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COMPARATIVE STUDY ON THE HEAT CAPACITY OF $ABa_2Cu_3O_{7-x}$ HIGH T_c SUPERCONDUCTING COMPOUNDS (A = Y, Eu, Ho).

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ABSTRACT

We report heat capacity results obtained on single phase polycrystalline samples of high T_c perovskite type superconductors $YBa_2Cu_3O_{7-x}$, $EuBa_2Cu_3O_{7-x}$, $HoBa_2Cu_3O_{7-x}$. The samples were obtained from the sintered product of well reacted A_2O_3, BaO_2 and CuO powders. The calorimetric measurements were performed in a computer controlled continuous heating adiabatic calorimeter in the temperature range 77 - 300 K.

The work is aimed to compare the thermal behaviour of compounds $ABa_2Cu_3O_{7-x}$ in which elements with different internal magnetic field are present. Particularly a study at temperature above the superconducting transitions was compared with others, to investigate by calorimetric measurements thermal effects already observed in YBCO system by anelastic relaxation measurements at various temperatures.

INTRODUCTION

After the discovery of the lanthanum based high T_c superconductors [1], rapidly followed by the higher T_c based superconductors, a growing effort of research was made after recognition of the close similarity of **these structures** to the simple ABO_3 perovskite structure (Ba(Pb,Bi)O_3 superconductor).

In the ABO_3 structure the stability of the crystal is mainly governed by the size factor of the costituent ions A and B. This suggested substitution of Y or Ba by other elments of similar ionic dimensions (for example the lanthanide elements or thallium)

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in $YBa_2Cu_3O_{7-x}$. The research led to the discovery of the other rare-earth based analogues of $YBa_2Cu_3O_{7-x}$ [2,3].

Although recently [4,5] **two more papers appearred on the thermal** characterization of the $YBa_2Cu_3O_{7-x}$ compounds, up to date the thermal properties of the rare-earth based superconductors $REBa_2Cu_3O_{7-x}$ have been comparatively not so much studied even if they can give important information on superconducting transitions from the theoretical point of view [6,7,8,9].

Moreover, some questions about $YBa_2Cu_3O_{7-x}$ remain still open. For example, how can the other thermal effects present in the heat capacity be connected to the superconducting characteristics and whether a first order phase transition is superimposed in the specific heat jump at T_c, as observed by Butera [5].

In this paper we report the heat capacity data of $YBa_2Cu_3O_{7-x}$, $EuBa_2Cu_3O_{7-x}$ and $HoBa_2Cu_3O_{7-x}$.

EXPERIMENTAL

We prepared the $ABa_2Cu_3O_{7-x}$ compounds by a solid state reaction [10] which was based on the thermal decomposition of BaO_2 instead of $BaCO_3$. Details were reported elsewhere [11].

Briefly, well dried stoichiometric amounts of A_2O_3, BaO_2 and CuO powders were mixed thoroughly in a rotating mixer, then were reacted in air at about 1220 K for 8 hours (heating rate 5÷10 K/min) and slowly cooled to room temperature.

The resulting product was characterized, as usual in our laboratory [12], structurally and magnetically, then it was powdered, pressed in cylindrical shape and sintered generally in flowing oxygen for 12 hours at 1220 K, 1210 K and 1250 K for $HoBa_2Cu_3O_{7-x}$, $EuBa_2Cu_3O_{7-x}$ and $YBa_2Cu_3O_{7-x}$ compounds, respectively. We have found that these temperatures give the best compromise between sintering conditions and diamagnetic characteristics at 90 K.

The sintered samples were again magnetically checked and X-ray and microprobe analysed confirming that they were single phase superconducting above 90 K.

The sample for the heat capacity measurements were obtained from the sintered product cutting pellets of 13 mm diameter weighing 2÷3 g.

The calorimetric measurements were performed in a computer controlled continuous heating adiabatic calorimeter [13].

For the purpose of comparing heat capacity of YBCO prepared via different sintering conditions we have prepared two single phase orthorhombic samples sintered in oxygen and in air. The best sintering condition for YBCO are reported elsewhere [11].

RESULTS AND DISCUSSION

In figure 1 and 2 C_p/T data for HoBCO and EBCO samples respectively, are presented in the 80÷110 K temperature range, showing the heat capacity jump at 91.5 K.

In figure 3 and 4 the heat capacity near the critical temperature of two YBCO samples, sintered in air and in oxygen respectively, are reported.

