Anomalies in heat capacity of YBa$_2$Cu$_3$O$_{6+x}$ in normal state

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The temperature dependence of heat capacity for the samples of 90 K phase of YBa$_2$Cu$_3$O$_{6+x}$ with $x > 0.4$, besides anomalies resulted from superconducting phase transition (at temperature $T_c$), anomalies in the range of normal state ($T > T_c$) are observed (for example, see $^{[12, 15, 16]}$).

The anomalies stably shown up in heat capacity and the corresponding singularities in other physical properties of YBa$_2$Cu$_3$O$_{6+x}$ inevitably raise the questions: to what subsystem of superconductor (the lattice one, magnetic one or electron one) - they are relevant, what processes they mark. Perhaps these processes are caused by the rise of incoherent pairing carriers of charge, by opening the pseudogap in the spectrum of spin excitations, by manifestation of wave of charge density, or by other phenomena $^{[1, 2, 3, 4, 5]}$. For clearing up the noted questions the investigations of heat capacity of YBa$_2$Cu$_3$O$_{6+x}$ in the range of the normal state seem to be topical.

In this work we analyze the precise experimental data on heat capacity of three sample of superconducting ceramics YBa$_2$Cu$_3$O$_{6+x}$ ($x = 6.85$, 6.90 and 6.95), which fall into a region of 90 K phase ($T_c \simeq 92$ K). Our investigation showed that three anomalies in the temperature interval 100–320 K were observed. The obtained results indicate that anomalies in heat capacity above $T_c$ mark the characteristic properties of YBa$_2$Cu$_3$O$_{6+x}$ - system rather than the imperfections of individual sample.

The measurements of heat capacity $C_p(T)$ were carried out in different laboratories by means of vacuum adiabatic calorimetry. We used the experimental points presented in $^{[12, 13, 14]}$.

We set the experimental heat capacity $C_p(T)$ in the range above $T_c$ to be presented by the expression

$$C_p(T) = C_v(T) + \gamma T + RA(T/T_0 - 1)\alpha + \delta C(T),$$

where $R$ is the universal gas constant. Here the term $C_v(T)$ describes the harmonic part of lattice heat capacity; the term $\gamma T$ consists in two components - the linear electron one and the linear anharmonic one; the term of $RA(T/T_0 - 1)\alpha$ is used to approximate the low-temperature wing of the another anomaly which is stably observed in the YBa$_2$Cu$_3$O$_{6+x}$ - system at the temperatures $T > 250$ K and which is caused by modification of the oxygen subsystem in the plane of chains CuO$_x$$^{[12, 13, 14]}$, the term $\delta C(T)$ describes the anomalous part of heat capacity (if it does exist). The harmonic part of the lattice heat capacity $C_v(T)$ is presented by known function of temperature with three parameters $\Theta_2$, $\Theta_4$ and $\Theta_6$, which correspond to the second moment of the phonon density of states, to the fourth moment and to the effective moment attributed to the upper limit of a phonon spectrum (the method of effective sum based on high temperature expansion of heat capacity $^{[17, 18, 19]}$). For each investigated sample the numerical values of parameters $\Theta_2$, $\Theta_4$, $\Theta_6$ and $\gamma$ (entered the expression (1)) were determined by least square method in the temperature interval 100–250 K. Then, two first terms were calculated and subtracted from the experimental heat capacity $C_p(T)$ above 100 K. Parameters of the term $RA(T/T_0 - 1)\alpha$ were determined by approximating the remainder in the interval 235–310 K (as an example see $^{[12, 13, 14]}$). With parameters determined in such a way we calculated the terms $C_v(T)$, $\gamma T$ and $RA(T/T_0 - 1)\alpha$ in the interval 100–350 K. It should be noted that these terms are nonoscillating smooth functions. For the sample $x = 0.85$ the second term $\gamma T$ (at 200 K) is less than 2% of the total heat capacity and the third term $RA(T/T_0 - 1)\alpha$ does not exceed 1.5% of the total heat capacity. For the others the orders of magnitude are the same.

In the temperature range of normal state the subtracting of smooth contributions $C_v(T)$, $\gamma T$ and $RA(T/T_0 - 1)\alpha$ from experimental heat capacity was car-
As a result the anomalies in the form of peaks higher then experimental scatter were discovered in the temperature intervals 110–200 K ($T_{\text{low}}$) and 260–290 K ($T_h$). The heights of peaks are different for the samples with different $x$. These anomalies are presented in Fig.1.

