Peculiarities of electronic heat capacity of thulium cuprates in pseudogap state

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Abstract Precise calorimetric measurements have been carried out in the 7 - 300 K temperature range on two ceramic samples of thulium 123 cuprates TmBa$_2$Cu$_3$O$_{6.92}$ and TmBa$_2$Cu$_3$O$_{6.70}$. The temperature dependence of the heat capacity was analyzed in the region where the pseudogap state (PGS) takes place. The lattice contribution was subtracted from the experimental data. The PGS component has been obtained by comparing electronic heat capacities of two investigated samples because the PGS contribution for the 6.92 sample is negligible. The anomalous behavior of the electronic heat capacity near the temperature boundary of PGS was found. It is supposed that this anomaly is due to peculiarities in $N(E)$ function where $N$ is the density of electronic states and $E$ is the energy of carriers of charge.

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Introduction

Last years a number of articles devoted to research of features of various properties, connected with so called pseudogap state (PGS), have appeared in periodicals. The PGS arises in underdoped yttrium 1-2-3 and lanthanum 2-1-4 superconductors in the temperature region above the line of superconducting transition ($T_c < T < T^*$) and at concentrations of carriers of charge, smaller than the critical value $p_c$ appropriate to the point of optimal doping (POD) (Fig. 1).
Hundreds publications were devoted to studying of unusual manifestations of the PGS in various properties. The most convincing proofs of existence of the PGS were received by direct methods - photoemission with the angular resolution (ARPES) and methods of electronic tunneling [1-3]. These data make evident an appreciable decrease of the density of electronic states in the field of PGS. The density of electronic states near the Fermi level has V-shaped minimum. If temperature increases and gets over a boundary line $T^*(p)$, this minimum disappears and the system goes out of the PGS.

At first the line $T^*(p)$ was perceived as a boundary of the region where NMR spin-lattice relaxation deviates significantly from the Korringa rule [4, 5]. Later it has been shown that experimental investigations of different physical properties determine different standings of the boundary of this state [6]. The border derived from the NMR measurements of the Knight shift or from the measurements of spin-lattice relaxation is marked in Fig. 1 with $T_{cr}(p)$. It is situated at higher temperatures, than the border derived from thermodynamic and kinetic properties $T^*(p)$. Such a discrepancy allows several researchers to suggest that there are two regions on the phase diagram, corresponding to weak and strong PGS [6]. Discussing the problem, we use the notations of ref. [6] throughout the work. The upper temperature boundary denoted by $T_{cr}$, is defined as a border of crossover phenomena in NMR experiments. The lower boundary is denoted traditionally by $T^*(p)$.

Two probable mechanisms of the PGS formation are discussed in the literature:

1. The Cooper pairs exist above the temperature of superconducting phase transition forming the incoherent paired states. The number of the pairs increases with decreasing temperature and at the temperature $T_c$ the incoherent pairing transforms into the correlated superconducting state [7, 8].

2. The charge carriers interact with the fluctuations of magnetic or charge short-range order (spin or charge density waves) [9-11]. Such an interaction can yield the V-shaped minimum in the density of electron states near the Fermi level [12].

It is difficult to recognize what mechanism of PGS formation is actual. Many authors suppose the second mechanism to be more plausible, than first [13].

Along with direct examinations of features of electronic states in PGS of 1-2-3 and 2-1-4 cuprate HTSC by the methods of ARPES and electronic tunneling, the studying of thermodynamic properties of these substances can
make a considerable contribution to the insight into the subject. The investigation of unusual peculiarities in thermodynamic properties of 1-2-3 and 2-1-4 cuprate HTSC was started by Junod and co-workers in the early 90s [14, 15]. Main investigations were carried out by Loram and co-workers after the middle of 90s [16-20] and are prolonged now. Such investigations are of great interest because of many problems in the theoretical interpretation of the phenomena observed. Another problem is the separation of the electronic contribution to the heat capacity. For the normal state above \( T_c \), the electronic contribution \( C_{el} \) is not greater than 2 - 3 % of total heat capacity. Change of \( C_{el} \) connected with PGS formation is significantly less, namely 0.2 - 0.3 % of total heat capacity. Thus, even minor error in the separation of lattice, electronic, and magnetic contributions can lead to a significant error in the values describing electronic properties of cuprate HTSC.

To determine the electronic contribution at the PGS in yttrium cuprates YBCO\(_{6+x}\), Loram and co-workers used the lattice heat capacity \( C_{lat} \) of dielectric YBCO\(_6\) as a reference value. Probable differences between the values for a reference substance and substance under investigation were corrected using the sum of Einstein functions. The parameters in the functions were derived from the fitting of experimental data at low temperatures. The extrapolation of these components into field of PGS has allowed authors to separate electronic heat capacity \( C_{el} \) of the cuprates investigated. This way of calculation yields the value of \( C_{el} \) containing also the differences in magnetic and anharmonic contributions. The approximation of the difference by Einstein functions and its extrapolation in the field of PGS can produce significant errors in the electronic contribution calculated.

