7. N. V. Dezhkunov, V. I. Kuvshinov, G. I. Kuvshinov, and P. P. Prokhorenko, Akust. Zh., 26, No. 5, 695-699 (1980).
8. G. I. Kuvshinov, N. V. Dezhkunov, V. I. Kuvshinov, and P. P. Prokhorenko, Inzh.-Fiz. Zh., 39, No. 5, 866-869 (1980).
9. G. I. Kuvshinov, P. P. Prokhorenko, N. V. Dezhkunov, and V. I. Kuvshinov, Intern. J. Heat Mass Trans., 25, No. 3, 381-388 (1982).
10. A. Sima, Theor. Princ. Eng. Comput. [Russian translation], 90, No. 1, 84-99 (1968).
11. V. A. Burtsev and V. V. Shamko, Zh. Prikl. Mekh. Tekh. Fiz., No. 1, 80-90 (1977).
12. B. A. Agranat and F. A. Bronin, Akust. Zh., 14, No. 2, 285-286 (1968).
13. P. P. Prokhorenko, N. V. Dezhkunov, and G. I. Kuvshinov, Izv. Akad. Nauk BSSR, Ser. Fiz.-Tekh. Nauk, No. 1, 71-73 (1979).
14. S. P. Kozyrev, Hydroabrasive Wear of Metals in Cavitation [in Russian], Moscow (1971).
15. B. Vyas and C. M. Preece, J. Appl. Phys., 47, No. 12, 5133-5138 (1976).
16. K. M. Pris (ed.), Erosion [in Russian], Moscow (1982), pp. 287-288.
17. O. K. Keller, G. S. Kratysh, and G. D. Lubyanitskii, Ultrasonic Cleansing [in Russian], Leningrad (1977).

THERMODYNAMIC CHARACTERISTICS OF THE SUPERCONDUCTING METAL-OXIDE $Bi_2Sr_2CaCu_2O_y$ IN THE LOW TEMPERATURE DOMAIN

Ya. A. Abeliov, E. M. Gololobov, G. V. Maiornikova, B. V. Novysh, N. A. Prytkova, Zh. M. Tomilo, and N. M. Shimanskaya

UDC 537.312.62

Results are presented of an experimental investigation of the specific heat of the superconducting metal-oxide $Bi_2Sr_2CaCu_2O_y$ in the 40-230 K range on whose basis the temperature dependences of the thermodynamic functions and the Debye temperature are computed.

An experimental investigation of the specific heat of superconductors is one of the important questions of the problem of the physics of superconductivity. With the discovery of high-temperature superconductivity (HTSC) this problem became still more urgent since the nature of the phenomenon has not been revealed and much that is contradictory is present in published data on the HTSC properties, including the specific heat. There is very little

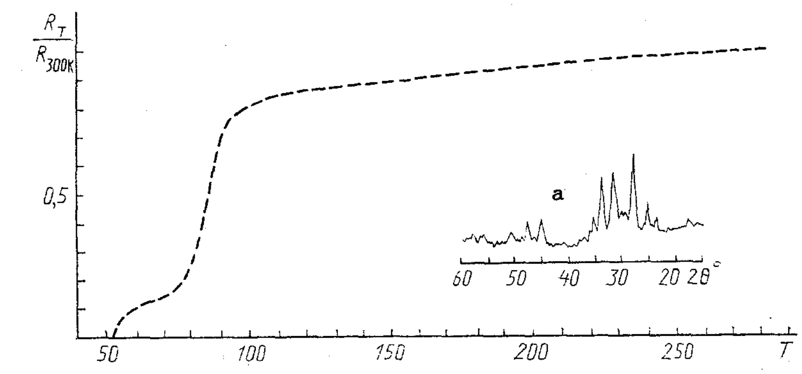

Fig. 1. Temperature dependence $R_T/R_{300\,K}$ for the superconducting metal-oxide $Bi_2Sr_2CaCu_2O_y$: a) x-ray diffraction pattern of this specimen. T, K; θ, deg.

Institute of Solid-State and Semiconductor Physics, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 6, pp. 990-994, June, 1990. Original article submitted June 30, 1989.

