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Low temperature heat capacities and thermodynamic functions of $Tl_2Ba_2CaCu_2O_y$ [α]

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Abstract

The heat capacity of the high temperature superconductor $Tl_2Ba_2CaCu_2O_y$ was measured by adiabatic calorimetry between 7 and 300 K. The sample was carefully synthesized by a method of powder calcination, and the properties were characterized and evaluated by X-ray powder diffraction, electrical resistivity and magnetic susceptibility measurements. The values of enthalpy, entropy and Gibbs energy were calculated from the heat capacity data. An anomaly due to the superconducting phase transition at 102 K was analyzed in terms of a fluctuation effect and the distribution of T_c. The effect of thallium deficiency on the superconducting phase transition was also examined.

INTRODUCTION

Since the discovery of the high T_c superconductivity of compounds containing thallium ions [1], the number of thermodynamic studies has further increased. However, only a few reports have been published so far about the heat capacities of the compounds [2–5]. The heat capacity is one of the most fundamental and important properties to be used for analyzing the phase transition between the superconducting state and the normal state. In the present study, the absolute value of the heat capacity has been determined for carefully synthesized samples of $Tl_2Ba_2CaCu_2O_y$. The thermodynamic functions such as enthalpy, entropy and Gibbs energy are calculated from the heat capacity data. The electrical resistivity and a.c. magnetic susceptibility have also been measured. The effects of heat treatment of the sample will be discussed by comparison with the previous results [5].

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EXPERIMENTAL

Sample preparation

The sample of $Tl_2Ba_2CaCu_2O_y$ was synthesized by a method of powder calcination of the high purity reactants Tl_2O_3, BaO_2, CaO and CuO. The starting materials in the ratio of 2.11 : 2 : 1 : 2 for thallium, barium, calcium and copper were mixed and ground with an agate mortar. The powder was pressed into a disk 15 mm in diameter and 5 mm thick under 150 MPa. The disk was wrapped with gold foil and put into an electric furnace heated at 1170 K for 10 min in a flowing oxygen atmosphere. After cooling to room temperature in the furnace, the disk was ground again. The specimen was heated in the same way at 1063 K for 60 min, and then cooled to room temperature in the furnace. The composition of the sample was $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$ as determined by gravimetric analysis; the oxygen content has not so far been determined, and the nominal value is used for convenience. After heat capacity measurements, the same specimen was used to prepare a second sample by a heat treatment for evaporating thallium at 1133 K for 24 h and at 1153 K for 30 min in a flowing oxygen atmosphere. The composition of the second sample was determined as $Tl_{1.94}Ba_2Ca_1Cu_2O_{7.91}$. The third sample of $Tl_{1.82}Ba_2Ca_1Cu_2O_{7.73}$ was prepared in the same manner from the second sample: heat treatment at 1133 K for 36 h and at 1153 K for 30 min. Heat capacities were also measured for the second and third samples in order to study the effect of thallium deficiency. Powder X-ray diffraction with Cu K_α radiation showed a single phase with no impurities for each sample.

Heat capacity measurements

The heat capacities were measured by using a laboratory-made adiabatic calorimeter between 7 and 300 K [6]. The sample of about 15 g weight was loaded into the calorimeter vessel. The vessel was evacuated and sealed with Wood's alloy after adding a small amount of helium gas (10 kPa at room temperature) to improve thermal uniformity within the calorimeter vessel. The sample contributed about 30% to the total heat capacity. The contribution of the helium gas was negligible compared with the heat capacity of the sample. The working thermometers mounted on the calorimeter vessel were a platinum resistance thermometer (type 5187L, H. Tinsley & Co., Ltd.) calibrated on the IPTS-68 between 13.81 and 373.15 K at the National Physical Laboratory in England, and a germanium resistance thermometer (model GR-200A-500, Lake Shore Cryotronics, Inc.) calibrated on the EPT-76 between 1.2 and 23 K. An a.c. automatic resistance bridge (type 5840D, H. Tinsley & Co., Ltd.) was used for the platinum resistance thermometer with a precision of 0.0001 K. The resistance of the germanium

thermometer was measured by the four-terminal method with a high precision digital voltmeter (model TR-6871, Advantest Co.) and a universal scanner (model TR-7200).

