The heat capacity and derived thermophysical properties of the high T_C superconductor $YBa_2Cu_3O_{7-\delta}$ from 5.3 to 350 K

R. Shaviv and E. F. Westrum, Jr.
Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

R. J. C. Brown
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

M. Sayer and X. Yu
Department of Physics, Queen's University, Kingston, Ontario K7L 3N6, Canada

R. D. Weir
Department of Chemistry and Chemical Engineering, Royal Military College, Kingston, Ontario K7K 5L0, Canada

The heat capacity of the perovskite high-T_C superconductor $YBa_2Cu_3O_{7-\delta}$ was measured from 5.3 to 350 K in an adiabatic calorimetric cryostat. A break in the heat-capacity curve, associated with the critical temperature for superconductivity was observed between 90.09 and 92.59 K. The transition temperature was identified as 91.44 K, and $\Delta C_{p,m}$ was calculated to be $0.559R$ at that temperature. The lattice heat capacity was evaluated by means of the recently developed Komada/Westrum phonon distribution model and the apparent characteristic temperature Θ_{KW} was calculated to be 107.7 K. The excess electronic heat capacity for the superconducting phase was evaluated and the energy gap was identified as 234. R K. Excess contribution, resulting from magnetic impurities, was noted below 20 K. Thermodynamic properties at selected temperatures are presented.

I. INTRODUCTION

The discovery of two new classes of superconducting materials first by Bednorz and Müller in La–Ba–Cu oxides[1] and later by Wu et al.[2] in Y–Ba–Cu oxides created a wave of excitement in the scientific community; many properties of these compounds were examined and reexamined, and numerous theoretical attempts at explaining the phenomena were made. These explanations, however, were only partially successful, and as this report is being written the mechanisms behind high T_C superconductivity are not yet fully understood. The interactions predicted by the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity[3] seemingly cannot account for the high T_C in the new materials. The BCS interactions, which are responsible for the creation of "Cooper pairs," that are responsible for the superconductivity in "normal" metals, are not strong enough to maintain superconductivity at "high" temperatures since thermal activation would break the weak bond that keeps the Cooper pair paired. It is, therefore, evident that new approaches to the understanding of superconductivity are required and new theories are in order.

The understanding of the thermodynamics of a compound is an integral part the general understanding of its chemistry and physics. In that respect heat-capacity mesurements are particularly attractive since they are very sensitive to transformations in the solid, are not affected by minor amounts of impurities, and phase transitions are easily ascertained by such measurements. In addition to probing phase transitions, heat-capacity measurements can supply valuable information about lattice vibrations, electronic density of states near the Fermi level, the magnitude of energy gaps, and low temperature electronic characteristics.

Since the discovery of the high-T_C materials, more than 100 papers on their specific heat have been published. However, the majority of these works were constrained to a limited temperature region (either very low temperatures $T < 20$ K, or the transition region). Many of these reports have been recently reviewed by Fisher et al.[4] and by Fischer et al.[5] The agreement between results obtained on different samples is usually poor. This may be attributed to different sample stoichiometry arising from different methods of synthesis and purification. Most of the samples that were used for evaluations of heat capacity (including the sample we used for this report) were neither single crystal nor single phase. Variations in synthetic methods were shown to cause variations in the magnitude of the drop in the heat capacity at the transition temperature, even in single phase samples.[6]

Recently we have reported heat-capacity measurements on $YBa_2Cu_3O_{7-\delta}$ in the vicinity of the superconducting transition.[7,8] In this report we extend our discussion to the temperature region between 5.3 and 350 K. We report heat-capacity data, thermodynamic functions from 10 to 350 K, and make an attempt to resolve the measured heat capacity into its component lattice and the electronic contributions. ΔC_p and gap energy are thus evaluated.

II. EXPERIMENTAL

A. Sample provenance

The sample was prepared by mixing stoichiometric amounts of Y_2O_3, BaO, and CuO so as to yield a 1:2:3 ratio of metals. Starting materials were checked by x-ray powder

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TABLE I. Molar heat capacities of $YBa_2Cu_3O_{6.9}$. ($R = 8.3144$ J K^{-1} mol^{-1}.)

