Thermochimica Acta, 137 (1988) 65–70
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

HEAT CAPACITY MEASUREMENTS OF THE HIGH T_c SUPERCONDUCTOR $YBa_2Cu_3O_{7-x}$

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(Received in final revised form June 7, 1988)

ABSTRACT

Recent reports of superconductivity at temperatures of 90-95 K in the Y-Ba-Cu-O chemical system have demonstrated that T_c higher than those generally considered attainable can be achieved in oxide systems. We report heat capacity results obtained on single-phase polycrystalline samples of high T_c perovskite-type superconductors.

INTRODUCTION

The discovery of superconductivity at temperatures of 90-95 K in the system Y-Ba-Cu-O [1] has triggered an explosive growth of interest in copper-based oxides. However, the thermal properties of these ceramic materials have received little comparative attention so far, even though they can provide a substantial insight into the theoretical aspect of superconducting transitions [2-4].

Work was initially directed to the study of the effect on the superconducting transition temperature (T_c) of the partial replacement of barium with another alkaline-earth, or yttrium with the trivalent rare-earths, in the search for ways of simulating "internal pressures". It was found, however, that although most rare-earth atoms are more or less magnetic, these substitutions did not change T_c by more than ±10% [5,6]. By contrast, it has become evident that the superconducting properties of "YBCO" samples were strongly affected by the preparation process, including cooling rate, quenching temperature, oxygen partial pressure during synthesis (determining the amount of oxygen present in the phase [7]) and the used chemical reaction.

$YBa_2Cu_3O_{7-x}$ oxides can be prepared *via* different processes, such as

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coprecipitation of citrates or oxalates or direct synthesis of the oxides or from the reaction of nitrates. The best known reaction follows from the decomposition of barium carbonate in the presence of Y_2O_3 and CuO [8,9]. We have also proposed the reaction of Y_2O_3 and CuO with barium peroxide [10,11] that appears the proper reaction for the synthesis of the $YBa_2Cu_3O_{7-x}$ phase.

We have also shown that it is possible to drive the oxygen content in the superconducting phase with simple vacuum heat treatment, to reach the critical oxygen concentration for maximum superconducting volume fraction at 77 K [12].

In this paper we refer results obtained during heat capacity measurements of samples of $YBa_2Cu_3O_{6.90\pm0.05}$.

EXPERIMENTAL

The preparation and characterization of the samples used in the calorimetric measurements have been described in detail elsewhere [11,13]. Briefly, a 30 g sample of $YBa_2Cu_3O_{7-x}$ was prepared using stoichiometric amounts of Y_2O_3 (4N - Atlantic Equipment Engineers), CuO (2N - Merck) and BaO_2 (1N5 - Merck) powders. The powders, well dried and thoroughly mixed, were heated to 1220 K in air at about 5 K min^{-1} in a pure alumina crucible for six hours, then slowly cooled to room temperature.

The material, a black sintered cylinder of the superconducting compound, was shown to be monophasic by powder X-ray diffraction with an orthorhombic cell constant of a=3.820(1) Å, b=3.890(1) Å, c=11.667(3) Å. This is in good agreement with the previous single crystal results [14]. Superconducting properties were checked *via* resistivity and magnetic susceptibility measurements [13] (Fig. 1).

A part of the sample was milled and sintered again to increase the density to value as high as 90% of the theoretical crystallographic density: in this case, too, a microprobe analysis confirmed that the sample was substantially monophasic [11].

The samples for the heat capacity measurements were prepared from the sintered product by cutting pellets of 13 mm diameter weighing about 2.5 g, then annealed in vacuum to obtain the maximum superconducting volume fraction at 77 K [12].

The calorimetric measurements were performed in a computer controlled continuous heating adiabatic calorimeter made by one of us [15].

