

Anomalous thermal properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in the 200–250 K range

R.A. VARGAS, W.R. AGUIRRE AND J.E. DIOSA

*Departamento de Física, Universidad del Valle
Apartado aéreo 25360, Cali, Colombia*

Recibido el 4 de abril de 1995; aceptado el 2 de febrero de 1996

ABSTRACT. Heat capacity data at normal pressure, $C_P(T)$, measured by a high-resolution a.c. calorimetric method on single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, provide evidence for a phase transition at $T_t = 220$ K in all the 90-K superconducting phases ($\delta \leq 0.2$). The amplitude of the heat capacity peak is relatively small, less than 3% of the total lattice contribution, and no latent heat was detected through the transition. The persistence of the $C_P(T)$ anomaly near T_t in samples that differ in oxygen-deficit δ indicates that the ordering process associated with this transition takes place in the CuO_2 planes.

RESUMEN. Datos de capacidad calorífica a presión normal, $C_P(T)$, medidos por un método de calorimetría a.c. de alta resolución en muestras monocristalinas de $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, suministran evidencia de una transición de fase en $T_t = 220$ K para todas las fases superconductoras a 90 K. La amplitud del pico de la capacidad calorífica es relativamente pequeña, menos que el 3% de la contribución total de la red cristalina, y no se detectó calor latente a través de la transición. La persistencia de la anomalía en $C_P(T)$ cerca de T_t en muestras que difieren en la deficiencia δ de oxígeno, indican que los procesos de ordenamiento asociados con esta transición tienen lugar en los planos de CuO_2 .

PACS: 74.30.-e; 74.40.+k; 74.70.-b

1. INTRODUCTION

In high-temperature oxide superconductors the role of defects on thermodynamic instabilities have been acknowledged to be very important [1]. All copper oxides having the perovskite-type structure are characterized by the presence of one or more CuO_2 planes whose $(\text{CuO}_2)^{2-}$ oxidation states of an antiferromagnetic and semiconductor parent compound are either oxidized or reduced by a doping mechanism to set in a metallic state and superconductivity. For the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($0 \leq \delta \leq 1$) (YBCO) system, the defects are oxygen atoms that occupy, in a random or ordered configuration, a fraction of $x/2$ ($x = 1 - \delta$) of available sites in the copper basal layer. In the YBCO tetragonal phase, the oxygen sites are randomly populated or completely vacant, with identical lattice constants in the a and b directions, and the material is nonsuperconducting. In the ordered state, depending on the oxygen content x , at least two orthorhombic, superconducting structures are known to exist [2, 3]: a single-cell phase OI (near $x = 1$) in which all the sites of the basal layer parallel to the b axis are occupied, and a double-cell phase OII (near

$x = 0.5$) with every second chain removed. In these orthorhombic phases the basal layer has undergone a distortion such that $a < b$.

There have been a number of experimental reports on phase behavior of YBCO that emphasize the effect of defect ordering and the corresponding structural distortion in different phases [4–10]. Furthermore, experimental observations (measurements of elasticity, heat capacity, neutron and X-ray diffraction, Raman, thermal expansion, piezoresistance, photoconductivity, thermoelectric power, etc.) have pointed out the existence of anomalies in many physical properties of YBCO in the vicinity of 220 K [11]. Attempts have been made to correlate these anomalies with some kind of structural or magnetic ordering [12, 13].

In this paper we report results from a sequence of calorimetric experiments in which we examined the phase behavior of superconducting single-crystal samples of the YBCO system within the 77–300 K temperature range, using a high-resolution a.c. calorimetric method. Our results show anomalous thermal response of the samples near 220 K that confirm previous experimental observations. A remarkable result is that the variations of the oxygen deficiency δ ($0 \leq \delta \leq 0.2$) hardly affects this behavior. Previously, we reported [14, 15] similar observations on polycrystalline samples of the 123 copper oxides in the same temperature range and in which a hysteretic-like behavior of the a.c. calorimetric traces were observed.

2. EXPERIMENTAL

We performed the heat capacity measurements on single crystals of YBCO which were grown by a flux technique similar to that described in Ref. [16]. The crystals were characterized by X-ray analysis, resistivity and Meissner effect experiments, showing they were superconducting single phase 90-K bulk superconductors. Moreover, the crystals were very shiny and showed very narrow transition at T_c (less than 0.5 K). The crystals were subject to thermal treatments at high temperature (≈ 700 K) in the appropriate oxygen partial pressure to slightly vary the oxygen content δ . The actual oxygen content of the crystals was estimated from a comparison with the transition temperature T_c [17], which was measured immediately after the thermal treatment.

