

# THERMAL EXPANSION OF THE SUPERCONDUCTIVE METALLIC OXIDE $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ IN THE LOW-TEMPERATURE RANGE

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*Dilatometry is used to study the temperature dependence of the coefficient of linear expansion in the high-temperature semiconductor  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  in the range 60–300 K. At temperature close to  $T_c$ , 125–140, and 200–400 K anomalies were observed in  $\alpha(T)$ . Temperature hysteresis was found in the quantity  $\Delta l/l$  measured during heating and cooling.*

The discovery of bismuth and thallium semiconductive materials not only expanded the class of high-temperature semiconductors (HTSs), but also the possibilities for study and use of high-temperature semiconductivity. However the question of the mechanism underlying this phenomenon still remains unanswered. Study of the thermophysical properties of an HTS, especially thermal expansion, provides information on the behavior of the phonon subsystem, which is important in clarifying the mechanism of high-temperature semiconductivity.

It has been shown in a number of studies of thermal expansion in the yttrium HTS system [1–9] that the temperature coefficient of the coefficient of thermal linear expansion (TLEC or  $\alpha$ ) shows an anomaly at temperatures close to the semiconductive transition temperature  $T_c$ , for  $T < T_c$  [1, 9], and at temperatures significantly above  $T_c$  [2, 7–9]. In [10, 12] anomalies were not found in the temperature dependence of the TLEC. Significant scattering has been noted in the value of the linear expansion coefficient itself [7]. Usually anomalies in  $\alpha(T)$  are related to lattice instabilities which manifest themselves in phase transitions, structural ordering, softening of the phonon spectrum, etc. For "classical" semiconductors with relatively high  $T_c$  (for example, A-15 type materials) it has been noted that such instability precedes the semiconductive transition, while some results indicate that high  $T_c$  values are related to the presence of such instability [13, 14]. The question of a similar correlation in HTS materials remains to be studied. Study of the temperature dependence of the TLEC will provide a definite contribution toward solution of this question.

We will note that data on the function  $\alpha(T)$  for the bismuth HTS system is scarce. At the present time the authors are aware of only the studies [15], [16]: [15] presented thermal expansion data only in the range 90–130 K for a polycrystalline Bi(Pb)—Sr—Ca—Cu—O specimen with composition 2223 and partial replacement of bismuth atoms by lead, while [16] also offered data for a bismuth semiconductive specimen, containing lead atoms in the range 30–300 K. Both studies recorded a  $\alpha(T)$  anomaly in the temperature range near  $T_c$ , while the latter study found an additional three anomalies: ~110, ~130, and ~160 K.

We will present below results of a study of temperature dependence of the TLEC in a semiconductive metallic oxide of composition  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (2212) in the temperature interval 60–300 K by the dilatometric method [17]. Specimen synthesis was carried out in a solid phase reaction from a mixture of finely dispersed powdered oxides  $\text{Bi}_2\text{O}_3$ , CuO, and carbonates  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  [18]. The specimen diffractograms (Fig. 1) show that it consists mainly of the 85° semiconductive phase 2212. Resistive measurements show that the temperature of completion of the semiconductive transition  $T_c^0$ , essentially determined by synthesis regimes, is equal to 66 K in the given case.

Experimental results on measurement of the temperature dependence of the TLEC of the compound  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  is shown in Fig. 2a in the form of the dependence  $\alpha(T)/T$  over the range 60–300 K. Measurements of relative specimen elongation  $\Delta l/l$  (Fig. 2b) were carried out with a cylindrical specimen ~20 mm long and ~8 mm in diameter during both cooling and heating. In contrast to the results of [15] hysteresis was observed in the TLEC

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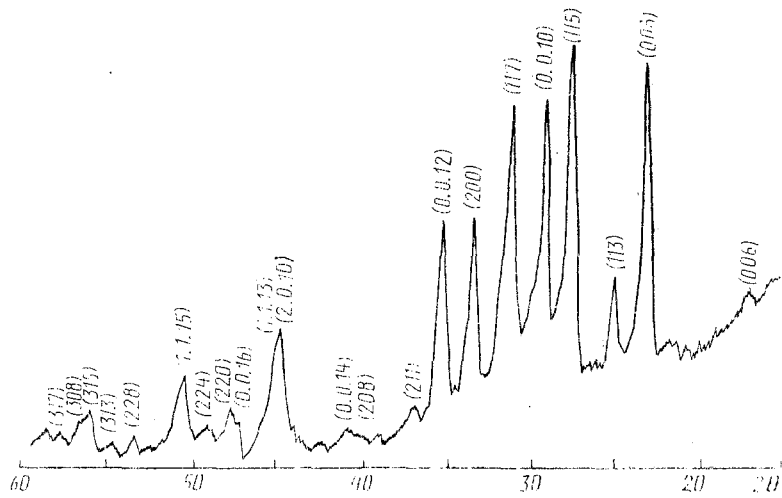


Fig. 1. Diffractogram of semiconductive metal oxide  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  ( $\text{CuK}_\alpha$  radiation,  $2\theta^\circ$ ).

