Contributions of Different Nature into Specific Heat of Superconducting Ceramics $NdBa_2Cu_3O_{6.87}$ at Low Temperatures

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Abstract

The specific heat of $NdBa_2Cu_3O_{6.87}$ sample within the temperature range of 5–320 K is measured. The contribution from the Schottky heat anomaly is calculated on the basis of energies of Stark components of the ground level ($^4I_{9/2}$) of Nd^{3+} ion. Electron component of specific heat at the normal state is revealed. Sommerfeld constant is obtained that determines electron state density in the vicinity of Fermi level. Harmonic component of the lattice specific heat is determined. The second and fourth momenta of the phonon state density function are calculated. Anomalous contribution into specific heat above 250 K is discovered which is due to oxygen disordering in Cu—O chains as well as the anomaly localized within the range of 260–290 K that is connected with the transition of $NdBa_2Cu_3O_{6.87}$ into a pseudo-gap state. The assumed decrease of electron state density accompanying the formation of pseudo-gap is calculated.

INTRODUCTION

The range of practical application of new superconducting materials based on compounds of the Ln – Ba – Cu – O systems (here Ln is lanthanide) is getting broader. This explains the necessity of wide-scale investigations of these compound properties. The series of properties and effects with unknown behaviour and nature requires further studies. One of important tasks to be solved when studying superconductors is the separation of phonon, electron and other components of specific heat from the total specific heat measured experimentally. The analysis of separate components of specific heat can allow one to obtain the most important characteristics of subsystems of different nature. Within the frames of these tasks, in the present study we measured specific heat of $NdBa_2Cu_3O_{6.87}$ superconductor within the temperature range of 5–320 K, calculated the contribution from Schottky thermal anomaly, separated the electron and phonon contributions to experimental specific heat, obtained its anomalous components, analysed electron and phonon characteristics of the compound under investigation.

EXPERIMENTAL

$NdBa_2Cu_3O_{6.87}$ sample was prepared from stoichiometric amounts of Nd_2O_3, $BaCO_3$ and CuO at the Ames Laboratory (Iowa State University, USA). The stoichiometric mixture was kept at 880 °C for 48–72 h and then cooled to room temperature. This procedure (heating – keeping – cooling) was done three times. Then the sample was annealed in oxygen. Annealing regime: exposure at 950 °C for 1 h, slow increase of temperature to 1050 °C and exposure for 48 h, cooling in the furnace to room temperature. Then the sample was annealed at 980 °C, at first in the air containing 1 % of oxygen (24 h), then in oxygen for 48 h, and cooled in the furnace to room temperature.

X-ray phase analysis and chemical analysis of the sample were carried out. Chemical analysis involved atomic absorption spectroscopy

(with respect to Nd, Cu and Ba contents) and iodometric titration (with respect to an oxygen content). The results of analyses showed that the sample is monophase and its composition is $NdBa_2Cu_3O_{6.87}$. The accuracy of oxygen index determination is ± 0.03 %. The sample was fine powder. Its mass was 4.025 g.

Specific heat was measured by adiabatic method using a set-up described in [1]. A sectional nickel calorimetric ampoule was used (for its structure, see [2]). The results of specific heat measurements with this calorimeter are in good agreement (see [3]) with the reference data for standard compound C_6H_5COOH [4].

Specific heat C_p of the compound $NdBa_2Cu_3O_{6.87}$ was measured at 130 points within the temperature range 5–320 K (Fig. 1). During the experiments, in order to provide equilibrium low-temperature state of the sample, the rate of its cooling from room temperature to 200 K was kept ~ 0.2 K/min (see [5, 6]). Mean square deviation of the experimental points from the curve representing smoothed $C_p(T)$ dependence is 1 % below 20 K, 0.2 % within the range of 20–80 K and 0.1 % above 80 K. The curve $C_p(T)$ exhibits an anomaly connected with the transition of the sample into superconducting state. The temperature of transition (T_c) is (95.5 ± 0.3) K. It was determined from the temperature of the minimum of $d(C_p(T)/T)/dT$ function within the range of 80–110 K. The derivative was determined using the first differences from the massive of experimental $C_p(T)$ values averaged over 3 points (Fig. 2). The jump of specific heat $\Delta C(T_c)$ is (3.3 ± 0.2) J/(mol·K).