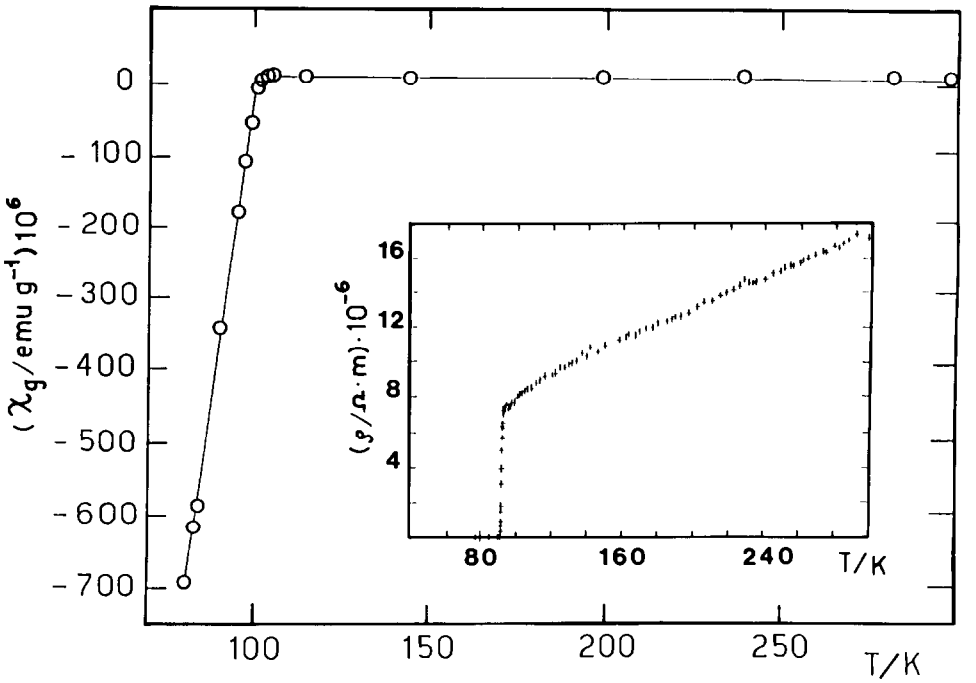

Fig. 1. Thermal behaviour of the magnetic susceptibility and electrical resistivity (inset) for the $YBa_2Cu_3O_{7-x}$ orthorhombic phase.

RESULTS AND DISCUSSION

Heat capacities data from 80 to 115 K are reported in Figs. 2 and 3. Assuming the relationship $\Delta C_p/T_c=1.43\gamma$, we can estimate the electronic specific heat coefficient from the specific heat jump at T_c: $\gamma=(2\div3)\times10^{-2}$ J mol^{-1} K^{-2} (±50% at least).

It is evident from the two figures that the estimation can be heavily affected from the smearing of the jump. Moreover, it is well known that in strong coupling the value of the constant can increase up to 2.5 and more whereas anisotropy may decrease it.

The low temperature electronic specific heat γ can also be cast in a parameter-independent form by the Bardeen, Cooper and Schrieffer's theory (hereafter symbols used as defined in Ashcroft and Mermin [16])

$$C_s/\gamma T_c = 1.34\,(\Delta(0)/T)^{3/2}\,e^{-\Delta(0)/T} \qquad (1)$$

where $\Delta(0)$ is the energy gap.

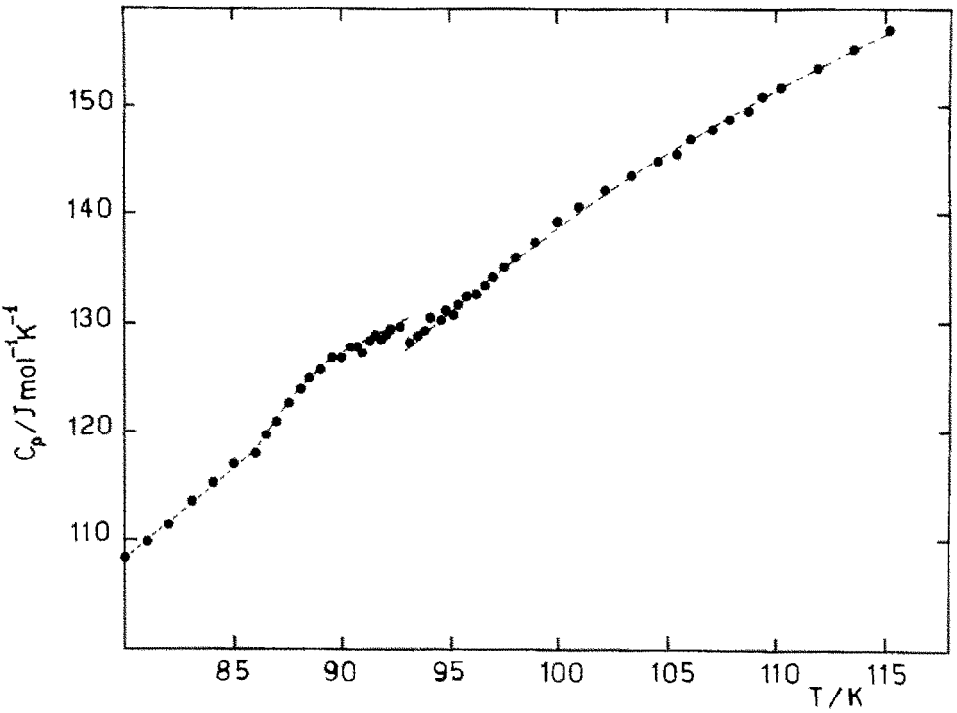

Fig. 2. Molar heat capacity of the $YBa_2Cu_3O_{6.90}$ compound versus absolute temperature.