Heat capacity was determined with a precision of 0.1%. The rate of energy input was varied depending on the temperature and the value of the heat capacity. During the experiments, no abnormal relaxation or hysteresis phenomena were observed.

The electrical resistivity and the relative a.c. magnetic susceptibility were measured by the four-terminal method (current density 0.05 A cm^{-2}) and the inductive method (1 kHz, 3 Oe) respectively.

RESULTS AND DISCUSSION

The measured molar heat capacities of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$ are shown in Fig. 1 and tabulated in Table 1. As the data are listed in chronological order, the temperature increment due to each energy input can be estimated from the adjacent mean temperatures. A typical second-order type of anomaly is observed at about 100 K which coincides with the electrical resistivity drop due to the superconducting phase transition. The heat capacity value seems to approach the classical limit of $45R = 374.1$ J K^{-1} mol^{-1} asymptotically above room temperature. The values of thermodynamic functions calculated from the present results are given in Table 2. The small contribution below 7 K was estimated by the method of smooth extrapolation to 0 K.

The electrical resistivity and a.c. magnetic susceptibility of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$ are shown together with the heat capacity anomaly in Fig. 2. With decreasing temperature, the drop in the electrical resistivity due to the superconducting phase transition commences at about 120 K and zero resistance is reached at 101 K. The Meissner signal in the a.c. magnetic susceptibility is observed below 104 K. The increase in heat capacity is also accelerated below about 110 K. The critical temperature and the heat

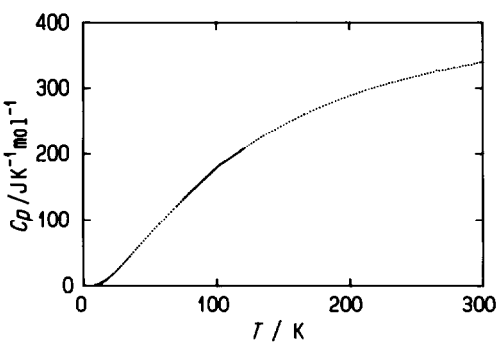

Fig. 1. Measured molar heat capacities of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$.

TABLE 1

Measured molar heat capacities of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$

T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)
Series 1		184.58	277.14	24.87	23.22
70.30	122.35	186.91	278.64	26.06	25.77
71.85	125.54	189.23	280.96	27.21	28.16
73.36	128.60	191.54	282.66	28.46	30.67
74.85	131.59	193.84	284.40	29.84	33.68
76.30	134.54	196.13	285.74	31.10	36.44
77.71	137.42	198.41	287.94	32.23	38.93
79.10	140.19	200.67	289.47	33.46	41.61
80.46	142.66	202.93	291.17	34.81	44.60
81.80	145.29	205.18	292.32	36.24	47.84
83.11	147.92	207.41	294.28	37.73	51.19
84.41	150.16	209.67	295.58	39.21	54.53
85.68	152.74	211.95	297.34	40.68	57.75
86.93	155.08	214.22	298.95	42.20	61.16
88.17	157.44	216.48	300.13	43.73	64.59
89.39	159.60	218.73	301.56	45.29	68.09
90.60	162.03	220.98	302.84	46.87	71.71
91.78	164.09	223.22	304.24	48.49	75.24
92.96	166.35	225.45	305.20	50.17	78.94
94.12	168.61	227.67	306.77	51.87	82.87
95.27	170.64	229.88	308.04	53.57	86.44
96.40	172.71	232.09	309.19	55.29	90.39
97.53	174.87	234.29	309.99	57.04	94.06
98.64	176.98	236.51	311.52	58.80	98.00
99.74	179.07	238.76	312.70	60.61	101.76
100.83	181.13	240.99	313.91	62.43	105.76
101.91	183.01	243.22	314.62	64.27	109.65
102.98	184.56	245.44	316.33	66.11	113.46
104.05	185.84	247.66	317.33	67.96	117.42
105.10	187.17	249.87	318.50	69.82	121.38
106.15	188.41	252.07	319.08	71.65	124.93
107.19	189.69	254.27	320.68	73.47	128.80
108.22	191.06	256.46	321.73	75.30	132.55
109.25	192.44	258.68	322.80	77.14	136.12
110.27	193.78	260.91	324.13	78.98	139.89
111.28	195.16	263.14	324.68	80.82	143.49
112.28	196.60	265.37	327.44	82.71	147.01
113.28	198.09	267.59	327.00	84.66	150.74
114.27	199.34	269.80	327.89	88.54	158.11
115.26	200.77	272.01	328.09	90.45	161.71
116.24	202.12	274.21	329.52	92.38	165.34
117.22	203.48	276.41	330.28	94.44	169.14
118.19	204.82	278.60	331.23	96.60	173.25
119.15	206.18	280.79	331.57	98.73	177.24
120.11	207.53	282.97	332.74	100.82	181.16