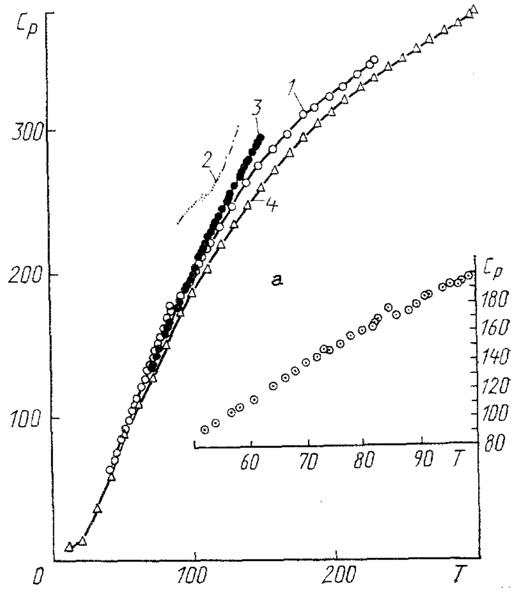

Fig. 2. Temperature dependence of the specific heat C_p (mJ/(g·K)) of bismuth superconducting materials: 1) $Bi_2Sr_2CaCu_2O_y$ (our data); 2) $(Bi + Pb)_2Sr_2Ca_2Cu_3O_y$ [3]; 3) $BiPb_{0.3}SrCaCu_2O_{5.8}$ [4]; 4) $Bi_2Sr_{2.3}Ca_{0.7}Cu_2O_y$ [8]; a) $C_p(T)$ in the 40-100 K temperature range.

TABLE 1. Experimental Values of Specific Heat of the Metal-Oxide $B_2Sr_2CaCu_2O_y$

T, K	c_p, J/(g·K)	T, K	c_p, J/(g·K)	T, K	c_p, J/(g·K)
40,9	0,0638	77,3	0,153	98,9	0,198
43,9	0,0701	78,0	0,156	100,0	0,197
45,5	0,0740	79,0	0,158	104,4	0,206
47,8	0,0819	80,0	0,160	111,8	0,220
52,2	0,0914	81,9	0,162	119,2	0,233
53,8	0,0975	82,5	0,166	128,9	0,247
56,8	0,104	83,4	0,169	138,9	0,262
58,0	0,110	84,8	0,176	148,9	0,275
60,3	0,113	86,1	0,172	158,4	0,287
62,9	0,118	87,6	0,175	168,1	0,297
64,1	0,123	89,8	0,179	178,4	0,308
66,0	0,127	91,5	0,183	188,0	0,315
68,0	0,132	92,2	0,186	198,0	0,323
70,2	0,138	94,2	0,190	207,9	0,329
72,0	0,143	96,1	0,192	218,0	0,337
73,4	0,146	97,5	0,192	227,9	0,345
74,8	0,148	98,0	0,194	229,8	0,346
76,3	0,151				

data on the investigation of the specific heat for the comparatively newly discovered class of high-temperature superconducting materials, the bismuth and thallium metal-oxides. The limited number of papers in which information is reported about the C_p of bismuth superconductors can be separated into two kinds: papers in which results on C_p are presented in the domain of just the superconducting transition [1-5], and papers executed in the domain of quite low temperatures (1-10 K) [1, 6, 7]. The specific heat is measured in [8] in the temperature range 10-300 K for a specimen of the composition $Bi_2Sr_{2.3}Ca_{0.7}Cu_2O_y$. According to [1-3, 5], an anomaly in the form of the maximum ($\Delta C \approx$ 5-6 mJ/(g·K)) is observed on the curve of the temperature dependence $C_p(T)$ during the transition into the superconducting state. No anomaly exceeding the measurement error is noted in [4] for T_k in the dependence $C_p(T)$. The data of [8] indicate strong fuzziness of the specific heat anomaly in the domain of the superconducting transition due to inhomogeneity of the specimen investigated.

To a great extent the composition and superconducting properties of bismuth metal-oxides depend on the synthesis conditions; consequently, the specimens obtained by different authors will be distinctive in their properties. No single-phase specimen of the Bi—Sr—Ca—Cu-O system having a narrow superconducting transition has been obtained up to now. The specimens investigated in [2-4] contained lead atoms, with which replacing approximately one-third the bismuth atoms the width of the superconducting transition ΔT_k diminished abruptly, while the value of the temperature for the termination of the superconducting transition $T_k{}^0$ rose to 100-110 K.