The anomaly $T_{\text{low}}$ occupies a wide temperature interval (110–200 K). It would probably consist in several components. One can see a separate peak in low-temperature region (110–140 K) for all the samples. The anomaly $T_m$ has two peaks approximately of the same height at 208 K and 225 K. The anomaly $T_h$ is located in the range 260–290 K with a peak at $\approx 275$ K.

Further investigations should answer the questions to what subsystem of superconductor – to lattice one, magnetic one or electron one – these anomalies are relevant, and what their nature is. In this work we consider the anomalies $T_h$ and $T_m$.

The analysis of experimental data shows that the correlation is evident between the temperature $T_h$ and the temperature of superconducting phase transition: $T_h \approx 3T_c$ (276 K = 3 x 92 K). Thus the anomaly $T_h$ looks like a temperature "echo" arising from superconducting phase transition at temperature $\approx 3T_c$.

The temperature "echo" discovered in three investigated samples is not the only example of such a phenomenon. Just the same temperature "echo" from superconducting phase transition arising at temperature $\approx 3T_c$ was observed in the heat capacity of the NdBa$_2$Cu$_3$O$_{6+x}$ and HoBa$_2$Cu$_3$O$_{6+x}$ compounds as well [15, 20].

The peculiarities in $T_h$ – range are characteristic for superconductors of YBa$_2$Cu$_3$O$_{6+x}$ system and they reveal themselves in different properties. For example, for the sample YBa$_2$Cu$_3$O$_{6.85}$ the derivative of electrical resistance $\rho'(T)/\rho'(200K)$ shows the sharp change just in the temperature range 260–300 K (see Fig.4 in [12]). Once more example of the anomalous behavior of electrical resistance we obtained for the sample YBa$_2$Cu$_3$O$_{6.90}$. The resistance $\rho(T)$ was measured in the temperature interval 4.2–730 K (Fig.2) by heating the sample in special regime [21]. On the curve $B$ in the range $T_h$, when the temperature decreases, the character of conduction changes from the semiconducting one to the metallic one. The deviation from semiconducting behavior begins at $\approx 275$ K. At this temperature some additional channel of the conduction arises in the sample. Otherwise the semiconducting behavior would continue further while temperature decreases. It is possible this process represents the same phenomenon which one we see in the heat capacity at temperature $T_h$.

One more example is presented in [4] where the coefficient of linear thermal expansion $\alpha(T)$ was measured along the three orthorhombic axes for single crystals YBa$_2$Cu$_3$O$_{6.95}$ and YBa$_2$Cu$_3$O$_{7+}$. At temperature $T_c$ along each axis the anomaly in $\alpha(T)$ was observed as a change of slope. Besides, for the sample YBa$_2$Cu$_3$O$_{6.95}$ the similar anomalies were observed along each axis at temperature $\approx 280$ K (in our denotes $T_h$). One can consider these anomalies, as an additional evidence of the temperature "echo" from superconducting phase transition (280K : 3 = 93.3K). It should be noted that anomalies in $\alpha(T)$ at temperature $T_h$ are present only in the sample $x = 0.95$, whereas in the sample $x = 1$ they are absent. This suggest that $T_h$ – process depend on the doping.

The connection between temperature $T_h$ and tempera-
ture of superconducting phase transition allows one to suppose that this anomaly reveals some process concerned with the rise of superconductivity, for example, with forming the Cooper pairs above the temperature of superconducting phase transition or with some other processes, from where the pseudogap in the single-particle spectrum comes.

The anomaly in heat capacity, as a peak at temperature $T_h$, evidences that this process happens as true phase transition rather than a crossover. This conclusion is in agreement with the view given in [23] that transition to superconducting phase transition allows one to agree with the view given in [23] that transition to superconducting phase transition allows one to understand the pseudogap phase is accompanied by some hidden break of symmetry.

The small amplitude of the observed anomaly results from microscopic size of the domains where the $T_h$ process happen. However, the great number of these domains in the sample (as many as the Avogadro number) gives the chance to observe it.

We assign a following meaning to introduced notion of the temperature "echo". At relatively high temperature the new phase arises in the short-range order which manifests itself by a phase transition ($T_h$ process). Yet another phase transition (when temperature decreases) is connected with development of the long-range order ($T_m$ process).

Anomaly $T_m$ (with two peaks at $\approx 210$ K and $\approx 230$ K) can be observed not only in our compounds YBa$_2$Cu$_3$O$_{6+x}$ and in (R)Ba$_2$Cu$_3$O$_{6+x}$ [3, 20], but one can note the similar anomaly in heat capacity of La$_{2-x}$Sr$_x$CuO$_4$ – compound [21].

