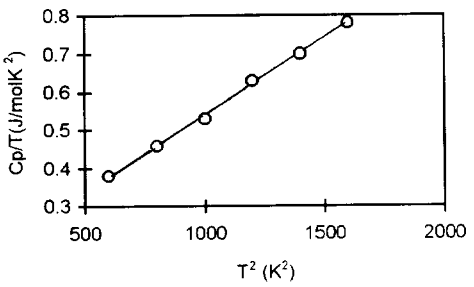

Fig. 7. C_p/T as a function of temperature squared.

It can be seen from Fig. 5, that C_p has an anomaly both at the superconducting transition ($T_c = 90$ K), as well as at temperatures near 230 K. This anomaly was described for the first time by Laegreid et al [31]. The peak of C_p is probably due to a phase transition because of structural changes. These changes, as is well known, are connected with a cubic–to–tetragonal structural phase transition in SrTiO3 at 105 K [32, 33]. Supporting evidence for a structural phase transition near 230 K can be found in a paper by Khachaturyan at al. [34], predicting a spinoidal decomposition line as a function of oxygen content which may be relevant.

IV. CONCLUSIONS

The heat transport is an important transport parameter with a significant impact on the possible technological applications of a given material. In addition, the magnitude and the temperature dependence of the thermal conductivity are powerful probes of the fundamental interaction processes taking place in a solid, since they provide the information about scattering phenomena. From the fact that thermal conductivity increases below T_c and has a peak near $T_c/2$, it has been deduced that phonon-carrier interaction is an important relaxation process. Specific heat measurements on a polycrystalline $YBa_2Cu_3O_{7-\delta}$ synthesized by the nitrate technology, show no deviations from linear behavior in C_p/T vs. T^2. The received value of $\Theta_D = 398$ K is in agreement with the results of other authors for YBCO samples obtained by other technologies. There seems to exist a remarkably good correlation between a γ–term [25] in the specific heat and a linear limiting temperature dependence of thermal conductivity. A glass–like structural transition is suggested to cause an anomaly in the specific heat at the vicinity of 230 K.

We conclude that the nitrate technology can produce $YBa_2Cu_3O_{7-\delta}$ superconductors with good qualities.

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