TABLE 1 (continued)

T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})	T (K)	C_p (J K^{-1} mol^{-1})
Series 2		285.15	334.04	102.86	184.42
121.27	209.27	287.32	334.54	104.88	187.00
122.80	211.75	289.49	335.26	106.87	189.43
124.51	213.80	291.65	335.30	108.83	192.00
126.21	216.04	293.80	337.28	110.77	194.65
127.90	218.19	295.96	338.38	112.68	197.25
129.68	220.44	298.10	339.36	114.56	199.86
131.55	222.42	300.24	339.47	116.43	202.56
133.41	225.24	*Series 3*		118.28	205.15
135.39	227.61	8.63	1.36	120.11	207.63
137.55	230.23	9.43	1.69	*Series 5*	
139.74	232.51	10.39	2.30	79.81	141.44
141.91	235.34	11.44	3.08	81.20	144.13
144.06	237.76	12.55	4.08	82.57	146.83
146.19	240.29	13.66	5.17	83.91	149.14
148.36	242.74	14.74	6.44	85.20	151.80
150.56	244.86	15.84	7.87	86.45	154.07
152.77	247.53	17.06	9.64	87.68	156.51
155.00	249.98	*Series 4*		88.89	158.59
157.20	252.23	12.26	3.89	90.08	160.96
159.40	254.14	13.35	4.90	91.26	163.14
161.58	256.50	14.47	6.11	92.43	165.28
163.74	258.68	15.58	7.45	93.60	167.52
165.89	260.90	16.70	8.93	94.76	169.67
168.03	262.34	17.86	10.64	95.92	171.85
170.31	264.99	19.04	12.52	97.09	174.03
172.72	267.03	20.23	14.60	98.28	176.21
175.12	269.24	21.35	16.57	99.49	178.56
177.50	270.91	22.44	18.58	100.70	180.88
179.88	273.32	23.62	20.84	101.88	182.90
182.23	275.33				

capacity jump of the superconducting phase transition are 104 K and 2.6 J K^{-1} mol^{-1} respectively. The shape of the heat capacity anomaly is rather rounded compared with that for the transition metal superconductors. It has been suggested that the fluctuation would contribute to the shape of the heat capacity anomaly in high temperature oxide superconductors because of the small value of the Bardeen–Cooper–Schreiffer (BCS) coherent length [7]. In the $YBa_2Cu_3O_y$ single crystal, the three-dimensional fluctuations and a rather large value of the superconducting Ginsberg–Landau order parameter n_{GL} have been reported [7,8].