TABLE 2. Values of the Coefficient γ for Bismuth Superconducting Metal-Oxides

Composition	γ, mJ/(mole·K^2)	γ, mJ/(mole·K^2)	T_k, K	Literature source
$Bi_2Sr_{2,3}Ca_{0,7}Cu_2O_y$	0,0436	39,34	80—100	[8]
$Bi_{1,6}Pb_{0,4}Sr_2Ca_2Cu_3O_y$	0,0147	15,00	92	[2]
$(Bi+Pb)_2Sr_2Ca_2Cu_3O_y$	0,0338	34,6	107	[3]
$BiSrCaCu_3O_y$	0,0343	21,36	85	[5]
$Bi_2Sr_2CaCu_2O_y$	0,0494	39,14	85	(Ours)

TABLE 3. Values of $H_{40-T}°-H_0°$(J/g) and $S_{40-T}°$ (J/(g·K))

T, K	$H^o_{40-T}-H^o_0$	S^o_{40-T}	T, K	$H^o_{40-T}-H^o_0$	S^o_{40-T}
40	0	0	175	26,8	0,256
45	0,333	0,0124	180	28,3	0,264
50	0,737	0,0209	185	29,8	0,272
55	1,21	0,0299	190	31,3	0,280
60	1,74	0,0391	195	32,9	0,288
65	2,34	0,0487	200	34,4	0,296
70	3,00	0,0584	205	36,0	0,304
75	3,71	0,0683	210	37,6	0,312
80	4,48	0,0782	215	39,2	0,319
85	5,30	0,0881	220	40,8	0,327
90	6,17	0,0981	225	42,5	0,334
95	7,09	0,108	230	44,1	0,341
100	8,05	0,118	235	45,8	0,348
105	9,06	0,128	240	47,5	0,356
110	10,11	0,137	245	49,2	0,363
115	11,20	0,147	250	50,9	0,370
120	12,3	0,157	255	52,6	0,376
125	13,5	0,166	260	54,4	0,383
130	14,7	0,176	265	56,1	0,390
135	15,9	0,185	270	57,9	0,396
140	17,2	0,195	275	59,6	0,403
145	18,5	0,203	280	61,4	0,409
150	19,8	0,212	285	63,2	0,416
155	21,2	0,221	290	65,0	0,422
160	22,5	0,230	295	66,8	0,428
165	23,9	0,238	298,16	67,9	0,432
170	25,4	0,247	300	68,6	0,434

We investigated the specific heat of the superconducting bismuth metal-oxide of composition $Bi_2Sr_2CaCu_2O_y$ (85 K is the superconducting phase) in the 40-230 K temperature range. Synthesis of the specimens was by the method of a solid-phase reaction from powders of the oxides Bi_2O_3, CuO and the carbonates $SrCO_3$, $CaCO_3$ at an 850°C temperature in air [9]. X-ray diffraction and resistive measurements showed (Fig. 1) that the specimen had a pseudo-tetragonal configuration with the lattice parameters $a \approx b \approx 5.4$ Å and $c \approx 30.7$ Å with $T_k \sim 85$ K (main phase) and $T_k° = 52$ K.

The specific heat was measured on an automated low-temperature calorimeter installation [10] in the adiabatic mode with a periodic delivery of heat for a maximal error ~2% in the whole temperature range investigated. Experimental values of the specific heat C_p of the high-temperature superconducting metal-oxide of composition $Bi_2Sr_2CaCu_2O_y$ are presented in Fig. 2 and Table 1. Part of the temperature dependence of the specific heat in the domain close to the superconducting transition is presented in Fig. 2a in an enlarged scale. The comparison between our experimental results on the specific heat and those of other authors [3, 4, 8] indicates their essential distinction (Fig. 2). Nonmonotoneity in the 75-100 K temperature band is observed on the $C_p(T)$ curve. An anomaly corresponding to the transition of the basic phase into the superconducting state appears in $C_p(T)$ at a temperature ~85 K. The jump in the specific heat ΔC_p determined from the difference between the maximal C_p in the anomaly domain and the extrapolation value of the dependence $C_p(T)$ before and after the transition equals 5.35 mJ/(g·K). The magnitude of the Sommerfield coefficient γ equal to 0.0494 mJ/(g·K^2) or 39.14 mJ/(mole·K^2) was computed in a weak coupling approxi-