The heat capacity measurements were performed on the YBCO samples by using an a.c. calorimeter, described previously [18]. The samples, typically of several square millimeters in area and about 0.15 mm thickness, were suspended from the heat reservoir by a pair of flattened type-K thermocouple wires, 25 μm in diameter, attached to the rear face of the sample with a minute amount of silicone rubber or graphite, depending on the operating temperature. The front face of the sample was periodically heated by a square power input of frequency $\omega/2\pi = 1.5$ Hz, from a beam of light source chopped at this frequency. The amplitude, $|T_{\text{ac}}|$, of the temperature oscillations (at frequency 1.5 Hz) induced at the rear face of the sample, was detected with the thermocouple and measured with a lock-in amplifier. Under desirable operating conditions for a.c. calorimetry [19], $|T_{\text{ac}}|$ is related to the heat capacity of the sample, $C_P(T)$, by $|T_{\text{ac}}| = P_1\omega^{-1}C_P^{-1}$, where P_1 is the effective input power to the front face of the sample. However, the a.c. method does not give the absolute value of the heat capacity when the heat flux to the sample is provided by means of mechanically chopped light, because the effective input power is unknown.

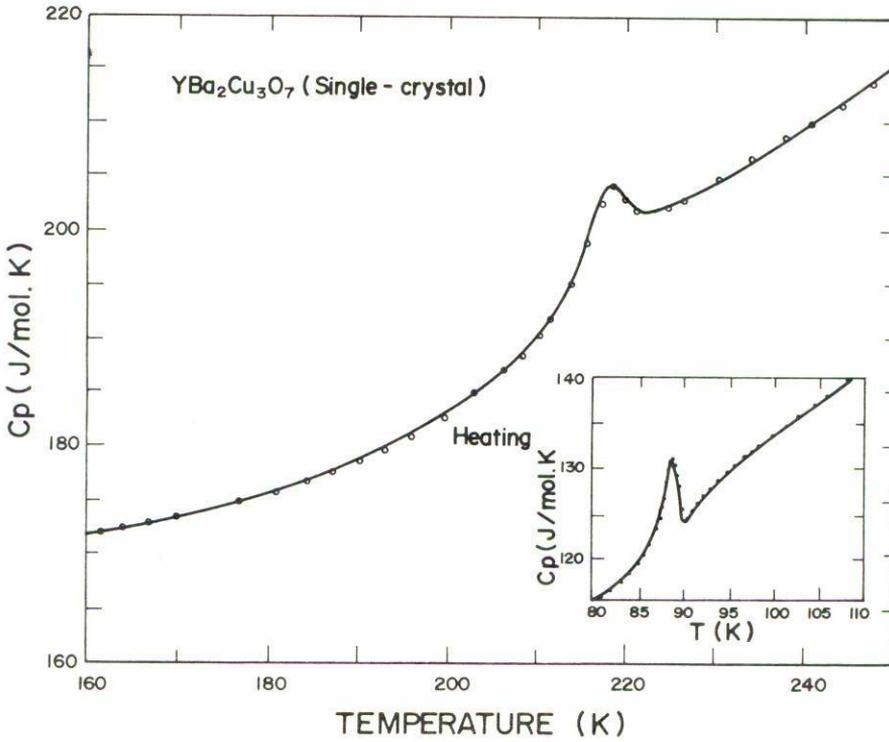


FIGURE 1. Temperature dependence of the heat capacity at normal pressure, $C_P(T)$, for a single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the 160–250 K temperature range. The inset shows the heat capacity data near the 90 K superconducting transition, indicating the high quality of the crystal. The solid line is drawn as a guide to the eye.

The calibration constant of the apparatus, P_1/ω was calculated by adjusting the data to that of Ref. [20] near 90 K.

3. RESULTS AND DISCUSSION

The a.c. calorimetric data of all single-crystal samples, tested in the temperature range between T_c and 300 K, consistently show anomalous features in the 200–250 K region. A marked $C_P(T)$ anomaly is observed in the vicinity of $T_t = 220$ K, with no latent heat suggesting the existence of a continuous phase transition at this temperature. The sharpness and the amplitude of the peak are retraced on subsequent temperature scans. In a magnified scale, Fig. 1 shows a typical $C_P(T)$ plot in this region for a single crystal YBCO. The inset shows the data for the same crystal in the region near $T_c = 90$ K, that reveals the high quality of the crystal for the magnitude of the heat capacity jump and the sharpness of the superconducting transition region (less than 0.5 K). For all samples, independent of their thermal history and oxygen deficiency δ ($0 \leq \delta \leq 0.2$), the 200–250 K temperature region of the $C_P(T)$ curves were essentially of the same shape, showing a small peak near 220 K.

