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Common thermal properties of high T_c oxide superconductors

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Abstract

A review of the thermal properties of some high T_c superconductors (specific heat, thermal decomposition, the influence of the quenching effect on electrical conductivity, thermal conductivity and thermoelectric power) is presented.

SPECIFIC HEAT OF BISMUTH AND THALLIUM SUPERCONDUCTORS

Bismuth and thallium high-temperature superconductors (HTSC) are being thoroughly investigated. The temperatures of transition to the superconducting state for these substances are higher than those for yttrium 123 HTSC [1,2]. The specific heat data, in combination with the results of the investigation of other physical properties, provide useful information. For example, the jump in specific heat is related to such basic parameters as the Sommerfeld constant, the density of the states on the Fermi surface, and the low-temperature heat capacity variation with initial Debye temperature [3].

We have noted that researches have not investigated the thermodynamic properties of bismuth and thallium superconductors (SC), and that it is practically impossible to obtain samples which can be used for this purpose. In general, they are more interested in other properties: the lattice specific heat (for a subsequent determination of Debye temperature and low-frequency modes), the normal-state electronic specific heat (for calculation of the Sommerfeld constant and the Pauly susceptibility), the superconducting state specific heat, etc.

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Calorimeters

Different types of calorimeters have been used to determine the specific heats of HTSC. As a rule, adiabatic techniques (with heat-pulse [4–9] and continuous heating [10] modes) and differential scanning calorimeters have been applied in the range 25–400 K. In the range of lowest temperatures, the best measurements have been made by dynamic methods which enable small samples to be investigated [11].

Samples

The preparation of high-quality samples of bismuth and thallium superconductors presents a great problem. The temperature in the synthetic zone has to be very close to the melting point. The reaction temperature has to be controlled with high precision. A multi-stage process with an intermediate grinding, was used to homogenize the preparations. Nevertheless, the resulting samples contained a mixture of phases; for instance, samples of Bi 2223 phase also contained, in general, 2234 and 1212 phases. It has been established that the addition of lead promotes the formation of bismuth 2223 superconducting phase [12].

Results

It is known that the Debye temperature calculated from the specific heat data is constant only at low temperatures ($T < \Theta_D/25$) [3]. For bismuth ceramics of different compositions, the initial Debye temperature values, Θ_0, are ≈ 240 K for 2212 phase [5,13–16] and ≈ 250 K for 2223 phase [16]. The Θ_0 values for thallium superconductors are 238 K for 2201 and 254 K for 2212 composition [17]. In other literature references, Θ_0 results are either very uncertain (for example < 300 K [16]) or are related to mixtures of phases [17,18]. Hence, the correct value of the initial Debye temperature may be obtained from $C_p(T)$ data only for the range below 10 K. Any attempts to calculate Θ_0 from specific heats for temperatures above 10 K (for the subsequent estimation of lattice specific heat and the evaluation of electronic specific heat) leads to considerable errors.

The specific heat anomaly at T_c is one of the most extensively documented physical properties of HTSC. A common feature of the specific heat T_c anomalies of bismuth and thallium SC is the gentle shape of the C_p jumps, unlike the sharp jumps of yttrium SC (Fig. 1). The heat capacity anomalies for Bi and Tl ceramics are so spread that there is no clear evidence for a jump. The values of the C_p jumps vary in different literature references, and this may be connected with the various extrapolation techniques used by authors in the T_c range (see Table 1). In refs. 4–6 and

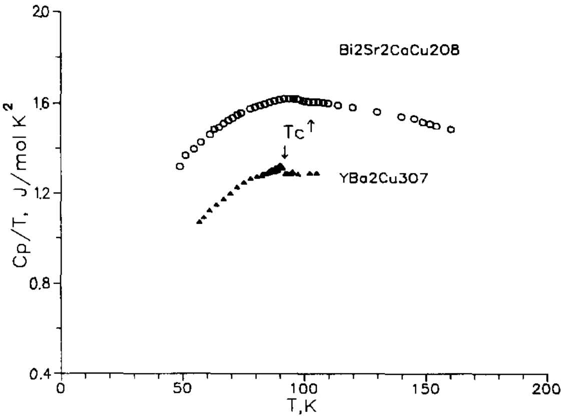

Fig. 1. Comparison of C_p/T jumps for bismuth [5] and yttrium [19] SC.