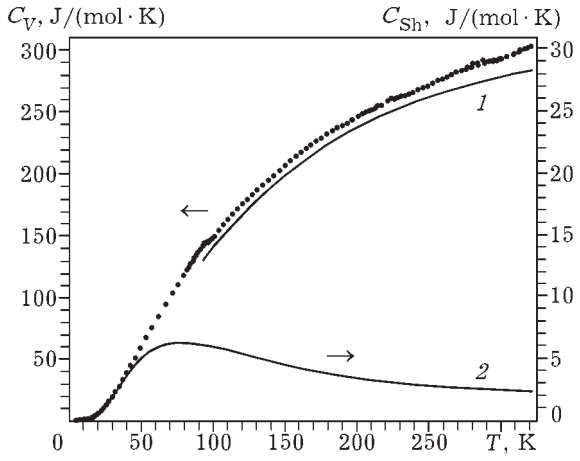

Fig. 1. Specific heat of $NdBa_2Cu_3O_{6.87}$: *1* – lattice specific heat $C_V(T)$, *2* – Schottky anomaly $C_{Sh}(T)$; points – experimental values.

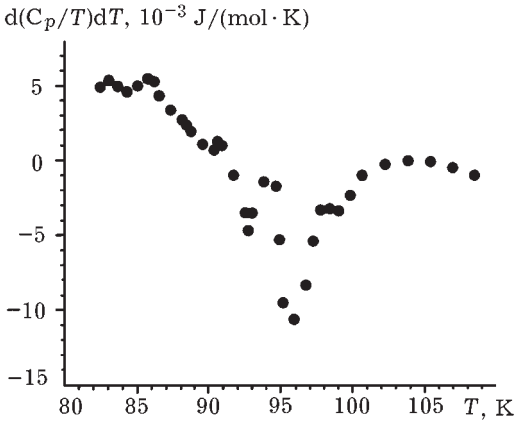

Fig. 2. The derivative $d(C_p/T)/dT$ within the temperature interval 80–110 K.

CALCULATIONS

In order to obtain reliable electron and phonon characteristics of the substance under investigation, it is necessary to reveal correctly the electron and lattice components of the total specific heat.

Low-temperature specific heat of superconducting oxides related to the systems Ln – Ba – Cu – O (Ln is a rare earth metal except La, Eu, Gd and Lu) contains the term C_{Sh} which is due to the Schottky effect. Specific heat C_{Sh} is connected with electron transitions between the components of the Ln^{3+} ion basic energy level split by the crystal field. The term C_{Sh} can be calculated if we know the splitting scheme and splitting parameters. This information is available for the compound under investigation. The basic term of the Nd^{3+} ion $^4I_{9/2}$ is ten-fold degenerated ($2J + 1$). It is split by crystal field into five Kramers doublets. The energies of the split components for the $NdBa_2Cu_3O_x$ samples with oxygen indices 6.98, 6.94, 6.73, 6.62, 6.44, 6.30 and 6.02 were obtained in [7] by means of inelastic neutron scattering. Using the results of [7] we calculated the energies of the split components for our sample (x = 6.87). The energies of the components were 0, 11.7, 20.1, 37.0, 115.5 MeV. These figures were used to calculate the specific heat C_{Sh} (T) (see Fig. 1).

Separation of electron and lattice contributions of specific heat obtained by subtracting $C_{Sh}(T)$ contribution from experimental C_p values was carried out using the method described in

[8, 9]. It was shown in [9] that the lattice specific heat in harmonic approximation (C_V) can be described by the analytical equation (in the region of high-temperature expansion applicability):

$$C_V(T) = 3N_A km\left\{1 - \frac{\theta_2^2}{12T^2} - \frac{\theta_4^4}{T^2\theta_*^2}\left[\frac{1}{12} + \frac{1}{\varphi(z)}\right]\right\} \quad (1)$$

$$\varphi(z) = e_z + e^{-z} - 2, \quad z = \frac{\theta_*}{T}, \quad T > \frac{\theta_*}{2\pi}$$