T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$	T/K	$C_{p,m}/R$
		$YBa_2Cu_3O_{6.9}$,	$M = 664.000g$ mol^{-1}		
Series I				**Series VII**	
67.409	4.520[a]	92.273	15.311	85.863	14.294
69.583	7.665[a]	92.586	15.178	87.209	14.567
72.555	8.194[a]	92.896	15.464	88.230	14.870
75.512	8.758[a]	93.311	15.391	88.896	15.027
77.993	9.047[a]	93.984	15.444	89.308	15.040
79.998	9.444[a]	95.066	15.688	89.616	15.207
82.011	9.877[a]	96.605	15.916	89.926	14.968
84.030	10.155[a]	98.346	16.187	90.209	15.395
86.049	10.663[a]	100.087	16.481	90.467	15.386
88.073	11.084[a]	102.032	16.820	90.727	15.284
90.100	11.471[a]			90.987	15.447
92.146	11.470[a]	**Series IV**		91.247	15.410
94.195	11.656[a]	5.573	0.208[a]	91.787	15.321
96.238	5.734[a]	6.287	0.107[a]	91.507	15.394
98.278	12.220[a]	7.409	0.041	92.088	15.224
100.318	12.541[a]	8.316	0.066[a]	92.393	15.387
102.362	12.768[a]	9.001	0.058	92.704	15.219
104.402	13.141[a]	9.784	0.069	93.014	15.500
106.444	13.453[a]			93.375	15.619
108.489	13.724[a]	**Series V**		93.844	15.413[a]
110.538	14.034[a]	5.888	0.012[a]	94.515	15.726
114.092	15.277[a]	6.614	0.037		
119.131	16.017[a]	7.235	0.040	**Series VIII**	
		8.029	0.046	96.942	15.959
Series II		8.764	0.054	101.459	16.748
57.816	8.035	9.543	0.065	110.270	18.160
60.915	8.751	10.418	0.079	122.796	20.085
63.847	9.412	11.287	0.099	131.485	21.362
66.948	10.101	12.137	0.123	136.501	21.994
70.213	10.821	12.992	0.152	141.573	22.682
73.640	11.569	13.852	0.185	146.588	23.337
77.241	12.348	14.723	0.225	156.713	24.547
81.022	13.189	15.599	0.273	161.826	25.107
84.996	14.115	16.477	0.327	166.941	25.655
88.524	14.887	17.364	0.390	172.059	26.163
91.025	15.350	18.260	0.458	177.694	26.725
93.068	15.393	19.131	0.534	183.842	27.284
95.117	15.860	20.000	0.615	189.992	27.815
97.161	15.845	20.908	0.709	196.139	28.341
99.206	16.337	21.862	0.816	202.294	28.856
101.846	16.813	22.857	0.938	208.969	29.370
105.641	17.431	23.900	1.071	216.162	29.887
109.816	18.106	24.995	1.219	223.349	30.356
114.347	18.800	26.146	1.383	230.540	30.811
119.377	19.572	27.347	1.568	237.747	31.232
124.408	20.332	28.603	1.776	245.463	31.673
129.455	21.077			253.690	32.119
134.515	21.768	**Series VI**		261.923	32.566
139.589	21.433	29.800	1.998[a]	270.159	32.967
144.674	23.129	31.067	2.220	278.397	33.336
		32.510	2.499	286.634	33.659
Series III		34.014	2.795	294.857	33.989
83.954	13.832	35.594	3.118	303.052	34.303
85.486	14.218	37.255	3.462	311.252	34.656
87.469	7.271[a]	38.998	3.827	319.449	34.997
88.385	9.294[a]	40.828	4.215	327.581	35.328
89.218	15.022	42.752	4.631	335.689	35.565
89.727	15.063	44.772	5.076	342.442	35.668
90.088	15.453	46.893	5.559		
90.402	15.439	49.120	6.069		
90.716	15.243	51.460	6.604		
91.027	15.268	53.924	7.158		
91.338	15.398	56.508	7.733		
91.650	15.249	59.224	8.358		
91.962	15.291	62.082	9.016		
		65.084	9.682		

[a]Not included in the calculation of thermodynamic properties.

diffraction. There was evidence that the BaO may have reacted with atmospheric water to form the hydrated hydroxide, and the diffraction pattern of the product contained four very weak reflections which could not be indexed on the cell described by LePage et al.[9]

The starting materials were mixed, heated at 10 °C min^{-1} to 910 °C, held at that temperature for 12 h, and cooled at 5 °C min^{-1} to 750 °C and then at 10 °C min^{-1} to room temperature. The product was ground, pressed into pellets and sintered at 930 °C with the same heating and cooling rates as in the first heat. The sample is believed to have the composition $YBa_2Cu_3O_{6.9}$.