We notice that the critical temperature (91.5 K) is unaffected by the sintering treatment but the sharpness of the transition is improved by high temperature sintering in O_2. These results are in agreement with the data of Junod et al. [4] who also analysed different samples prepared with different reaction

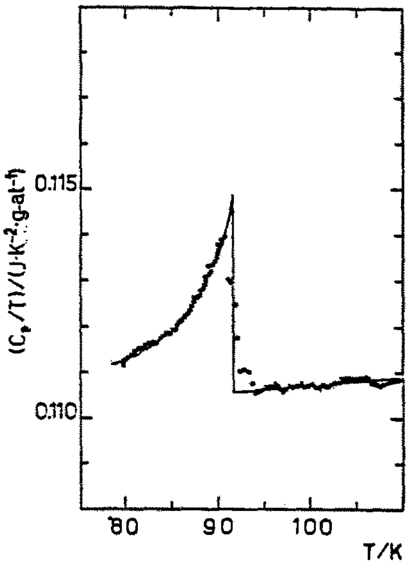

Fig. 1. C_p/T thermal behaviour of $HoBa_2Cu_3O_{7-x}$ near T_c.

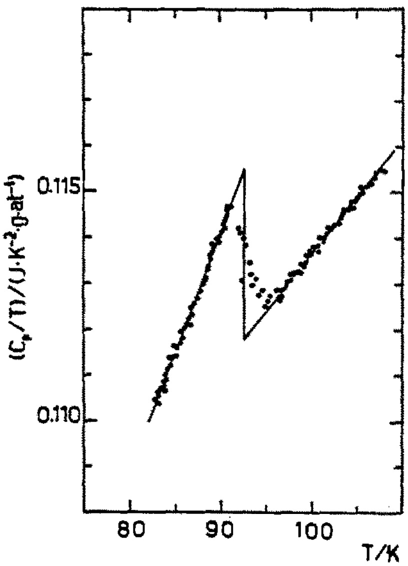

Fig. 2. C_p/T thermal behaviour of $EuBa_2Cu_3O_{7-x}$ near T_c.

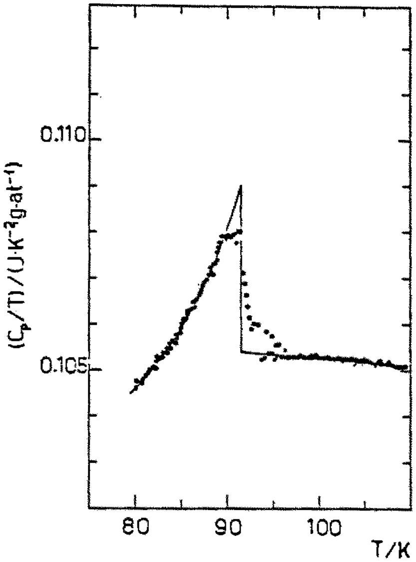

Fig. 3. C_p/T thermal behaviour of $YBa_2Cu_3O_{7-x}$ near T_c (sintered in air).

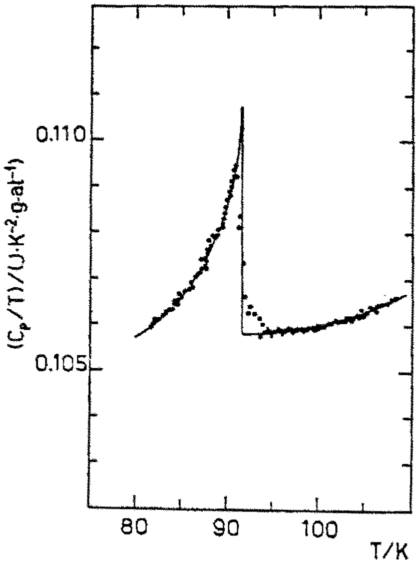

Fig. 4. C_p/T thermal behaviour of $YBa_2Cu_3O_{7-x}$ near T_c (sintered in oxygen).

routes and observed the same shape of the heat capacity jump at T_c.

Notwithstanding the smearing of the jump, the extrapolated value of the jump is only partially affected by it, even if it is difficult to determine the functional dependence of the jump itself. No volume change was observed by Bayot et al. [14] and David et al. [15] in their thermal expansion measurements at T_c.

Thermal expansion measurements and the jump of heat capacity can be connected together by the Ehrenfest's relation

$$dT_c/dP = V_m \cdot \Delta\alpha \cdot T_c/\Delta C_p$$

from which we can deduce the pressure dependence of the critical temperature ($dT_c/dP = 4\ 10^{-2}$ K $Kbar^{-1}$) taking the value of Bayot et al. $\Delta\alpha = 2.4\ 10^{-7}$ [14].