The aim of this work is to use the experimental results for the sample close to the optimal doping as the reference data. We think that this way of calculation of electronic contribution in the PGS is more correct.

**Experimental**

The calorimetric measurements of TmBa\(_2\)Cu\(_3\)O\(_{6.92}\) and TmBa\(_2\)Cu\(_3\)O\(_{6.70}\) were carried out using automatic low-temperature vacuum adiabatic calorimetric system. The equipment was described elsewhere [21] but only one exception: the calorimeter we used was made of copper and covered with silver instead of that made of pure nickel [21]. Internal volume of the calorimeter was about 6 cm\(^3\). Heat capacity of empty calorimeter was measured in the temperature range 6 - 310 K. The accuracy of the calorimetric results was
tested using the standard reference sample - benzoic acid. Our results agree
with reliable data for benzoic acid taken from the literature [22-24] within
the limits of ±2 % over the temperature range 6 - 10 K, 0.5 % for 10 - 30
K, 0.2 % for 30 - 60 K, and 0.1 % above 60 K. During the measurements,
temperature increase at the heat pulse was 1 to 2 K at \( T < 30 \) K and 3 - 5 K
over the temperature range 30 - 300 K. The average deviation of the exper-
imental values from the smoothed curve was about 0.02 % at temperatures
100 – 300 K. The deviation increased with decreasing temperature, growing
up to 1 % at 10 K. A total of 300 - 400 experimental points were performed
for each sample.

Ceramic \( \text{TmBa}_2\text{Cu}_3\text{O}_X \) was synthesized in the solid-state reaction ac-
cording to the standard procedure using high-purity oxides \( \text{Tm}_2\text{O}_3 \), \( \text{BaO} \),
and \( \text{CuO} \). Before the synthesis, the oxides \( \text{Tm}_2\text{O}_3 \) and \( \text{CuO} \) were annealed
at 750°C and 700°C, respectively, to remove volatile impurities. The syn-
thesis was performed in a corundum crucible in the temperature range from
800 to 900°C, step by step with an interval of 25°C, for 25 hours each. Be-
fore each step, the sample was thoroughly ground in an agate mortar. To
receive the sample with optimal oxygen content \( X = 6.92 \), the heating was
performed in an atmosphere with excess amount of oxygen. The sample with
\( X = 6.7 \) was prepared from the sample with \( X = 6.92 \) which was annealed in
air at \( T = 590°C \), then quenched into liquid nitrogen and annealed at 100°C
for two days.

Thulium cuprates were chosen for the investigation instead of yttrium
cuprates because aluminum impurity in thulium cuprate after the synthesis
in a corundum crucible was several tens lower than in yttrium cuprate. \( \text{X-ray}
\) powder diffraction showed ceramics \( \text{TmBa}_2\text{Cu}_3\text{O}_X \) to be nearly monophase
and to contain the impurities of \( \text{Tm}_2\text{BaCuO}_5 \) and \( \text{BaCuO}_2 \). Total amount
of these phases was not greater than 2-3 %. The analysis showed that the
amount of impurities did not change when the oxygen content decreased
from 6.92 to 6.70. The analysis of structural factors sensing to homogeneity
of oxygen distribution (orthorhombicity and broadening of basal reflections)
has shown a high degree of homogeneity both in the sample with \( X = 6.92 \)
and with \( X = 6.70 \).

**Results and Discussion**

Heat capacity \( C_p \) is the sum of several contributions

\[
C_p = C_{harm} + C_{anh} + C_{el} + C_{magn},
\]

(1)
where $C_{\text{harm}}$ is the contribution from harmonic vibrations in a lattice, $C_{\text{anh}}$ is that from anharmonicity, $C_{\text{el}}$ and $C_{\text{magn}}$ are the electronic and magnetic contributions, respectively. $C_{\text{el}}$ contains the contribution from the heat capacity of ordinary Fermi particles ($C_s$) that constitutes the major portion of $C_{\text{el}}$ for the sample 1 with $X = 6.92$. Besides $C_s$, $C_{\text{el}}$ in the sample 2 with $X = 6.70$ contains the contribution from the PGS ($C_{\text{PGS}}$). In the sample with $X = 6.92$, a very small contribution of $C_{\text{PGS}}$ can also be, since the PGS in 1-2-3 cuprates disappears at $X \approx 6.97$.

