THERMODYNAMIC STUDY OF HIGH-TEMPERATURE SUPERCONDUCTORS $YBa_2Cu_3O_x$ AND $Bi_2Sr_2CaCu_2O_y$

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UDC 537.312.62

We show experimentally that the heat capacity curves for the superconductors with compositions $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$ interact the heat capacity curves of their corresponding glasses near the superconducting transition temperatures.

Intensive studies of the thermodynamic properties of high-temperature superconductors (HTSC) have led to the development of a certain scheme, which is based on the additivity of heat capacities, for searching and interpreting the data. As a rule the "scenario" of such studies consists of the following stages: first, the discontinuity in the electronic heat capacity at the superconducting transition temperature is determined; second, the lattice contribution to the heat capacity, which may be described by the Debye function, is isolated; and, third, the linear contribution γT, predicted by the Anderson model [1], is found, etc. However, despite a large number of experimental investigations, the data on thermal properties – primarily on the heat capacity of the superconducting compounds Bi–Sr–Ca–Cu–O – is clearly inadequate due to the multiphase nature of the investigated samples, which leads to large differences in the obtained results and to difficulties in their interpretation. At the present time certain differences in the behavior of the heat capacities of different classes of HTSC have been observed. For example, the linear electronic contribution to heat capacity has not been observed in superconductors based on Bi [2-4]. In this connection, new approaches and methods are necessary in order to reveal the general trend in the behavior of the thermodynamic properties of all high-temperature superconductors.

The goal of the present work is to determine the common features in the behavior of the thermodynamic properties of two high-temperature yttrium–barium ceramic superconductors $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$. For that purpose, based on the working hypothesis about the primary role of the phonon contribution to the high-temperature superconductivity mechanism and the independence of the phonon spectral frequencies of the structure at $T = T_c$, we investigated the thermodynamic properties of superconductors $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$ and of glass oxides with the same compositions.

The superconductors $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$ were prepared by using one of the more interesting modern techniques which entails melting the charge in a solar furnace by the lining method in a cold container and then thermally treating the quenched molten material. Some of the distinguishing characteristics of this method are the absence of sources for contaminating the samples which result from melt interacting with crucible walls; the high homogeneity of the material due to melt heating and to the uniform conditions during quench cooling; the completeness of the synthesis because of chemical reactions taking place in liquid phase; and the speed of sample preparation. We should separately point out the advantages of solar technology for the study of thermodynamic properties. Since the separate contributions to thermal capacity – in particular, the linear electronic component γT – might be due to the impurity compounds which form during the intermediate sample grinding step in traditional methods for obtaining HTSC, this might lead to an incorrect understanding of the mechanism for high-temperature superconductivity. The application of solar technology (and thereby the elimination of the intermediate grinding step), opens up the possibility of synthesizing standardized HTSC materials for the study of their thermodynamic properties.

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1062-0125/92/6201-0001$12.50

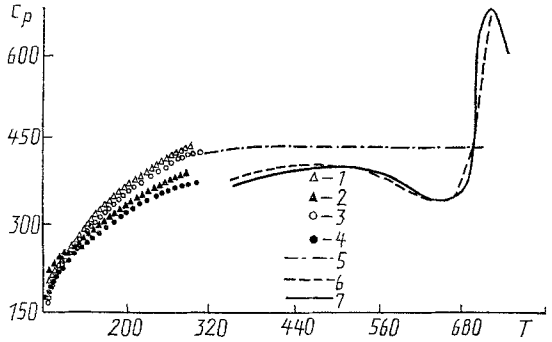

Fig. 1. Temperature dependence of heat capacity in the temperature range 80-300 K: 1) superconducting $YBa_2Cu_3O_x$; 2) quenched $YBa_2Cu_3O_x$; 3) superconducting $Bi_2Sr_2CaCu_2O_y$; 4) quenched $Bi_2Sr_2CaCu_2O_y$; 5) extrapolation of our data for superconducting $Bi_2Sr_2CaCu_2O_y$; 6, 7) data of Inoue [6] for $BiSrCaCu_2O_y$ and $Bi_{1.3}SrCaCu_2O_y$ glasses. Units: c_p (J/kg·K); T (K).

The charge was prepared from Y_2O_3, $BaCo_3$, and CuO powders for the 1:2:3 compound and from Bi_2O_3, SrO_2, $CaCO_3$, and CuO powders for the 2:2:1:2 compound. The charge was not subjected to thermal treatment prior to melting. Following the rapid liberation of CO during the carbonate decomposition, the compound was held briefly at 1500-1600°C. Quenched samples were prepared by rapidly cooling the collapsing melt droplets by using two water-cooled blocks with high-speed electromagnetic shutters. The melt cooling rate was at least 10^5 deg/sec. Next, in order to impart superconducting properties, the quenched samples received a thermal treatment. The 1:2:3 system received a single anneal at 950°C in air and was then cooled slowly in flowing oxygen. The 2:2:1:2 system received a single anneal at 800-820°C and was then cooled quickly by extracting the samples from the furnace.