Here N_A is the Avogadro number; k is Boltzmann constant; m is the number of atoms in the formula used to determine the mass of mole; θ_* is temperature that characterizes the limiting frequency of the phonon spectrum; θ_2, θ_4 are characteristic temperatures connected with the second and fourth momenta μ_2 and μ_4 of the function $g(\omega)$ ($g(\omega)$ is the spectral density of phonon modes) by the relation

$$\theta_{2n}^{2n} = (\hbar / k)^{2n}\mu_{2n}, \; n = 1, 2$$

where $\hbar$ is Planck's constant. The momenta μ_{2n} are determined as

$$\mu_{2n} = \int_0^\infty g(\omega)\omega^{2n}d\omega / \int_0^\infty g(\omega)d\omega$$

Specific heat $C(T)$ including harmonic lattice and electron components can be written as a sum:

$$C(T) = C_V(T) + \gamma T \quad (2)$$

where $C_V(T)$ is described using (1). If data on $C(T)$ are available, it is possible to determine the parameters γ, θ_2, θ_4, θ_* and calculate lattice specific heat ($C_V(T)$) and electron specific heat (γT). In order to determine the parameters, equation (1) should be transformed into the equation of straight line by substituting

$$X(\theta_*, T) = \frac{1}{2}\left[1 - \frac{12T^2}{\theta_*^2} + \frac{12}{\varphi(\theta_* / T)}\right] \quad (3)$$

$$Y(\gamma, T, C) = 12T^2\left[1 - \frac{C(T) - \gamma T}{3N_A km}\right] \quad (4)$$

The straight line equation will be:

$$Y = \theta_2^2 - \theta_4^4 X \quad (5)$$

In order to determine optimal parameters, it is necessary to choose γ (incorporated into Y) so that the experimental specific heat C_i and temperature T_i in the coordinates of (3) and (4) were best fitted by the straight line equation. The parameters of this equation determine θ_2 and θ_4. Thus, optimal values are determined as the values corresponding to the minimum of the functional

$$\sum_i [Y(\gamma, T, C_i) - \theta_2^2 + \theta_4^4 X(\theta_*, T_i)]^2$$

Calculation technique is described in more detail in [8, 10].

Equation (2) above $T = \theta_*/(2\pi)$ describes also experimental constant-pressure specific heat $C_p(T)$ within the temperature range where this value does not contain any anomalous contributions and where non-linear (with respect to temperature) anharmonic component of the specific heat does not exceed random error of experimental results. For the case of metals and superconductors being in the normal state $\gamma T = \gamma_0 T + \gamma_A T = (\gamma_0 + \gamma_A)T$ (here γ_0 is Sommerfeld constant, $\gamma_0 T$ is electron specific heat, $\gamma_A T$ is the component of anharmonic specific heat linear with respect to T).

The specific heat of the sample $NdBa_2Cu_3O_{6.87}$ in the normal state was analysed using the procedure described above. The parameters of γ, θ_2, θ_4, and θ_* were calculated from the experimental specific heat within 100–215 K temperature range after the subtraction of C_{Sh} contribution. Specific heat in X, Y coordinates and the approximating straight

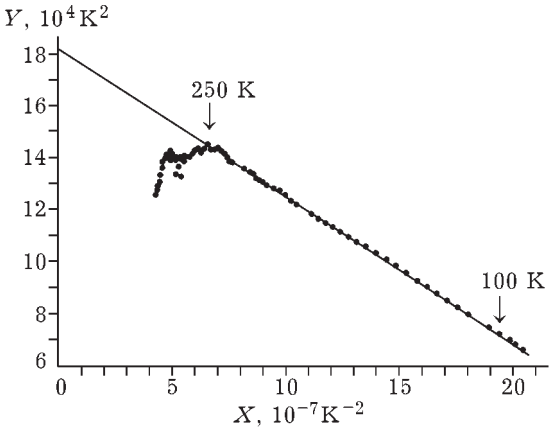

Fig. 3. Experimental specific heat of $NdBa_2Cu_3O_{6.87}$ in X, Y coordinates (see equations (3) and (4) in the text), and the approximating straight line Y at optimal parameters.

line (5) at optimal parameters are shown in Fig. 3. One can see that the linear dependence $Y(X)$ is well fit within 100–250 K temperature range. The parameters obtained in the calculation are: $\gamma/m = (\gamma_0 + \gamma_A) = (2.0 \pm 0.3)$ mJ·K^{-2}·mol^{-1}, $\theta_2 = (426.1 \pm 4.4)$ K, $\theta_4 = (488.3 \pm 7.0)$ K, $\theta_* = (586.3 \pm 12)$ K.