The lattice contribution $C_{\text{harm}}$ was calculated by fitting the experimental data to the sum of Debye and Einstein functions according to the procedure described in [25]. The fitting was performed at low temperatures. The sum of the electronic, magnetic, and anharmonic terms $\gamma_{\text{anh+el+magn}} = (C_{\text{anh}} + C_{\text{el}} + C_{\text{magn}})/T$ for the samples investigated is shown in Fig. 2 as a function of temperature over the temperature range 100 - 300 K. We suppose that the anharmonic and magnetic contributions to the heat capacity for both samples are nearly identical. At least, we state with certainty that the difference between those contributions is much greater for YBCO$_6$ and YBCO$_{6+X}$, compared by Loram [16-20], than for TmBa$_2$Cu$_3$O$_{6.7}$ and TmBa$_2$Cu$_3$O$_{6.92}$. The reason is the difference in structure and in magnetic order between the compared yttrium cuprates.

Our experimental data were treated in the following way. After subtraction of lattice contribution from total heat capacity, the function $f(T)$ was derived:

$$f(T) = \{C_{\text{anh}}(X=6.92) / T + \gamma_{\text{el}}(X=6.92) + C_{\text{magn}}(X=6.92)/T\} - \{C_{\text{anh}}(X=6.70)/ T + \gamma_{\text{el}}(X=6.70) + C_{\text{magn}}(X=6.70)/T \}.$$  \hspace{1cm} (2)

The function $f(T)$ is shown in Fig. 3. If the anharmonic and magnetic contributions are nearly the same, the difference is

$$f(T) = \Delta \gamma_s - \gamma_{\text{PGS}}(X=6.70).$$  \hspace{1cm} (3)

The first term is positive and increases slightly with increasing temperature [26]. Function $\Delta \gamma_s(T)$ has no extremum. Hence, the wavy anomalies in the Fig. 3 are caused by the second term in equation 3. The minimum of the $f(T)$ is the result of the maximum of the function $\gamma_{\text{PGS}}(X = 6.70)$ that exists in the temperature range 200 - 250 K. The $f(T)$ tends to zero as
temperature increases up to 300 K indicating that the PGS transforms into other state.

Moca and Janko [26] have analyzed the experimental data on electronic heat capacity measured by Loram and co-workers. The analysis was based on the first point of view mentioned above: the incoherent Cooper pairs exist in the PGS. Moca and Janko supposed that $\gamma_{el}$ consists of two contributions:

$$\gamma_{el}(T) = \gamma_s(T) + \gamma_p(T), \quad (4)$$

where $\gamma_s(T)$ is the single-particle contribution from Fermi particles. This contribution is similar to the first term in Eq. 3. It increases slightly and monotonically with increasing temperature. The second term in Eq.4, $\gamma_p(T)$ is the contribution from the formation of the incoherent Cooper pairs. According to Ref. [26], $\gamma_p(T)$ depends on temperature like $(T*/T)^3 \exp(-2T*/T)$ with a maximum near $T = T^*$. According to analysis of the data reported by Loram et al., the authors [26] suppose the position of maximum of $\gamma_{el}(T)$ to shift to lower temperatures when the oxygen content increases. For the cuprate with $X = 6.7$, the maximum of function $\gamma_{el}(T)$ was estimated to be within the temperature range 120 to 130 K [26]. The experimental results in Fig. 3 clearly show that there is no maximum over the temperature range 120 - 130 K.

If there is a systematic error in the separation of harmonic and anharmonic contributions, the error in the electronic contribution can be as high as tens percent. Such an error in the calculations is equivalent to the experimental error of 0.1 - 0.2 % in the total heat capacity. It means that we analyze the function $C_p(T)$ in trying to recognize its peculiarities comparable with an accuracy of the experiments. This illustrates how complicated it is to extract the electronic heat capacity and correctly determine its features.

It is possible to assume, that observed anomalies are related to impurities in samples. In fact, copper oxide is a starting material for the synthesis and it undergoes two phase transitions, at $T = 212.6$ K and $T = 229.5$ K [28]. Nevertheless, to produce such an effect in heat capacity, the samples have to contain at least 4 or 5 % of copper oxide. We carefully investigated the samples by means of X-ray powder diffraction with a limit of detection about 2 - 3 % in searching for the copper oxide impurity. No traces of CuO were found. Besides, the effect observed in Fig. 3 is in the difference between heat capacities of two samples. The sample with $X = 6.70$ was received after gentle heat treatment (at 590°C) of the sample with $X = 6.92$. Copper oxide starts
to decompose at 1061°C and it means that both of the samples contain the same amount of CuO. The probable effect of the phase transitions in copper oxide should be eliminated in the evaluation of the \( f(T) \) function (Eq. 2). Thus, the copper oxide impurity cannot explain the anomalous behavior of the heat capacity. The amplitude of the anomalous heat capacity, by our data, decreases as the sample composition approaches the point of optimal doping. These facts lead us to the conclusion that the peculiarities observed are connected with the transformation of the samples into the PGS.