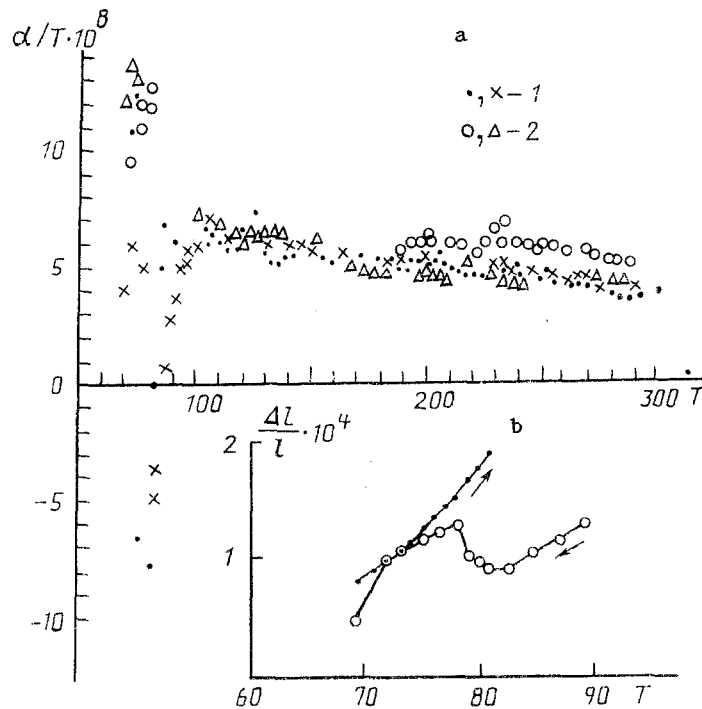


Fig. 2. Temperature dependences of  $\alpha(T)/T$  ( $\text{K}^{-2}$ ) (a) and  $\Delta l/l$  (b) of compound  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (1, cooling; 2, heating),  $T$ , K;  $\alpha/T \cdot 10^8$ ,  $\text{K}^{-2}$ .

behavior within the temperature range studied. At temperatures close to  $T_c$ , there is a minimum in  $\alpha(T)$  extending into the region of negative TLEC values. Such behavior of the linear expansion coefficient has been noted for the yttrium semiconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [6] and a thallium semiconductor with composition  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  [19]. The temperature dependence obtained here for the 2212 bismuth semiconductor also shows an anomaly in the temperature range 125–140 K and at 200–240 K (Fig. 2a).

In a study of specific heat  $C_p$ , elastic, and other properties [20, 21] anomalous behavior was also noted, with [20] finding hysteresis in the temperature dependence of elastic characteristics of high-temperature semiconductors, while [21] explained anomalous behavior of some of these characteristics (specific heat, elastic properties, IR-absorption) by a structural phase transition in the temperature range  $\sim 200$  K, accompanied by increase in the crystalline lattice parameters in that range. The authors of [22] also used a structural phase transition to explain the

hysteresis loop they observed, dependent on the rate of change of temperature, in the region 200-240 K while studying acoustical characteristics of the polycrystalline semiconductor  $(\text{Bi}_{0.8}\text{Pb}_{0.2})_2\text{Sr}_2\text{Ca}_3\text{Cu}_4\text{O}_y$ .

As is shown in [23], the appearance of a negative TLEC is possible in connection with certain features of the phonon spectrum in the low frequency region. The actions of the long-distance binding forces in the crystalline lattice which develop upon polarization of atoms lead to a reduction in the frequencies of the acoustic branches of the phonon spectrum near the edge of the Brillouin zone. With consideration of the differing dispersion of acoustic oscillations of all polarizations appearance of a negative TLEC can be expected with the highest probability in materials which have an open (loose) structure, such as that of high-temperature semiconductors.

Thus, using the dilatometric method, we have experimentally studied the temperature dependence of the thermal expansion coefficient in the high-temperature metal oxide semiconductor  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  in the range 60-300 K. Anomalies were found in  $\alpha(T)$  in temperature ranges close to  $T_c$ , 125-140 K, and 200-240 K. Hysteresis was found in measurements during cooling and heating regimes. Clarification of these anomalies will require additional studies of other properties of the compound  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ .

#### NOTATION

Here TLEC,  $\alpha$  — denotes the thermal linear expansion coefficient;  $T_c$ , semiconductive transition temperature; 2223,  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ ; 2212,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ ;  $T_c^0$ , temperature of completion of semiconductive transition;  $\Delta l/l$  relative elongation;  $C_p$ , specific heat at constant pressure.

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