The dependence $C_V(T)$ was calculated according to equation (1) with the mentioned above θ_2, θ_4 and θ_* values (see Fig. 1).

In [10], for $YBa_2Cu_3O_{6.85}$ the value $\gamma_A/m \approx 0.08$ mJ·K^{-2}·mol^{-1} was obtained. The compounds $NdBa_2Cu_3O_{6.87}$ and $YBa_2Cu_3O_{6.85}$ are isostructural. Similar behaviour of the frequency distribution function $g(\omega)$ and similar character of the changes in the frequency spectrum with changing temperature provide similar behaviour of anharmonic components of the specific heat γ_A of these compounds. The expected spectral shift (due to the difference in atomic masses when yttrium is replaced by neodymium) causes only insignificant change in γ_A/m (by ~0.003 mJ·K^{-2}·mol^{-1}). Because of this, it was assumed that γ_A for $NdBa_2Cu_3O_{6.87}$ is the same as that obtained in [10] for $YBa_2Cu_3O_{6.85}$. Taking this correction into account we obtain $\gamma_0/m = (1.9 \pm 0.3)$ mJ·K^{-2}·mol^{-1}.

Above 250 K experimental points deviate from the approximating straight line (see Fig. 3). This is the evidence of the appearance of additional term $\delta C_S(T)$ in specific heat. In order to reveal this new contribution, we subtracted C_V component together with C_{Sh} and γT from the experimental specific heat ($\Delta C_S(T) = C_p - C_V - C_{Sh} - \gamma T$). The result is shown in Fig. 4. Against the background of γT one can see that the additional component has a complicated appearance and is most likely the sum of two contributions. One of them increases monotonically and another is localized in the interval 260–290 K.

It is shown in [10] that there are two anomalous contributions in the specific heat of 90° superconductors of the system Y – Ba – Cu – O above 250 K. One of them appears as an anomaly within the temperature range 260–290 K and is connected with the transition of superconductor in a pseudo-gap state. This state is

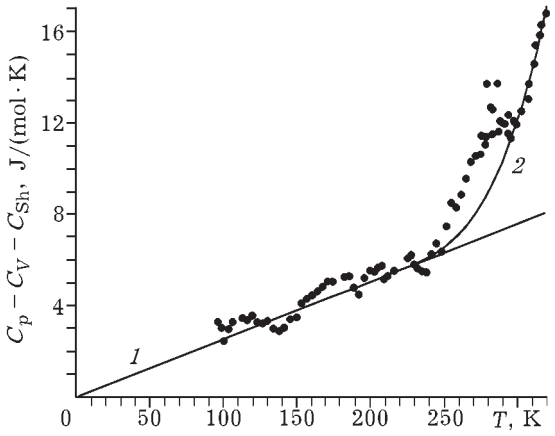

Fig. 4. The difference $C_p - C_V - C_{Sh}$ (points), the calculated contribution of γT (*1*) and anomalous component of specific heat $C_{an}(T)$ (*2*).

formed as a result of the decrease in electron state density at the Fermi level. The decrease in state density can be explained by the formation of incoherent coupled charge carriers. The second contribution is due to oxygen disordering in the chains Cu—O which is completely realized at temperatures above 320 K. In the interval of 260–320 K we observe only the low-temperature wing of this anomaly. The total additional contribution into specific heat of $NdBa_2Cu_3O_{6.87}$ at $T > 250$ K (see Fig. 4) and the anomalous contribution discovered in the same temperature range in yttrium superconductors [10] are similar in their temperature dependence and are comparable by order of magnitude. This gives the grounds to assume that their nature is the same.

In order to separate the anomalous contributions to $NdBa_2Cu_3O_{6.87}$ specific heat, we used the procedure described in [10]. The consideration of phase transitions related to ordering, when carried out, for example, in the Bragg – Williams and Kirkwood approximations (see, for example, [11]), gives an exponential decrease in anomalous heat capacity at low temperatures (close to 0 K). Within the intermediate temperature range below T_c, the dependence of specific heat is described by complicated combinations of exponential functions depending on long-range order parameter and effective temperature. It is convenient to replace these functions within a limited temperature range with a function of the type $A(T - T_0)^\alpha$ where A and α are constants. This function was used in the present study to describe a low-temperature wing of the anomaly due to