Several different pellets were prepared from the sample. The resistance of one of the pellets was measured using four-terminal connections, with a thermocouple attached to the pellet. The resistance dropped by about two orders of magnitude at approximately 92 K; a small residual resistance of unknown origin persisted below this temperature.

The powder diffraction pattern of the final product is in excellent agreement with the pattern described by Cava et al.[10] with $a = 3.8202(3)$ Å, $b = 3.8885(3)$ Å, and $c = 11.684(1)$ Å.

B. Calorimetric technique

The subambient heat capacity of $YBa_2Cu_3O_{6.9}$ was measured by adiabatic calorimetry over the temperature range 5.3 to 345 K in the Mark XIII adiabatic cryostat which is described in a separate paper.[11] The sample was contained in a gold-plated, oxygen-free, high-conductivity, (OFHC) copper calorimeter (laboratory designation W-99). The calorimeter has a mass of 10.21 g with an internal volume of 11 cm^3. The temperature of the calorimeter was measured with a Leeds & Northrup platinum encapsulated, platinum resistance thermometer (in an entrant well) which was calibrated by the U.S. National Bureau of Standards against IPTS-48 and is considered to reproduce the thermodynamic temperature scale within 0.03 K from 5 to 300 K.

The 17.3 g calorimeter sample represents about 0.026 moles when 664.600 g mol^{-1} is selected as the molecular mass. The stoichiometry of the sample is not known but it has been assumed that the value of δ is 0.1 in the formula $YBa_2Cu_3O_{7-\delta}$. This may be inferred from the sharpness of the superconducting transition, the thermal history of the sample and measured lattice parameters.[12,13] Hence the molecular formula $YBa_2Cu_3O_{6.9}$ was used to calculate the molar heat capacity of the compound. To facilitate rapid thermal equilibration, 3.34 kPa of helium gas at 300 K were introduced after evacuation. The calorimeter was then sealed, placed in the cryostat, and cooled. The heat capacity of the empty calorimeter represented 60% to 70% of the total heat capacity at temperatures below the transition temperature and about 50% at higher temperatures. The precision of a single data point is about 0.5% below 15 K and is reduced to 0.1% at higher temperatures. This error propagates to about 1% for the calculated thermodynamic functions at room temperature.

III. RESULTS AND DISCUSSION

The experimental heat capacity of $YBa_2Cu_3O_{7-\delta}$ is listed in Table I and plotted in Fig. 1. Values of the heat capacity
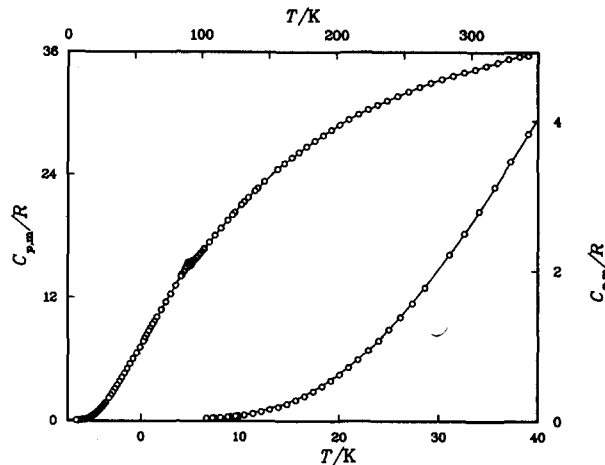

FIG. 1. Molar heat capacity of $YBa_2Cu_3O_{7-\delta}$. A magnified scale of the low temperature end is shown at the lower right corner.

are shown as a function of temperature in the vicinity of the transition in Fig. 2. Thermodynamic functions at selected temperatures are presented in Table II.