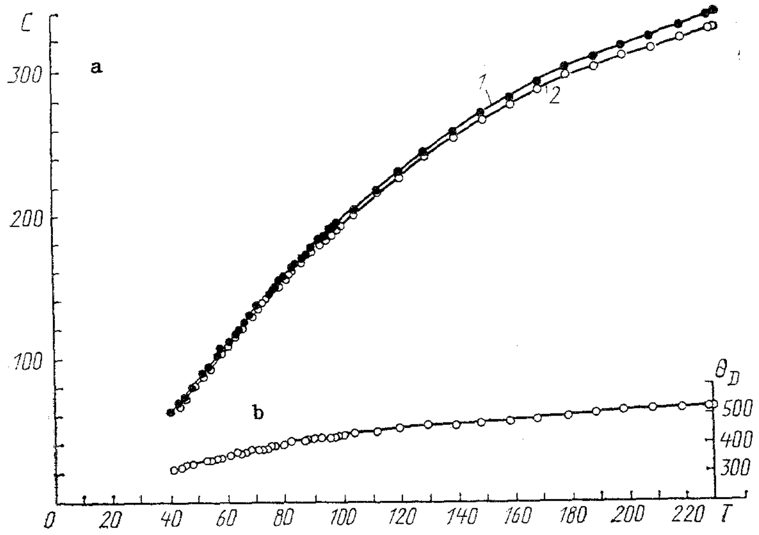

Fig. 3. Temperature dependences of C_f (mJ/(g·K)) (1), C_V (mJ/(g·K)) (2) (a) and the Debye temperature θ_D (K) (b) for $Bi_2Sr_2CaCu_2O_y$.

mation. Presented in Table 2 are γ for high-temperature bismuth superconductors known from bibliographic sources. The value of γ we obtained is close to the value presented in [8].

The electron contribution C_e to the specific heat of $Bi_2Sr_2CaCu_2O_y$ is computed in the Sommerfeld approximation for temperature above T_k with $\gamma = 0.0494$ mJ/(g·K²). In the temperature domain below T_k the change in γ from 0 at T = 0 [7] to 0.494 mJ/(g·K²) at $T = T_k$ is taken into account in the computation of $C_{el}(T)$. The maximal contribution of the electron component of the specific heat to C_p equals ~3% at 230 K.

The phonon component $C_f = C_p - C_{el}$ is presented in Fig. 3. We estimated the value for the specific heat at constant volume C_V with the anharmonic component taken into account by using the semiempirical formula [11]

$$C_V = C_f(1 - AC_fT),\ A = \alpha^2 V/\varkappa C_f^2,$$

where α is the coefficient of volume expansion ($45\cdot10^{-6}$ K⁻¹ [12]), V is the specific volume of $Bi_2Sr_2CaCu_2O_4$ (0.15 cm³/g), ϰ is the multilateral compression factor ($3.26\cdot10^{-3}$ GPa⁻¹ [13]), and C_f is the phonon specific heat (~370 mJ/(g·K)).

Because of the lack of information about the compressibility of bismuth metal-oxides the average value for three yttrium superconductors presented in [13] was used in the computations. The temperature dependences of C_f and C_V are represented in Fig. 3. The anharmonic correction to the phonon component $C_f - C_V$ at 230 K is ~7% according to our computations.