In spite of numerous attempts made to determine $\Delta(0)$ for the new ceramics by different measurements, the results have been generally unsatisfactory [17]. However, if the value $2\Delta(0)/k_BT_c=5.5$, derived from inelastic relaxation measurements [18] is used in the formula, we obtain a γ value of about $5x10^{-2}$ $J\,mol^{-1}\,K^{-2}$ in agreement with the calorimetric results.

From the thermodynamic point of view, the jump of the specific heat C_s-C_n (respectively the heat capacity in the superconducting and in the normal state) of first-kind superconductor can be correlated with the dependence of the critical field H_c from the temperature by Rutgers' relation

$$C_s - C_n = \mu_o V_m T_c / 4\pi (\partial H_c/\partial T)_P^2 \qquad (2)$$

but if this formula is applied to our results in the range of magnetic fields where the behaviour of the superconductors is perfect (i.e. as far as $H<H_{c_1}$) with the molar volume $V_m=1.04x10^{-4}$ $m^3\,mol^{-1}$ and $(\partial H_{c_1}/\partial T)_P=-6x10^2$ $A\,m^{-1}\,K^{-1}$ [5], ΔC_p is a hundred times too big, whereas if the value $(\partial H_{c_2}/\partial T)_P = -6x10^5 A\,m^{-1}$

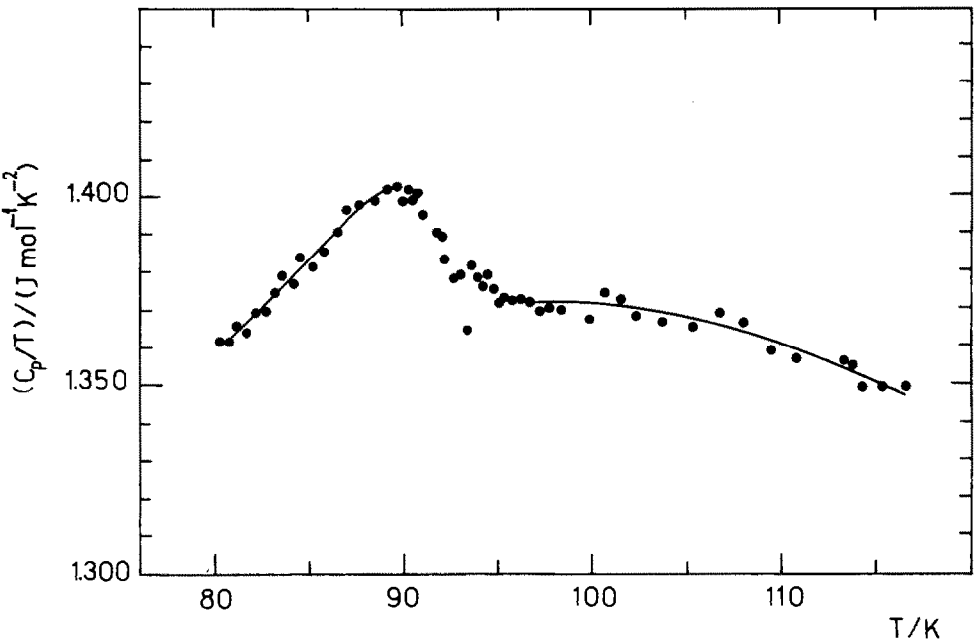

Fig. 3. Thermal behaviour of the C_p/T ratio for the $YBa_2Cu_3O_{6.90}$ compound.

K^{-1} is used, ΔC_p is too small by a factor of 10^4.

These results confirm the second-kind behaviour of this superconductor. This is reasonable considering that the molar volume of the superconducting phase varies very much with the magnetic field, passing from $V_m=1.04\times10^{-4}$ $m^3\ mol^{-1}$ for $H<H_{c_1}$ to $V_m=0$ for $H>H_{c_2}$.

Heat capacity measurements, extended to 185 K have confirmed the existence of the thermal effect at about 167 K already observed by inelastic relaxation measurements [18] on $YBa_2Cu_3O_{7-x}$ prepared by the $BaCO_3$ technique. Work is in progress to ascertain the exact nature of this effect.

ACKNOWLEDGEMENTS

The suggestions and helpful discussions of prof. Aldo Iandelli are gratefully acknowledged.

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