Moreover from the heat capacity jump and making use of the Rutgers's relation we can determine the thermodynamic critical field

$$(\partial H_c/\partial T)_p^2 = (4\pi/V_m\mu_o)\ (\Delta C_p/T_c)$$

from which we obtain $(\partial H_c/\partial T)$ that is practically the same for YBCO and HoBCO (- 1000 Oe K^{-1}), but a bit less for EBCO (- 900 Oe K^{-1}).

We have not observed in any one of our samples the lambda transition at 86.6 K reported by Butera [15]; on the contrary we found thermal effects at different temperatures also reported by others [9,16].

One of such effects at 165 K is shown in figure 5. At the present we are not able to explain the origin of these effects nor whether they are connected in some way with the superconductivity. However we found that they were not reproducible.

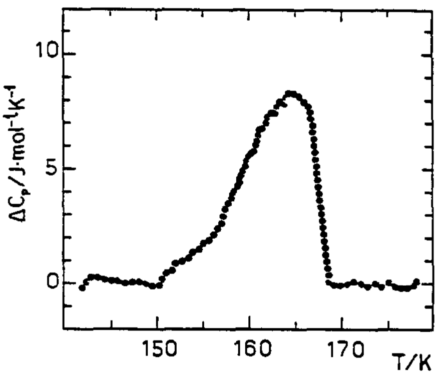

Fig. 5. Analysis of the anomaly at 165 K subtracting from the data a quadratic background fitted to points taken in the temperature range 140÷180 K for the YBCO sample sintered in air.

We have not detected, in zero magnetic field, latent heat at the critical temperature (91.5 K) that was observed by Butera [15]: from his data we should conclude that a first order transition (with a volume change) is superimposed at T_c. However since he worked with a 30 g sample while we used a 2-3 g sample it is possible that our sensitivity was not sufficient.

On the other hand a first order superconducting-normal state transition is expected if the sample is immersed in a magnetic field: the relative thermal effect can be calculated from the relation

$$q = -(\mu_0/4\pi)TH_cV_s(dH_c/dT)$$

Work is in progress to ascertain the amount of the thermal effect in low magnetic fields.

REFERENCES

1 J.G. Bednorz and K.A. Müller, Z.Phys. B, 64 (1986) 189.

2 K. Kadowaki, Y.H. Huang, M. van Sprang and A.A. Menovsky, Physica B, 145 (1987) 1.

3 F. Izumi, H. Asano, T. Ishigoki, E. Tokoyama Huromaki, Y. Ukida, N. Watanabe and T. Nishikawa, Jpn.J. Appl. Phys., 26 (1987) 87.

4 A. Junod, A. Bezinge and J. Muller, Physica C, 152 (1988) 50.

5 R.A. Butera, Phys. Rev. B, 37 (1988) 5909.

6 H. Takagi, S. Huchida, K. Kitazawa, K. Kishio, K. Fueki and S. Tanaka, Proc. Eur. Workshop on High T_c Superconductors and Potential Applications, Genova (Italy), 1-3 July 1987, p. 241.

7 M.V. Nevitt, G.W. Crabtree and T.E. Klippert, Phys. Rev. B, 36 (1987) 2398.

8 S.E. Inderhees, M.B. Salamon, T.A. Friedmann and D.M. Ginsberg, Phys. Rev. B, 36 (1987) 2401.

9 G. Cannelli, R. Cantelli, F. Cordero, G.A. Costa, M. Ferretti and G.L. Olcese, Phys. Rev. B, 36 (1987) 8907.

10 G.A. Costa, M. Ferretti, G.L. Olcese, M.R. Cimberle, C. Ferdeghini, G.L. Nicchiotti, A.S. Siri and C. Rizzuto, J. Crystal Growth 85 (1987) 623.

11 G.A. Costa, M. Ferretti and G.L. Olcese, J. Crystal Growth (in press).

12 G.A. Costa, M. Ferretti, M.L. Fornasini and G.L. Olcese, Solid State Commun., 65 (1988) 469.

13 G.A. Costa, J. Thermal Analysis, 30 (1985) 1293.

14 V. Bayot, C. Dewitte, J.P. Erauw, X. Gouze, M. Lambricht and J.P. Micheraud, Solid State Commun., 64 (1987) 327.

15 W.I.F. David, P.P. Edwards, M.R. Harrison, R.Jones and C.C. Wilson, Nature, 331 (1988) 245.

16 T. Laegreid, K. Fossheim, E. Sandvold and S. Julsrud, Nature, 330 (1987) 637.