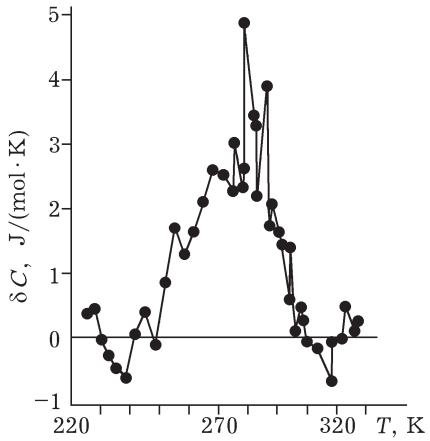

Fig. 5. Anomalous component of specific heat of $NdBa_2Cu_3O_{6.87}$ within the temperature range 260–290 K.

oxygen ordering. Parameter α was found to be 5. Figure 5 shows the separated anomaly of specific heat $\delta C(T)$ with a maximum at $T^* \approx 285$ K which is connected, as in [10], with the transition of superconductor from the normal state into a pseudo-gap one. The entropy of transition $\Delta S = (0.34 \pm 0.04)\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$. Linking the discovered anomaly with the formation of the pseudo-gap and using the equation $\Delta\gamma = \Delta S/T^*$ given in [12] we can calculate the decrease of electron state density $\Delta\gamma$ near the Fermi level. The resulting value $\Delta\gamma/m \approx 0.1\ \mathrm{mJ \cdot K^{-2} \cdot mol^{-1}}$ is only 5 % of γ_0/m. It is difficult to discover such a small change when analysing regular behaviour of $\gamma_0(T)$. The authors of [13] analysing the fraction of the charge carriers lost (at the Fermi level) for $YBa_2Cu_3O_x$ did not find that the decrease of electron state density can start at temperatures of about 285 K. They did not connect the appearance and developing of the pseudo-gap with phase-transition phenomena.

CONCLUSION

To conclude, the main results of the investigation of $NdBa_2Cu_3O_{6.87}$ specific heat are as follows. On the basis of experimental data on specific heat, the harmonic contribution of the lattice specific heat is calculated for temperatures above 93 K, the second and the fourth momenta of the phonon spectrum are calculated, as well as its effective boundary frequency. The electron specific heat of the superconductor under investigation is revealed for its normal state; the Sommerfeld constant that defines the electron state density near the Fermi level is determined. An anomalous contribution into specific heat due to oxygen disordering in Cu – O chains is revealed. An anomaly localized within the range 260–290 K is discovered which is due to the transition of superconductor in the pseudo-gap state. Assuming that the transition discovered (at 285 K) is connected with the formation of pseudo-gap, the decrease in electron state density at the Fermi level is calculated.

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REFERENCES

1 G. I. Frolova, L. E. Reznik and I. E. Paukov, *J. Chem. Thermodynamics*, 21 (1989) 25.
2 V. N. Naumov and V. V. Nogteva, *PTE*, 5 (1985) 86.
3 E. B. Amitin, Yu. F. Minenkov, O. A. Nabutovskaya *et al.*, *ZhFKh*, 64 (1990) 1755.
4 N. P. Rybkin, M. P. Orlova, A. K. Baranyuk *et al.*, *Izmeritel'naya tekhnika*, 5 (1974) 29.
5 A. N. Lavrov, *Phys. Lett. A*, 168 (1992) 71.
6 V. V. Nogteva, I. N. Kuropyatnik, A. N. Lavrov *et al.*, *Phys. Stat. Sol. (a)*, 157 (1996) k. 13.
7 P. Allenspach, J. Mesot, U. Staub *et al.*, *Z. Phys. B*, 95 (1994) 301.
8 V. N. Naumov, *Phys. Rev. B*, 49 (1994)13247.
9 V. N. Naumov, G. I. Frolova and T. Atake, *Thermochim. Acta*, 299 (1997) 101.
10 V. V. Nogteva, V. N. Naumov and A. N. Lavrov, *ZhFKh*, 72, 10 (1998) 1798.
11 V. M. Loktev and V. M. Turkowski, *Cond. mat.*, 9707191 (1997).
12 V. N. Naumov, F. S. Rakhmenkulov, V. E. Fedorov and A. V. Mishchenko, *ZhFKh*, 57, 1(1983) 33.
13 W. Y. Liang, J. W. Loram, K. A. Mirza *et al.*, *Physica C*, 263(1996)277.