Recent theoretical investigations examined the electronic systems interacting with charge or spin short-range fluctuations [13, 29]. The interaction is shown to be responsible for the formation of pseudogap structure near the Fermi level. The evaluations based on the mean field approximation fail to describe correctly the properties of the system. At proper consideration of the fluctuations in the PGS it is found that, besides V-shaped minimum, the sharp peaks in the density of electronic states can form [13, 29]. It would appear reasonable that the effective value \( N(E) \) near the Fermi level can be very complex and sensitive to the changes in the system near the PGS. In that case the transformation into the PGS can go with complex anomalous behavior of various physical properties. First of all, these are the properties connected with the density of states of charge carriers. We suppose that the observed anomalous behavior of the electronic heat capacity is the result of the transformation. Probably, the same phenomenon is responsible for unusual function \( C_p(T) \) for lanthanum 2-1-4 cuprates described in [27]. We assume that our experimental data for thulium cuprates, together with the results on the heat capacity of lanthanum 2-1-4 cuprates [27], can be qualitative confirmation of the theoretical calculations of Sadovskiy et al.

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REFERENCES

1. Randeria M, Campuzano J.C. cond-mat/9709107.
2. Randeria M, cond-mat/9710223.
3. Ding H. et al. Nature V. 382, 51 (1996).
4. Millis A., Monien H., Pines D. Phys.Rev. B, 42, 1671 (1990).
5. Gorny K. et al., Phys.Rev.Lett., 85, 177 (1999).
6. Schmalian J., Pines D., Stojkovich B., Phys.Rev.B, 60, 667 (1999).
7. Geshkenbein V.B., Ioffe L.B., Larkin A.I., Phys.Rev.B, 55, 3173 (1997).
8. Gusynin V.P., Loktev V.M., Sharapov S.G., GETP. 115, 1243 (1999).
9. Schmalian J., Pines D., Stojkovich B., Phys.Rev.Lett., 80, 3839 (1998).
10. Kuchinskiy E.Z., Sadovskiy M.V., GETP., 115, 1765 (1999); E-prints archive, cond-mat/9808321 (1998).
11. Posazgennikova A.I., Sadovskiy M.V., GETP, 115, 632 (1999); E-prints archive, cond-mat/9806192 (1998).
12. Sadovskiy M., Kuchinskiy E.Z., Physica C, 341-348, 879 (2000).
13. Sadovskiy M.V., Uspehi Phys.Nauk, 171, 539 (2001).
14. Junod A., Graf T., Sanchez, et al. Physica B, 165-166, 1335 (1990).
15. Junod A., et al., Physica C, 168, 47 (1990).
16. Liang W.Y., Loram J.W., Mirza K.A., et al., Physica C, 263, 277 (1996).
17. Loram J.W., Mirza K.A., Cooper J.R., et al., Physica C, 282-287, 1405 (1997)
18. Loram J.W., et al., J. Supercond. 7, 234 (1994).
19. Loram J.W., Tallon J.L., Physica C, 349, 53 (2001); cond-mat./0005063.
20. Loram J.W., Tallon J.L., Williams G.V.M., Physica C, 338, 9 (2000).
21. Bessergenev V.G., Kovalevskaya Ju. A., Paukov I. E., Starikov M. I., Opperman N., Reichelt W., J. Chem.Therm., 24, 85 (1992).
22. Rybkin N.P., Orlova M.P, Baraniuk A.K. Izmeritel’nyaya tekhnika, No 7, 29 (1974).
23. Moriya K, Matsuo T, Suga H., J. Chem. Therm. 14, 1143 (1982).
24. Sorai M., Kayi K., KanekoY., J.Chem. Therm., 24, 167 (1992).
25. Zhdanov K.R., Rahmenkulov F.S., Fedorov V.E., Mischenko A.V. Phyzika Tverdogo Tela, 30, 1119 (1988).
26. Moca C.P., Janko B., E-prints arXiv: cond-mat/0105202 v1.
27. Loram J.W., et al., J. Phys. Chem. Solids, 59, 2091 (1998).
28. Junod A., et al., J. Phys.: Condens. Mat., 1, 8021 (1989).
29. Sadovskiy M.V., Kuchinskiy,GETP , 117, 613 (2000).
Fig. 1. Schematic phase diagram for the cuprates
Fig. 2. Electronic, anharmonic, and magnetic contributions to the heat capacity of thulium cuprates
Fig. 3. Function $f(T)$