Recently, a new type of analysis has been developed for the broadening in the heat capacity anomaly at the superconducting transition temperature, taking account of the effect of sample inhomogeneity [9]. A gaussian

TABLE 2

Thermodynamic functions of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$

T (K)	$C_p(T)$ (J K^{-1} mol^{-1})	$H(T)-H(0)$ (J mol^{-1})	$S(T)-S(0)$ (J K^{-1} mol^{-1})	$-[G(T)-H(0)]/T$ (J K^{-1} mol^{-1})
10	2.11	5.32	0.71	0.17
20	14.16	77.56	5.24	1.36
30	34.02	315.0	14.59	4.09
40	56.24	765.9	27.41	8.26
50	78.63	1440.4	42.36	13.56
60	100.5	2336.8	58.65	19.70
70	121.7	3448.4	75.74	26.48
80	141.8	4767.1	93.32	33.73
90	160.8	6280.7	111.12	41.34
100	180.3	7982.8	129.04	49.21
110	194.2	9855.0	146.87	57.28
120	207.8	11865.7	164.36	65.48
130	220.8	14009.5	181.51	73.75
140	233.1	16279.6	198.33	82.05
150	244.5	18667.8	214.80	90.35
160	255.0	21165.6	230.92	98.63
170	264.6	23764.0	246.67	106.88
180	273.3	26453.8	262.04	115.08
190	281.4	29227.6	277.04	123.21
200	289.0	32079.7	291.66	131.27
210	296.0	35004.9	305.93	139.24
220	302.3	37996.9	319.85	147.14
230	307.9	41048.4	333.42	154.94
240	313.2	44153.7	346.63	162.66
250	318.6	47312.8	359.53	170.28
260	323.7	50524.2	372.12	177.80
270	328.0	53783.7	384.42	185.22
280	331.6	57081.9	396.42	192.55
290	335.4	60416.3	408.12	199.79
300	340.5	63794.3	419.57	206.92

distribution of T_c characterized by a width δ is introduced, and the electronic heat capacity $\langle C(t)\rangle$ is given as

$$\langle C(t)\rangle = \frac{\int dt' C(t') \exp\left[-(t-t')^2/\sigma^2\right]}{\int dt' \exp\left[-(t-t')^2/\sigma^2\right]}$$

where t is the reduced temperature, $t=(T-T_c)/T_c$; $C(t)$ is expressed as $C(t)=C_n(t)+C_s(t)+C_{nf}(t)+C_{sf}(t)$; C_n, C_s, C_{nf} and C_{sf} are electronic heat capacities of the normal state, superconducting state, fluctuation above T_c and fluctuation below T_c respectively. The electronic heat capacities in

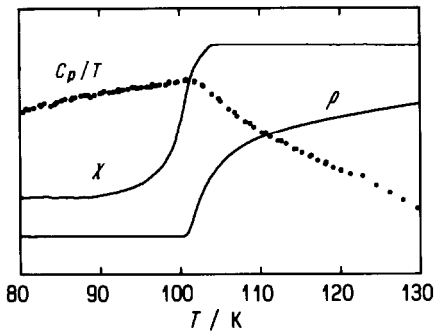

Fig. 2. Anomalies in heat capacity, electrical resistivity and magnetic susceptibility due to superconducting phase transition of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$.

the normal state ($C_n(t)$) and the usual BCS superconducting state ($C_s(t)$) are expressed as

$$C_n(t) = \gamma T_c(1 + t)$$

and

$$C_s(t) = R\gamma T_c(1 + t)(1 + \beta t)$$

respectively, where R is the parameter specifying the height of the heat capacity jump at T_c ($R = 2.43$ in the BCS weak coupling limit). The fluctuation contributions are expressed above and below T_c as

$$C_{nf}(t) = \alpha\gamma T_c t^{-1/2}$$

and

$$C_{sf}(t) = \frac{\alpha}{\sqrt{2}}\gamma T_c(-t)^{-1/2}$$

TABLE 3

Parameters obtained by fitting to the inhomogeneous smearing model of three-dimensional fluctuation with $n_{GL} = 2$

R	2.331
β	1.125
α	0.2115
γ	20.89 mJ K^{-2} mol^{-1}
δ	0.07205
a	8.175 mJ K^{-1} mol^{-1}
b	1811.6 mJ K^{-2} mol^{-1}
c	−0.785 mJ K^{-3} mol^{-1}