The total heat capacity of this compound is assumed to be the sum of the excess contributions and the lattice contribution. It is also assumed that the lattice heat capacity is not affected by the transition. According to the BCS theory[3]

$$\frac{C_{el,s}}{\gamma T_C} = 9.17 \cdot e^{-E_g/2RT}$$

when $C_{el,s}$ is the electronic heat capacity of the superconducting phase, E_g is the energy gap, and γ is the electronic heat capacity coefficient. Hence from a plot of ln $(C_{el,s}/T_C)$ vs $1/T$ the energy gap can be evaluated if γ is known. For most metals the experimental heat capacity, at low temperatures, follows the Debye limiting rule $C_p/T = \gamma T + \beta T^3$, and thus γ can be readily evaluated from the intercept on the abscissa of a C_p/T vs T/K plot. Such a plot is presented in Fig. 3 for temperatures up to 20 K. Since Debye-like behavior is not observed and no straight line can be drawn to fit the
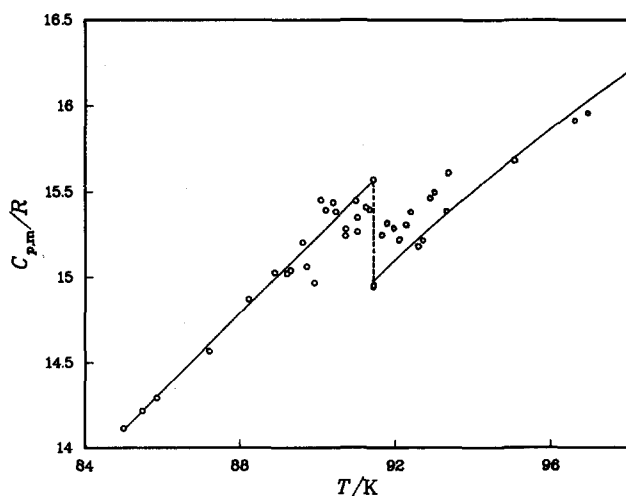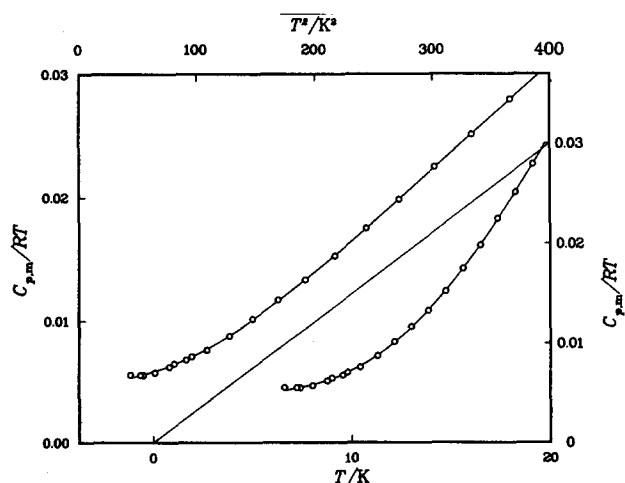

FIG. 2. Molar heat capacity for $YBa_2Cu_3O_{7-\delta}$ in the vicinity of the superconducting transition. Small differences between series cause what appears to be a reduced precision over the region (see the text).

TABLE II. Thermodynamic properties at selected temperatures for YBa$_2$Cu$_3$O$_{6.9}$. ($R = 8.3144$ J K^{-1} mol^{-1}.)

T/K	$C_{p,m}^0/R$	$\Delta_0^T S_m^0/R$	$\Delta_0^T H_m^0/R$ K	$\Phi_m^0(T,0)/R$
0.0	0.0	0.0	0.0	0.0
10	0.072	0.049	0.272	0.022
15	0.240	0.104	0.977	0.039
20	0.617	0.219	3.024	0.068
25	1.218	0.417	7.517	0.116
30	2.026	0.708	15.548	0.190
35	2.991	1.091	28.043	0.290
40	4.042	1.558	45.603	0.418
45	5.134	2.097	68.53	0.574
50	6.258	2.696	97.00	0.756
60	8.541	4.039	171.02	1.189
70	10.775	5.524	267.62	1.701
80	12.949	7.106	386.31	2.277
90	15.21	8.763	527.3	2.905
91.44	15.31	9.007	549.3	2.999
100	16.48	10.424	685.0	3.574
110	18.10	12.070	857.8	4.272
120	19.71	13.715	1047.0	4.990
130	21.14	15.35	1251.3	5.724
140	22.47	16.97	1469.4	6.469
150	23.75	18.56	1700.6	7.222
160	24.93	20.13	1944.1	7.980
170	25.97	21.67	2198.8	8.741
180	26.92	23.19	2463.3	9.501
190	27.81	24.67	2737.0	10.261
200	28.66	26.11	3019.4	11.017
210	29.45	27.53	3310.0	11.770
220	30.16	28.92	3608.1	12.518
230	30.78	30.27	3912.9	13.261
240	31.35	31.60	4223.5	13.997
250	31.91	32.89	4539.8	14.727
260	32.46	34.15	4861.7	15.45
270	32.97	35.38	5189.	16.17
280	33.41	36.59	5521.	16.87
290	33.79	37.77	5857.	17.57
298.15	34.10	38.71	6134.	18.14
300	34.17	38.92	6197.	18.27
325	35.24	41.70	7064.	19.96
350	35.62	44.33	7953.	21.61