The resolvable $C_P(T)$ anomaly in the 200–250 K temperature region reflects an intrinsic property of the YBCO system, since it is not shown any systematic dependence of the anomaly on the sample quality or thermal history as correlated to the sharpness of the superconducting transition at T_c [21, 22]. These calorimetric results can be correlated with anomalies observed by other experimental techniques and confirm the existence of a phase transition of the YBCO compounds around 220 K, with a very small change of enthalpy (less than 3%) compared with the total contribution of the lattice and other degrees of freedom of the sample. A remarkable result is that the variations of the oxygen deficiency δ hardly affect the anomalous thermal behavior of YBCO in the 200–250 K temperature range, so this behavior cannot be connected with oxygen ordering in the basal planes or conducting carrier concentrations and their mobilities, since they depend on the oxygen content x . On the other hand, the sheets of stoichiometry CuO_2 containing square planar copper are almost independent of the oxygen deficit δ , therefore, the persistence of the anomaly for different value of δ would imply that the structural instabilities associated with the 220 K phase transition is taken place in the CuO_2 planes, at least on a local length scale.

In summary, a high-resolution periodic thermal analysis serves as sensitive probe of thermodynamic instabilities in good-quality single-crystal samples of YBCO. The measurements yield complementary information regarding previous experimental observations that have pointed out the existence of anomalies in other physical properties of YBCO in the vicinity of 220 K [11].

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Colombian Research Agency-COLCIENCIAS and the International Program in The Physical Science, IPPS, of Uppsala University, Sweden. They thank Dr. P. Prieto, in the Physics Department of the University of Valle, Cali, for supplying them with high quality YBCO single crystals.

REFERENCES

1. K.B. Blagoev and L.T. Wille, *Phys. Rev.* **B 48** (1993) 6588, and references therein.
2. D. de Fontaine, G. Ceder, M. Asta, *Nature* **343** (1990) 544; *J. Less-Common Metals* **164-165** (1990) 108.
3. M. Goldman, C.P. Burmester, L.T. Wille, R. Gronsky, *Phys. Rev.* **B 52** (1995) 1331.
4. R. Beyers, T.T. Ahn, G. Gorman, V.Y. Lee, S.S.P. Parkin, M.L. Ramírez, K.P. Roche, J.E. Vázquez, T.M. Gür and R.A. Huggins, *Nature* **340** (London) (1989) 619.
5. J.D. Jorgensen, S. Pei, P. Lightfoot, A.P. Paulikas and B.W. Veal, *Physica C* **167** (1990) 571.
6. B.W. Veal, A.P. Paulikas, H. You, H. Shi, Y. Fang, J.W. Downey, *Phys. Rev.* **B 42** (1990) 6305.
7. H. You, J.D. Axe, X.B. Kan, S. Hashimoto, S.C. Moss, J.Z. Liu, G.W. Grabtree, and J.D. Lam, *Phys. Rev.* **B 38** (1988) 9213.
8. A.K. Sood, K. Sankaran, V.S. Sastry, M.P. Janawadkar, C.S. Sundar, J. Janaki, S. Vijayalakshmi, and Y. Hariharan, *Physica C* **156** (1988) 720.

9. C.N.R. Rao, R. Nagarajan, A.K. Ganguli, G.N. Subbanna, and S.V. Bhat, *Phys. Rev. B* **42** (1990) 6765.
10. Z. Hiroi, M. Takano, Y. Bando, T. Takeda, and R. Kanno, *Physica C* **158** (1989) 269.
11. S.L. Bud'ko, H.H. Feng, M.F. Davis, J.C. Wolfe, and P.H. Hor, *Phys. Rev. B* **48** (1993) 16707, and references therein.
12. O. Cabeza, A. Pomar, A. Díaz, C. Torrón, J.A. Veira, J. Maza, and Félix Vidal, *Phys. Rev. B* **47** (1993) 5332 and references therein.
13. Q. Wang, G.A. Saunders, D.P. Almond, M. Cankurtaran, K.C. Goretta, *Phys. Rev. B* **52** (1995) 3711.
14. R.A. Vargas, M. Chacón, J.C. Tróchez and I. Palacios, *Phys. Letters A* **139** (1989) 81.
15. R.A. Vargas and M. Chacón, *Rev. Mex. Fís.* **37** (1991) 303.
16. J.Z. Liu, M.D. Lan, P. Klavins, and R.N. Shelton, *Phys. Lett. A* **144** (1990) 265.
17. R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck Jr, L.W. Rupp Jr, *Physica C* **165** (1990) 419.
18. R.A. Vargas and A.J. Sánchez, *Rev. Mex. Fís.* **31** (1985) 663.
19. P.F. Sullivan, and G. Seidel, *Phys. Rev. B* **173** (1968) 679.
20. O. Beckman, L. Lundgren, P. Nordblad, L. Sandlund, P. Svedlindh, T. Lundström and S. Rundqvist, *Phys. Lett. A* **125** (1987) 425.
21. K. Ghiron, M.B. Salamon, and M.A. Hubbard, *Phys. Rev. B* **48** (1993) 16188.
22. J.W. Loram, K.A. Mirza, J.R. Cooper, and W.Y. Liang, *Phys. Rev. Lett.* **71** (1993) 1740.