29, the authors noted the effect of thermal history on the specific heat anomaly in bismuth SC (Fig. 2). It can be seen that the values of the C_p jumps for Bi and Tl ceramics are close to those for yttrium HTSC. Only in ref. 30 is the $\Delta C/T_c$ value highly anomalous (320 mJ K^{-2} mol^{-1}). In refs. 4 and 18 the authors noted that the main anomaly consisted of two or three small jumps (Fig. 3).

The nature of the temperature dependence of the electronic specific heat varies at the point of transition of the superconducting state: below T_c, the $C(T)$ curve has an exponential feature and is linear above T_c [31]. For yttrium ceramics in the range below T_c, in addition to the exponential term, the linear term of the specific heat is also present [32,33]. This is associated with the HTSC properties, as well as with the properties of admixtures, owing to the high normal electronic term [34–37]. For bismuth and thallium samples, the main superconducting phase may include other superconducting phases (in this case, the temperature dependence of the

TABLE 1

Values of the heat capacity anomalies of yttrium, bismuth and thallium superconductors given in the literature

YBCO		BSCCO		TBCCO	
$\Delta C/T_c$	Ref.	$\Delta C/T_c$	Ref.	$\Delta C/T_c$	Ref.
68	20	50	4	17	6
47	21	49.5	26	35	17
67	17	21	27	20	17
22	22	20	28	5	18
62	23	16	18	3	12
48	24			25	8
33–39	25				

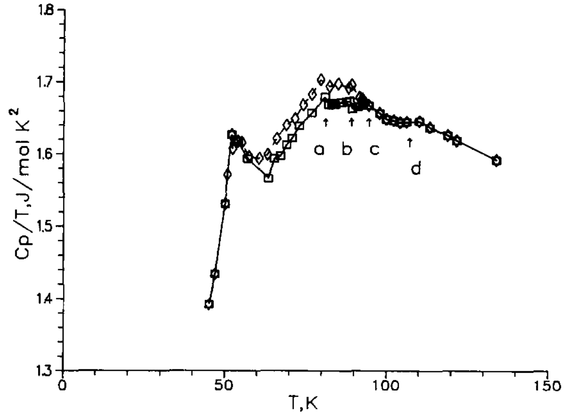

Fig. 2. C_p/T versus T curves of bismuth SC [4] before (□) and after (◇) cooling to 4 K (a, b, c, d are specific heat jumps).

specific heat featured a set of jumps [5,6]) as well as normal conducting phases. But in the literature, it has been shown that below T_c, the linear term is absent in the specific heat of Bi ceramics, [38] (Fig. 4).

The heat capacity curves of bismuth and thallium SC display the anomalies in the form of gently convex maxima (Figs. 5 and 6), which are not associated with the SC transition [5,6]. The temperature range 200–240 K has attracted attention because of reports concerning the anomalies on the $C_p(T)$ curves of YBCO. In ref. 39, it was shown that these anomalies are associated with the lubricant used in the experiments. But in ref. 40, after careful measurement of the lattice parameters of $YBa_2Cu_3O_x$ between 80 and 300 K, the authors concluded that there is a structural instability above T_c which is affected by the oxygen content. In particular, they fixed an

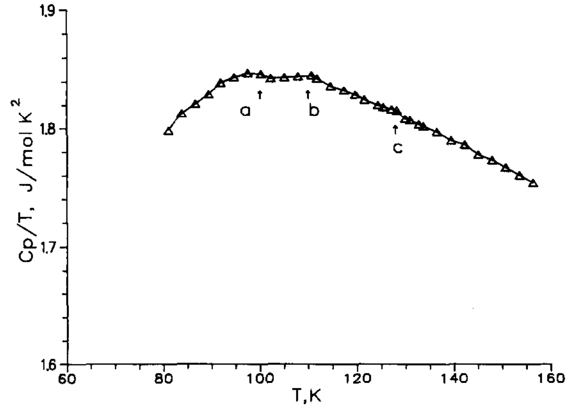

Fig. 3. C_p/T versus T curve for thallium 2223 SC (a, b, c are specific heat jumps).