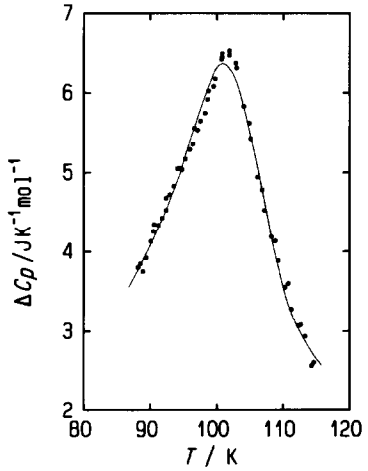

Fig. 3. Electronic heat capacities of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$. Solid line shows the result of least-squares fitting.

respectively, assuming a conventional three-dimensional fluctuation with $n_{GL} = 2$. The lattice contribution near T_c is approximated as

$$C_{\text{lattice}} = a + bT + cT^2$$

The least-squares fitting with eight parameters R, β, α, γ, δ, a, b and c described above has been carried out by using the Marquardt method. The values of the parameters are given in Table 3. The electronic heat capacity thus obtained is shown in Fig. 3. The electronic heat capacity coefficient γ is obtained as 21 mJ K^{-2} mol^{-1} and the coherence length ξ_0 as about 5.4 Å from the value of $\alpha = k/8\pi\xi_0^3\gamma T_c$. The value of R is close to 2.43 (expected in the BCS weak coupling limit), and the width of distribution of T_c is about 7 K. Thus, we could fit the parameters by assuming a conventional three-di-

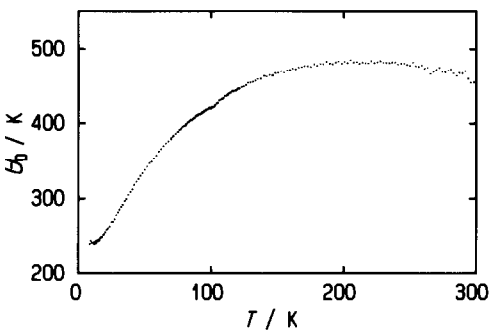

Fig. 4. Debye characteristic temperatures of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$ assuming three degrees of freedom for each atom.

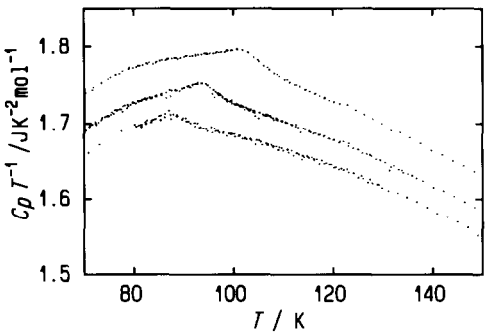

Fig. 5. Heat capacity anomalies due to the superconducting phase transitions of $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$, $Tl_{1.93}Ba_2Ca_1Cu_2O_{7.91}$ and $Tl_{1.82}Ba_2Ca_1Cu_2O_{7.72}$.

mensional fluctuations with $n_{GL} = 2$. However, it should be noted that more detailed analysis is required for a higher quality of sample with a narrow distribution of T_c.

The Debye characteristic temperatures, assuming the three degrees of freedom for each atom, are shown in Fig. 4, The decrease in the Debye characteristic temperature with decreasing temperature indicates a high density of state of low frequency lattice vibrational modes which should correspond to the layered structure of $Tl_2Ba_2CaCu_2O_y$.

The heat capacity measurements were made also for the second and the third samples to see the effect of thallium deficiency. A preliminary report of the results has been published [5]. The heat capacity anomalies of the three samples are shown in Fig. 5. The critical temperatures of the superconducting phase transition and the heat capacity jumps ΔC_p are determined as 104, 96 and 89 K, and 2.6, 2.8 and 2.2 J K^{-1} mol^{-1} for $Tl_{2.10}Ba_2Ca_1Cu_2O_{8.15}$, $Tl_{1.94}Ba_2Ca_1Cu_2O_{7.91}$ and $Tl_{1.82}Ba_2Ca_1Cu_2O_{7.72}$ respectively. The critical temperature decreased monotonically with the decrease in the abundance of Tl atoms. The heat capacity jump is remarkably small for the third sample. The superconductivity of this compound might be damaged by the deficiency of the Tl atom.

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