Values of the thermodynamic enthalpy $H_{40-T}{}^0 - H_0{}^\circ$ and entropy $S_{40-T}{}^0$ functions computed in the 40-300 K temperature range by using interpolation functional dependence $C_f(T) = -Be^{-\xi(T-\beta)} + C$, where B = 0.403 (J/(g·K)), $\xi = 8.7\cdot10^{-3}$ (K⁻¹); β = 20 (K⁻¹); C = 0.398 (J/(g·K)) are presented in Table 3. Value of $H_{40-298.16}{}^0 - H_0{}^\circ$ equals 67.93 J/g (60,350 J/mole) and of $S_{40-296.16}{}^0$ equals 0.4317 J/(g·K) (384 J/(mole·K)). As a comparison, we present the standard values of the thermodynamic functions for $La_{1.8}$-$Sr_{0.2}CuO_4$ [14]: $H_{298.15}{}^0 H_0{}^\circ$ = 70.84 J/g (27,990 J/mole) and $S_{298.15}{}^0$ = 0.4548 J/(g·K) (179.7 J/mole·K).

The data we obtained for $C_V(T)$ were used to compute the temperature dependence of the Debye temperature of the superconducting metal-oxide $Bi_2Sr_2CaCu_2O_y$ (Fig. 3). As in the case of the superconducting compound $YBa_2Cu_3O_{7-y}$ [15], a monotonic growth of $\theta_D(T)$ is observed from 318 to 530 K for $Bi_2Sr_2CaCu_2O_y$ in the 40-230 K temperature range, which can be an indication of the laminar structure of this compound.

Thus, we measured the specific heat of the superconducting metal-oxide of composition $Bi_2Sr_2CaCu_2O_y$. An anomaly in $C_p(T)$ is detected in the area of the superconducting transition

$T_k \sim 85$ K. Contributions of the electron and phonon components of the specific heat are estimated in the weak coupling and Sommerfeld approximations.

NOTATION

T_k, temperature of the transition to the superconducting state; ΔT_k, width of the superconducting transition; $T_k{}^0$, termination of the superconducting transition; a, b, c, crystalline lattice parameters; C_p, specific heat at constant pressure; C_{el}, electron specific heat; C_V, specific heat at constant volume; γ, Sommerfeld coefficient; H, enthalpy; S, entropy; and θ_D, Debye temperature.

LITERATURE CITED

1. R. A Fisher, S. Kim, S. E. Lacy, et al., Phys. Rev., 38, No. 16, 11,942-11,945 (1988).
2. Z. Chen, H. Liu, Z. Mao, et al., Physica C., 156, No. 5, 834-836 (1988).
3. R. Jin, F. Shi, Q. Ran, et al., Physica C., 158, Nos. 1/2, 255-257 (1989).
4. F. Seidler, P. Bohm, H. Geus, et al., Physica C., 157, No. 2, 375-394 (1989).
5. S. L. Juan, J. W. Li, W. Wang, et al., Int. J. Mod. Phys. B (Singapore), 4, Nos. 3-4, 421-425 (1988).
6. M. Sera, S. Kodoh, K. Fukuda, et al., Solid-State Commun., 66, No. 10, 1101-1103 (1988).
7. K. Kumagai and Y. Nakamura, Physica C., 152, No. 4, 286-288 (1988).
8. K. S. Gavrichev, V. E. Gorbunov, I. A. Konovalova, et al., Neorgan. Mater., 24, No. 12, 2078 (1988).
9. E. M. Gololobov, N. A. Prytkova, Zh. M. Tomilo, et al., Pis'ma Zh. Éksp., Teor. Fiz., 48, No. 7, 384-386 (1988).
10. V. M. Malyshev, G. A. Mil'ner, and E. L. Sorkin, Prib. Tekh. Éksp., No. 6, 195-197 (1985).
11. N. N. Sirota, Thermodynamics and Statistical Physics [in Russian], Minsk (1969).
12. D. P. Almond, B. Chapman, and G. A. Saunders, Supercond. Sci. Technol., 1, No. 3, 123-127 (1988).
13. I. V. Aleksandrov, A. F. Goncharov, and S. M. Stishov, Pis'ma Zh. Éksp. Teor. Fiz., 47, No. 7, 357-360 (1988).
14. K. S. Gavrichev, V. E. Gorbunov, and I. A. Konovalova, Neorgan. Mater., 23, No. 12, 2101-2105 (1987).
15. E. M. Gololobov, E. L. Mager, Z. V. Mezhevich, et al., Vestsi Akad. Navuk BSSR, Ser. Fiz.-Mat. Navuk, No. 1, 70-71 (1988).