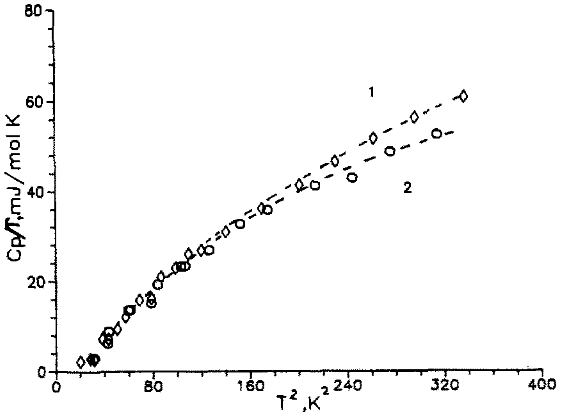

Fig. 4. C_p/T versus T^2 curves for bismuth 2212 (1) and 2122 (2) SC.

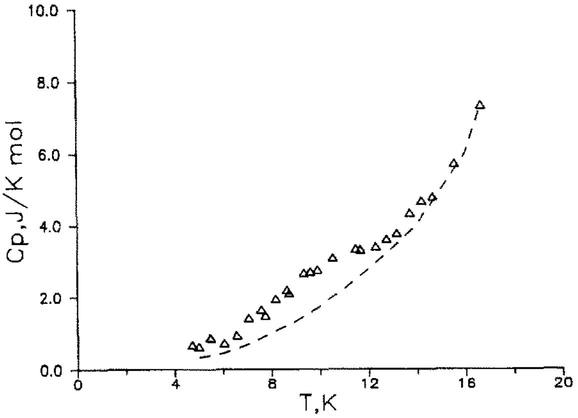

Fig. 5. The specific heat anomaly of thallium SC [6].

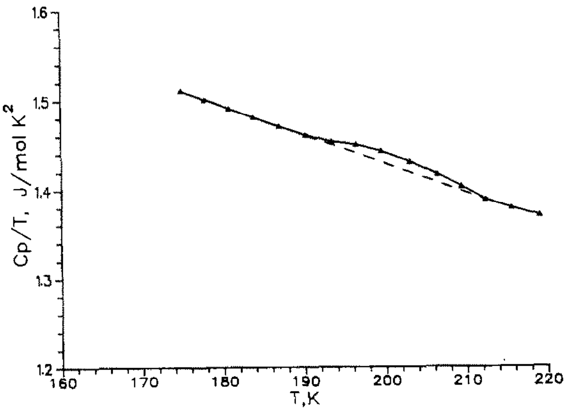

Fig. 6. The gently convex specific heat anomaly of bismuth SC [5].

anomaly at 240 K. We believe that it will be very interesting to perform a detailed investigation in the range above T_c for bismuth and thallium SC.

INVESTIGATION OF THE THERMAL PROPERTIES OF SOME HIGH T_c OXIDE SUPERCONDUCTORS

In recent years, several families of high T_c oxide superconductors have been investigated in the Ln–Ba–Cu–O (where Ln is Y or a rare earth), Bi–Ca–Sr–Cu–O and Tl–Ba–Ca–Cu–O systems. Many of the high T_c materials are thermodynamically unstable [41], therefore it is important to know the thermal properties and the behaviour of the materials at elevated temperatures.

Thermal analyses methods (DTA and TGA) have been used to study ceramic superconductors in the systems $La_{2-x}M_xCuO_{4-\delta}$ (for M = Ca, Sr and Ba) and $LnBa_2Cu_3O_{7-y}$ (for Ln = Y, Gd or Ho) under dynamic conditions of heating, assuming the compounds are typical members of the 123 family [42,43]. To obtain an overall picture of the thermal decomposition process of cuprate superconductors, the thermal properties of the "father" of the SC family, La_2CuO_4, have been studied [44]. Above 1150°C, it decomposes according to the equation

$$2La_2CuO_4 \xrightarrow{(-yO_2)} 2La_2CuO_{4-y} \rightarrow 2La_2O_3 + Cu_2O + (0.5 - y)O_2$$

This process is similar to the decomposition of other compounds in the Ln_2CuO_4 family [45].

It is possible for us to give some real results for the thermal properties of superconducting materials of different compositions. For the 1–2–3 type of superconductors, the oxygen content of the ceramic sample $YBa_2Cu_3O_{6.85}$ (A) in which the oxygen content was determined by a volumetric method [46] and a parallel iodometric titration. From the ideal structural formula of $YBa_2Cu_3O_7$ (Fig. 7), with orthorhombic unit cell parameters a = 3.8206

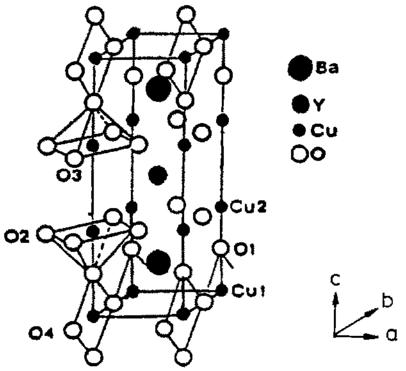

Fig. 7. The structure of $YBa_2Cu_3O_7$.