The temperatures of these two peaks almost coincide with the points of magnetic phase transitions in pure CuO: 212 K and 230 K [23, 26]. The estimation carried out for the sample $x = 0.85$ shows that this anomaly can’t be attributed to the impurity of pure CuO, otherwise it would demand $\approx 20$ mol % of impurity to supply the observed contribution to heat capacity, which absolutely disagrees with characteristic of the sample.

We dare to say that to account for anomaly $T_m$ in cuprate systems, one can use the available idea of coexisting the antiferromagnetism with superconductivity. The presence of two kind of antiferromagnetism was discussed theoretically in [23] and also some experimental evidence were presented in [27, 28, 29, 30]. The presence of antiferromagnetism coexisting with superconductivity was revealed by elastic neutron scattering in superconductors of the family La$_2$CuO$_4$ [27, 28] and also in superconductors YBa$_2$Cu$_3$O$_{6.5}$ and YBa$_2$(Cu$_{1-y}$Co$_y$)$_3$O$_{7+\delta}$ [22, 23]. It is possible that anomaly $T_m$ marks the phase transition in this magnetic subsystem (the Neel point).

In Fig.3 the $x$ dependence of entropy of $T_m$ – and $T_h$ – processes is presented. The dependence $S_h(x)$ is a dome with maximum just in the range of optimal doping ($x \approx 0.90$).

When $x$ decreases below the optimal doping range the entropy $S_h(x)$ decreases as well. It is possible that it reduces to zero at the lower boundary of 90 K phase of YBa$_2$Cu$_3$O$_{6+x}$ – compound. When $x$ increases above the optimal doping range the entropy $S_h(x)$ decreases again. It looks as if $S_h(x)$ reaches the zero value at $x = 7$. The absence of anomaly $T_h$ in the samples YBa$_2$Cu$_3$O$_{6+x}$ with $x = 7$ is also confirmed by the data of $\alpha(T)$ – dependence [3] (see above). Thus, the $T_h$ – process seems to accompany the superconductivity of 90 K phase of YBa$_2$Cu$_3$O$_{6+x}$ – compounds.

The entropy $S_m(x)$ sharply decreases when $x$ increases above the optimal doping. It is possible that it achieves its ultimate zero value (disappearance of anomaly $T_m$) in so called overdoped range, somewhere at $x$ less then 7. When $x$ decreases in the range lower than 6.85 the entropy $S_m(x)$ increases yet, but its rise slows down now. It is possible that dependence $S_m(x)$ passes through a maximum at some value $x$ and then it decreases, reaching the zero value at the lower boundary of superconducting phase ($x \approx 6.4$).
The curve $S_m(x)$ intersects the curve $S_h(x)$ in the point of optimal doping. In this point the entropies of $T_m$ and $T_h$ processes are equalized. It is possible that this condition just determines the point of optimal doping.

In summary, the accurate description of regular contributions allows us to reveal the anomalies in temperature intervals $T_{low}$ (110–200 K), $T_m$ (205–230 K) and $T_h$ (260–290 K) for all the samples YBa$_2$Cu$_3$O$_{6+x}$ ($x = 0.85, 0.90$ and 0.95).

It has been discovered that between the temperature $T_h$ and the temperature of superconducting phase transition $T_c$ the correlation takes place $T_h \sim 3T_c$. Thus the anomaly $T_h$ can be considered as a temperature "echo" from superconducting phase transition. The analysis of data has shown that such a temperature "echo" is observed for the samples YBa$_2$Cu$_3$O$_{6+x}$ and (R)Ba$_2$Cu$_3$O$_{6+x}$, it being observed not only in heat capacity but also in other properties. The anomaly $T_h$ can be believed to reflect some process which is connected with the arise of superconductivity.

For the explanation of anomaly $T_m$ the idea was used about the existence in the cuprate superconductors of the second antiferromagnetic subsystem, this antiferromagnetism coexisting with the superconductivity. The anomaly $T_m$ (230 K) is believed to mark the phase transition (the Neel point) in this magnetic subsystem.

The dependence $S_h(x)$ of anomaly $T_h$ shows that $T_h$ process accompanies the superconductivity of 90 K phase of YBa$_2$Cu$_3$O$_{6+x}$ compounds: its entropy has a maximum in the range of optimal doping and possibly disappears on the boundaries of this phase. The curves $S_h(x)$ and $S_m(x)$ intersect each other in the point of optimal doping. It is possible that just this condition determines the point of optimal doping of superconductor.

It should be noted that the discovered anomalies mark new lines on the phase diagram of YBa$_2$Cu$_3$O$_{6+x}$ – compounds.

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