TABLE III. Optical wave numbers used as weighted Einstein functions in the LEM-1 program for calculations of Θ_{KW} for the lattice heat capacity.[a]

Symmetry	Wave number (cm^{-1})
A_g	515, 373, 347, 159, 132
B_{2g}	586, 541, 348, 160, 70
B_{3g}	573, 510, 462, 158, 94
B_{1u}	555, 502, 375, 319, 199, 161, 109
B_{3u}	130, 555, 361, 291, 238, 116, 62
B_{2u}	576, 533, 429, 289, 237, 106, 156

[a] Reference 15.

which is an arithmetic averge of 56 previously published values[4] is adopted throughout this report.

The lattice contribution to the heat capacity was evaluated by means of the Komada/Westrum approximation to lattice heat capacity.[14] The approximation is based on a calculation of an estimated phonon spectra based on known lattice heat capacity and a set of physical parameters. Known lattice vibration frequencies can be incorporated in the approximated spectra as Einstein functions. A characteristic temperature Θ_{KW} is then calculated to represent the approximation. A constant Θ_{KW} indicates that the same density of state function can be used to reproduce the heat capacity over an extended temperature region[14] by extrapolation or interpolation. Such approximated spectra may not be unique but they provide a good prediction for lattice heat capacity beyond the experimental range. In the present calculation 36 lattice frequencies, which were obtained in a lattice dynamical calculation,[15] were used as internal branches in the phonon spectrum, resulting in 36 weighted Einstein functions in the C_v approximation. These frequencies are listed in Table III. The electronic heat capacity in the normal phase (i.e., $C_{el,n} = \gamma T$) did not enter the calculation of Θ_{KW} and was subtracted from the experimental heat capacity for the purpose of this calculation. Θ_{KW} was then calculated by the LEM-1 computer program.[16] Θ_{KW} as a function of temperature is presented in Fig. 4. Θ_{KW} is constant over the

data, γ cannot be evaluated from the present data. Debye-like behavior at low temperatures was observed by several authors and several different values of γ were proposed. The value $\gamma = (28.2 \pm 10)$ mJ mol^{-1} K$^{-2} = 3.4 \times 10^{-3}$ R/K
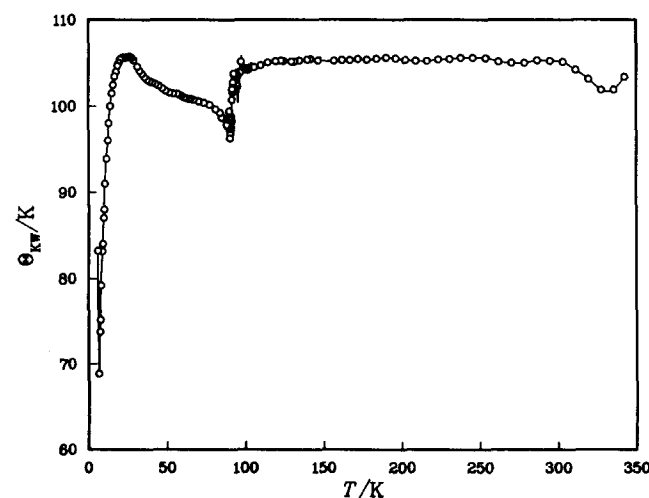

FIG. 3. C_p/T vs T^2 (top left corner), and C_p/T vs T (insert, lower right corner) for YBa$_2$Cu$_3$O$_{7-\delta}$.

FIG. 4. Θ_{KW} vs T for YBa$_2$Cu$_3$O$_{7-\delta}$.

entire nonsuperconducting temperature region. The drop in Θ_{KW} above 300 K is attributed to additional contributions from anharmonicity which start to take effect. The superconducting transition is clearly seen as a break in Θ_{KW} at the transition temperature. The apparent Θ_{KW} is lower in the superconducting region because of the excess electronic contribution.