Å, $b = 3.8853$ Å, and $c = 11.6757$ Å, it is clear that oxygen is evolved in the early stages of the TGA heating curves.

The thermal decomposition of SC samples under different gas compositions was investigated. The overall thermal decomposition mechanism is connected with the partial pressure of oxygen in the crucible–sample–gas system.

From Fig. 7, several steps in the thermal decomposition of A can be suggested: the initial oxygen evolution from the O(4) sites in the range 300–420°C; a second oxygen evolution above 400–440°C and up to near 750°C, during the dissociation of oxygen from the O(3) and O(2) sites, with practically equal values of dissociation energy; above 850°C, evolution of some of the oxygen from the O(1) sites occurs and (as a result), there is a common structural destruction and full dissociation of the high T_c oxide superconductors [47].

Concerning the thermal properties of superconducting phases in the systems Bi–Ca–Sr–Cu–O and Tl–Ba–Ca–Cu–O with T_c values near 77 K or below, in some opinions, this temperature may reflect other partial parameters of these materials (e.g. evolution under heat treatment in air, interaction with the crucible, evaporation of high T_c components, for example, lead- and thallium-containing materials).

The thallium concentration in the whole volume of sample during thermal decomposition of the SC phases 2212, 2223 and 2334 in the Tl–Ba–Ca–Cu–O system (independent of the conditions of synthesis or the thermal destruction mechanism) may be used for the correct interpretation of the process.

THE QUENCHING EFFECT AND ITS INFLUENCE UPON ELECTRICAL CONDUCTIVITY, THERMAL CONDUCTIVITY AND THERMOELECTRIC POWER OF TEXTURED HIGH T_c BISMUTH CERAMIC

Bismuth-based oxides, a new class of high T_c superconductors, have provided opportunities for conducting comparative studies [1]. High T_c superconductors in the Bi–Sr–Ca–Cu–O system are more stable than 123 compounds and it is probable that there will be other mechanisms of superconductivity.

The $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) sample was prepared by solid-state reaction from a mixture of evaporated Bi, Sr, Ca and Cu nitrates at 820°C for 50 h in air [48]. Analyses of the phases were carried out by atomic absorption spectroscopy. For the phase $Bi_2Sr_2CaCu_2O_{8+\delta}$, $0.4 \le \delta \le 0.6$. From the X-ray powder diffraction data the pseudo-tetragonal cell parameters are $a = 5.40$ Å and $c = 30.9$ Å.

BSCCO pellets ($8 \times 3 \times 2$ mm^3) or discs (10 mm in diameter, 1.5–2.0 mm thick) were calcined at 820°C for 8 h and cooled at 7 K min^{-1} to room temperature. Pellets were subjected to the resistivity measurements and the

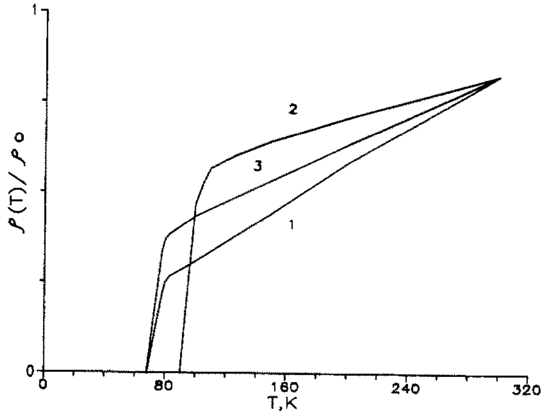

Fig. 8. Temperature dependences of electrical resistivity of BSCCO before and after quenching: curve 1, before quenching; curve 2, after quenching in liquid nitrogen; curve 3, after annealing at 500°C.

discs to thermal conductivity and thermal electrical power measurements. Both pellets and discs were textured using a precision procedure with the preferred orientation of the crystallites being along the *c*-axis.