The x-ray phase analysis was carried out on the DRON-2 diffractometer using the CuK line. The superconducting properties of the samples were monitored by measuring resistivity $\rho(T)$ and magnetic susceptibility $\chi(T)$. The electric resistivity was measured by the four-contact method with alternating current (10 mA), using the In–Ga eutectics for contacts. The sensitivity of the resistance measurement was at least 10^{-6} Ω. We studied thermodynamic properties using four types of samples: sample No. 1 ($YBa_2Cu_3O_x$ superconductor) has the orthorhombic structure of the 1:2:3 phase and the unit cell parameters $\gtrsim$ = 3.82 Å, b = 3.90 Å, and c = 11.71 Å. The presence of the secondary phases – Y_2BaCuO_5, BaCuO, and CuO – that were revealed by chemical analysis is within the noise level of the measurement. The x-coefficient for oxygen content is 6.82-6.91. Sample No. 2 ($Bi_2Sr_2CaCu_2O_y$ superconductor) predominantly contains ($\lesssim$80%) the 2212 phase, whose structure we attribute to the tetragonal crystal system with unit cell parameters a = 5.39 Å and c = 30.65 Å. There are also trace amounts of admixed CuO and 2201 phases and of unidentified compounds. Samples 1 and 2 exhibited metallic conductivities with a sharp single-step superconducting transition. Below we list the values of resistivity (from resistance measurements) and SC transition parameters (from magnetic measurements):

	Sample No. 1	Sample No. 2
T_c^{onset}, K	97	87
ΔT_c, K	2	4
ρ(300 K), mΩ·cm	10	2.5
$\rho(T_c^{onset})$, mΩ·cm	3	1

Sample No. 3 (quenched $YBa_2CU_3O_x$) was prepared by rapid melt quenching. The speed of quench used in preparing the material did not allow us to obtain a single amorphous state of the solid material. Our x-ray analysis revealed an amorphous phase including $BaCuO_2$ and Y_2O_3. Sample No. 4 (quenched $Bi_2Sr_2CaCu_2O_y$) is composed of a completely amorphous phase. Its x-ray photograph contains one broadly-spread peak near $2\varphi = 30°$, which is typical only of an amorphous phase. In the temperature range 77-300 K, samples 3 and 4 exhibited a semiconducting conductivity type and did not have a SC transition.

The heat capacity c_p of the samples was studied using the adiabatic calorimeter method with periodic heat input. The temperature was measured with the platinum resistance thermometer TSPN-3. The error in measuring heat capacity did not exceed 0.3%. Samples with masses of about 5 g were placed inside the calorimeter which was then sealed in helium gas. In each separate measurement we first determined the starting sample temperature and then supplied the heater with the power necessary to raise the temperature by $\Delta T \approx 1.7\text{-}2.0$ K in 20 min; next, the heat was turned off and the final temperature of the sample was measured for 15 min. The 15 min interval was chosen so that the temperature behavior of the calorimeter would not knowingly exceed the principal temperature dependence. (As a matter of fact, an acceptable drift was established within $\tau \approx 10\text{-}12$ min). The result of the measurements are shown in Fig. 1. Two features deserve attention: first, the intersection of the heat capacity curves of the superconductors with the curves of their respective amorphous materials occurs near their superconducting transition temperature; second, the heat capacity curves of the high-temperature superconductors for $T > T_c$ are above and for $T < T_c$ are below the heat capacity curves of their respective glasses. The discovered regularities provide a method for identifying thermodynamically similar points in superconductors – namely, the critical superconducting transition temperature is characterized by the equality of the heat capacities of the superconductor and of its respective glass.

The reason why we attribute the important results obtained in the present work to the discovered regularity in the heat capacity behavior of the investigated materials is due in part to the fact that the heat capacity of superconductors for $T > T_c$ is greater than and for $T < T_c$ is less than the heat capacity of the corresponding glasses in the working temperature range 77-300 K. If we regard heat capacity as the rate of change of entropy with temperature, then there is a temperature range in which the entropy of the crystal superconductor is greater than the entropy of the glass with the same composition. Since entropy is a measure of disorder in the system, then this conclusion is to a certain degree incorrect. It is appropriate to ask ourselves here the question that was posed by Stishov [5]: "Is the presence of excess (in comparison to the crystal) entropy a necessary property of every spatially disordered state of matter?" In his work Stishov provides the following answer:

"In the supercooled state the heat capacity of the liquid is always greater than the heat capacity of the crystal. At the same time the difference in the two heat capacities increases with decreasing temperature. This fact, which was first noted by Kauzman, imposes a strict lower bound on the existance region of the liquid phase. Actually, the higher the heat capacity of the liquid, the greater the rate of decrease of the liquid's entropy as the temperature decreases. Upon extrapolating the heat capacity of the supercooled liquid into the low-temperature region and calculating its entropy, we must conclude that there is a certain temperature T_K where the heat capacity of the system should decline sharply. In the opposite case, lest crystallization or vitrification occurs as the temperature is lowered further, the entropy of the system at $T = 0$ will be less than the entropy of the crystal obtained by equilibrium crystallization (Kauzman's paradox). In fact, the vitrification temperature is always higher than the Kauzman's temperature T_K, and, as a result, the total change of entropy for all liquid and glass cooling paths from the melting temperature to $T = 0$ is smaller than the entropy of the liquid at the melting point. To maintain balance, we must consider that the entropy of glass at $T = 0$ is nonzero. That value has been called the "residual" entropy. Therefore, glasses do not satisfy the Nernst heat theorem."

In order to follow the behavior of the heat capacity abbove 300 K, we present the data of Inoue et al. [6] for the Bi–Sr–Ca–Cu–O glasses and the approximate values of the heat capacity for crystalline $Bi_2Sr_2CaCu_2O_y$ above 300 K (see Fig. 1) using the results of Urbach et al. [3] who determined the Debye temperature of the Bismuth ceramic to be $\Theta = 230$ K.

Clearly, the heat capacity of the crystal over a significant range of temperatures (100-700 K) is greater than the heat capacity of the glass. The same holds true for the yttrium compound. Consequently, we conclude that the "residual" entropy of the oxide glasses $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$ is large and, according to our estimates, is on the order of the entropy of the corresponding high-temperature superconductors at $T = T_c$. If our hypothesis is verified, we would have a thermodynamic criterion for bounding the existence region of high-temperature superconductivity (at the critical superconducting transition temperature in high-temperature superconductors, there is an accumulation of entropy which is equal in value to the "residual" entropy of the corresponding glass). The presence of such a thermodynamic criterion opens up great possibilities for obtaining new high-temperature superconductors with high superconducting transition temperatures and for predicting their values.

In conclusion, we studied superconducting and amorphous materials with compositions $YBa_2Cu_3O_x$ and $Bi_2Sr_2CaCu_2O_y$. Certain regularities that allow for the determination of thermodynamically similar points in high-temperature superconductors were discovered. We proposed a thermodynamic criterion bounding the existence region of high-temperature superconductivity.

NOTATION

T, absolute temperature; $\rho(T)$, electrical resistivity; $\chi(T)$, magnetic susceptibility; T_c, superconducting transition temperature; c_p, specific heat capacity at constant pressure; T_K, Kauzman temperature; Θ, Debye temperature.

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HEAT EXCHANGE DURING THE BOILING OF HELIUM ON THE SURFACE OF $YBa_2Cu_3O_7$ HTSC-CERAMIC

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UDC 536.248.2.001.5

We investigate the heat transfer and crises in the nucleate and film boiling of helium on flat metal-oxide ceramic heaters at pressures 0.006-0.165 MPa.

In [1-2] we investigated heat transfer characteristics during the boiling of nitrogen on the surfaces of high-temperature superconducting $YBa_2Cu_3O_7$ ceramic samples. There are grounds for thinking that high-temperature superconductors (HTSC) with very large upper critical magnetic fields might be used efficiently at helium temperatures, for example, for current leads [3, 4] and for the solenoid windings of superconducting magnetic systems for fields above 20 T [5]. For these reasons the determination of the heat exchange characteristics of HTSC ceramics with liquid helium is of interest. The critical current density of modern HTSC-conductors at T = 4.2 K exceeds 10^5 A/cm^2, and the significant level of heat release during the transition to the normal state makes the heat transfer crisis the primary objective of our investigation. Depending on the technique used for the preparation of composite current-carrying components, the superconductor might either be in direct contact with the cryogenic medium or be separated from it by a sheath made of a normal metal; the present investigation is applicable to the first case.

The experiment was carried out inside a glass Dewar flask at pressures between 0.006 and 0.165 MPa. In the study we used $YBa_2Cu_3O_7$ HTSC ceramic samples which were 14 mm in diameter, 7-mm thick, and thermally insulated and an electric heater with three thermocouples; the sample design is the same as described in Baranets et al. [1, 2]. Due to the low thermal conductivity of HTSC-ceramics [6] for $q \geq 10^3$ W/m^2, the internal temperature of the samples was sufficiently high, which allowed us to use copper–constantan thermocouples in order to determine the temperature. The temperature of heat transfering surfaces was found by extrapolation. Experiments were conducted on four samples with volume porosities between 10% and

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Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 62, No. 1, pp. 10-15, January, 1992. Original article submitted April 30, 1991.

1062-0125/92/6201-0004$12.50