A plot of the excess heat capacity in the superconducting phase is shown in Fig. 5. The total excess contribution is the sum of the superconducting and the nonsuperconducting electronic heat capacity. Based upon Meisner effect studies we have concluded that only 5% to 10% of the electrons are not superconducting, and their heat capacity is, therefore, smaller than the experimental error. The heat capacity of the superconducting electrons, was then calculated using the relation

$$C_{el,s} = C_{exptl} - C_{lat},$$

when C_{exptl} is the experimental heat capacity and C_{lat} is the lattice contribution calculated using the program LEM-3[16] with $\Theta_{KW} = 107.70$. The thus calculated $C_{el,s}$, along the electronic heat capacity which would have been expected for the nonsuperconducting phase ($C_{el,n}$), are presented in Fig. 5. The figure reveals several interesting features. Some excess heat capacity is observed above the transition temperature and up to about 120 K. This residual excess contribution, although not large, is significant and probably indicates that phenomena associated with the superconductivity persist above the critical temperature. It is believed that this excess contribution is real and is not due to experimental error nor to an artifact resulting from the approximation. A similar phenomenon was previously observed by Gordon et al.[17] over a smaller temperature range.

No excess contribution was detected between 120 and 350 K. The anomaly at about 220 K which was reported by Laegreid et al.[18,19] and by Calemczuk et al.[20] is not observed in the present study. The crossover between the electronic heat capacity of the normal state $C_{el,n}$ and that of the superconducting state $C_{el,s}$ is observed at about 35 K. The excess contribution $C_{el,s}$ seems to be no larger than the experimental
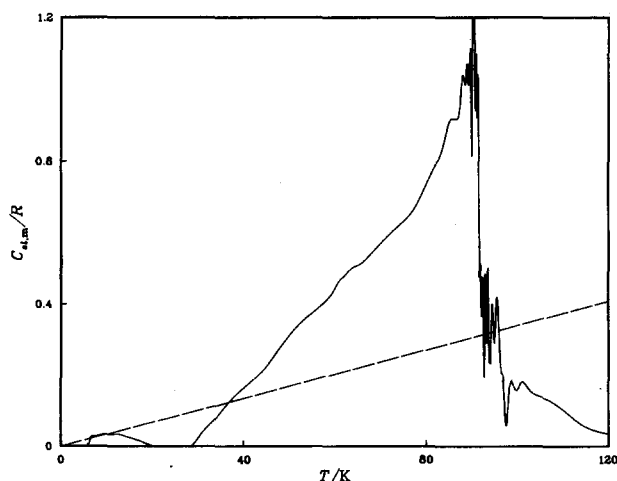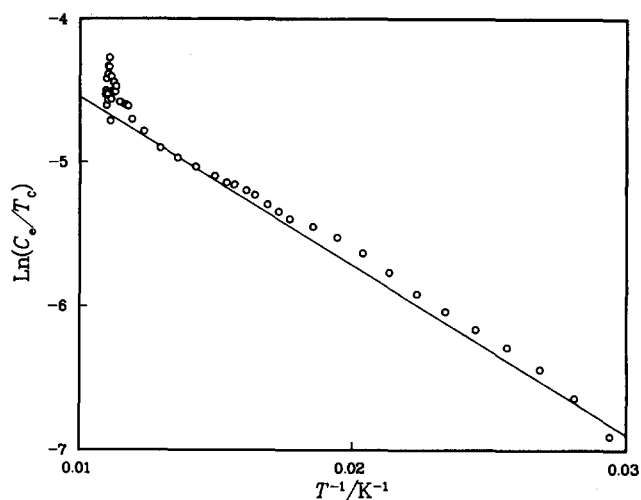

FIG. 6. Excess heat capacity for $YBa_2Cu_3O_{7-\delta}$ in the superconducting phase plotted as $\ln(C_{el,s} \cdot T_C^{-1})$ vs $1/T$.

tal error up to about 30 K. Below 20 K, however, additional excess contributions are evident. The origin of these is not totally clear, but it is believed to be in ordering of magnetic impurity phases.[4] These impurities may also give rise to Schottky contributions with maxima at the vicinity of 5 K or lower. In our experiment we were able to observe only the high-temperature tail of these contributions.