Using these conditions of synthesis, the resistivity superconducting transition curve showed T_0 near 65–70 K (Fig. 8). In optimal conditions, the sample (curve 1, Fig. 8, initial resistivity $\rho_0 = 1.3 \times 10^{-3}$ Ω cm^{-1}) was annealed at 830°C for 3–4 h after which the specimen was quenched in liquid nitrogen; this showed T_c near 90 K (curve 2, $\rho_0 = 4 \times 10^{-3}$ Ω cm^{-1}). The specimen mass change because of oxygen loss was $\Delta m/m$ (initial) $\approx 0.2\%$, corresponding to $\Delta\delta \approx 0.1$. After quenching, the unit cell of BSCCO was slightly elongated along the tetragonal *c*-axis at constant cell volume; the relative increase of *c* was $\Delta c/c \approx 0.003$. The quenching effect

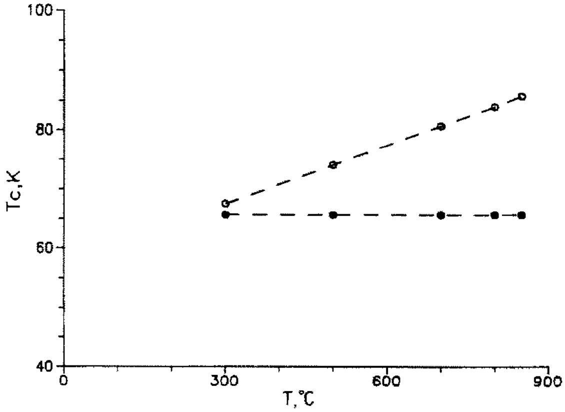

Fig. 9. Dependence of T_c on quenching temperature: ●, initial specimen; ○, quenched sample.

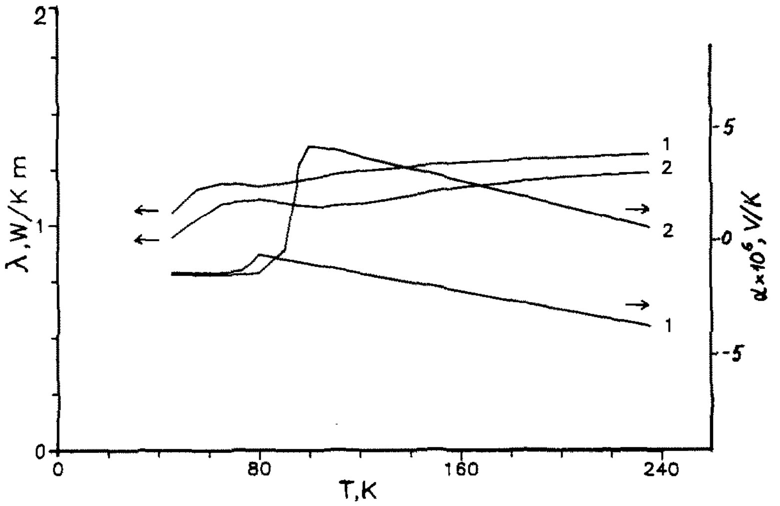

Fig. 10. Thermal conductivity and thermoelectric power of BSCCO at low temperatures: 1, initial specimen; 2, quenched specimen.

has a hysteresis: at 500°C for 7–8 h, the transition temperature returns from 90 K to the initial value of 68 K (curve 1, Fig. 8, $\rho_0 = 1.28 \times 10^{-3}$ Ω cm^{-1}). The specimen mass has no hysteresis and the oxygen loss in the quenching procedure does not recombine in BSCCO, the cell parameters remaining unchanged.

The dependence of T_c on quenching temperature is shown in Fig. 9. Usually, at quenching temperatures of 300, 500 and 700°C, BSCCO samples have no oxygen loss, i.e. $\Delta\delta = 0$. Thus, the increasing T_c is the result of lattice deformation. Figure 9 confirms the decisive role of lattice deformation as a consequence of quenching. We note that the superstoichiometric oxygen content is an important feature of BSCCO resistivity in the normal state. In the region $T > 2T_c$, the resistivity follows the equation $\rho(T) = A + BT$ (A is the residual resistivity and B a linear term), i.e. the quenching causes the superconducting system to approach the metal–insulator transition.

Figure 10 shows the thermal conductivity of BSCCO and the thermoelectric power. It is obvious that the quenching procedure decreases the thermal conductivity of the specimens up to almost 10–15% from the initial value. From the Wiedemann–Franz law, we estimated the upper limit of free carriers in the overall thermal conductivity to be ≈ 10% at 100 K. We believe that phonons are responsible for the thermal properties.

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