The excess heat capacity in the superconducting state is shown in Fig. 6 as $\ln(C_{el,s} \cdot T_C^{-1})$ vs T^{-1}. The plot should be linear with a slope of $E_g/(2R \text{ K})$. The result is indeed a straight line with a slope of -117 which corresponds to an energy gap of $E_g = 234R$ K. Below 30 K the electronic heat capacity is too small and disappears into the experimental error. Previously we have reported[8] the presence of two energy gaps with $E_{g1} = 36.16R$ K and $E_{g2} = 220.24R$ K for this material. This implied the presence of additional superconducting phase(s) at low temperatures. The presence of two energy gaps, although not common, is well established in other superconducting materials,[21] and additional superconducting phase(s) have been observed in YBCO compounds.[22] There are two major differences between the previous analysis[8] and the present one: 1. The value of $\gamma = 1.443 \times 10^{-3}R$ K that was previously used[23] was revised to $\gamma = 3.4 \times 10^{-3}R$ K based on a larger set of data. 2. The previous assumption that only 15% of the electrons was involved in the superconductivity was proven to be incorrect; it is now assumed that 90% to 95% of the electrons are involved in the process.

The intercepts on the abscissa in Fig. 6 is $\ln(C_{el,s} \cdot T_C^{-1}) = -3.371 = y(0)$. According to the BCS theory this intercept is related to γ by $y(0) = \ln(9.17\gamma)$ or $9.17 = e^{y(0)} \cdot \gamma^{-1}$. The current results yield $e^{y(0)} \cdot \gamma^{-1} = 10.1$ which is not far from the BCS prediction.

The superconducting transition appears to be a second order transition. During the course of the experiment four passes through the transition were made (series I, II, III, VII in Table I). The first series was not included in the final calculation since an equipment breakdown caused erroneous results. The last two series were used to map the transition and to identify the transition temperature. A small dif-

FIG. 5. Excess heat capacity in the superconducting region.—: electronic heat capacity of the superconducting phase; − −: electronic heat capacity of the nonsuperconducting phase.

ference between the two series is observed. In the first of the two experimental heat capacity reaches a maximum of 90.09 K and drops to a minimum at 92.59 K. In the second the maximum is found at 90.99 K and the minimum at 92.09 K. The center of the transition does not differ much between the two series but the first is much wider. It is not clear if the difference in the width of the transition is the result of experimental error or a real phonomenon due to thermal history. The transition temperature was selected to be 91.44 K which is the average of the mean temperatures of the two series. ΔC_p—the total drop in the heat capacity at the transition temperature—is calculated as the difference between the electronic heat capacity in the normal and the superconducting states

$$\Delta C_p = C_{el,s}(T) - C_{el,n}(T), \quad T = T_C.$$

The lattice heat capacity does not enter the calculation of ΔC_p since it is assumed that it is unaffected by the transition. The heat capacity of the superconducting electrons at the transition temperature can be found from Fig. 6. The electronic heat capacity in the normal state is γT. Hence

$$\Delta C_p/R = T_C \cdot e^{-4.655} - \gamma T_C$$
$$\Delta C_p/R = 0.870 - 0.0034 \times 91.44 = 0.559.$$

This value is slightly smaller but within experimental error of the value given by Gordon *et al.*[17] and is in agreement with the BCS prediction for a weakly coupled superconductor. The lattice heat capacity at the transition temperature is 14.639R. Thus C_p corresponds to 3.82% of the total heat capacity at the transition temperature.

IV. CLOSING REMARKS

The traditional method of resolving the electronic contribution in the heat capacity of a superconductor, i.e., by evaluating the lattice heat capacity in terms of the Debye characteristic temperature is less satisfactory than using, for example, the Komada/Westrum approximation. This report makes use of this approach to evaluate the lattice contribution of the superconducting phase. The excess contributions are small for the entire superconducting phase. Moreover, one should be cautious when conclusions are drawn from excess contributions approaching the experimental error. Such is the case at temperatures lower than 30 K. However, it is evident that the Komada/Westrum approximation provided the necessary tool for a reliable analysis of the experimental results.

Several important factors that influence the heat capacity and the transition temperature—such as the role of oxygen vacancies, the effects of isotope substitution, etc.—are not studied in this report. These will be the subjects of future studies and future experiments.

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