Thermoelectric Power Measurements of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ up to $950^\circ \text{C}$ and Their Application to Test the Band Structure near $E_F$

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Four-probe resistivity ($\rho$) and thermoelectric power (TEP) measurements were carried out on samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ up to $950^\circ \text{C}$, in air and in flowing oxygen at 1 bar. Below 700 K the TEP is small and increases rapidly above it, reaching, at 1200 K, $+140 \mu \text{V/K}$ in air and $+120 \mu \text{V/K}$ in oxygen. At the changeover temperature (700 K) the slope of $\log \rho$ vs. $T$ changes abruptly. These results are interpreted in terms of a model of transport of carriers in a narrow band, which is full for $\delta = 1$ and half-filled for $\delta = 0$. Possible origins for such a narrow band are discussed in detail.

KEY WORDS: $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$; resistivity; thermoelectric power.

Recent publications [1-3] have reported a steep increase with temperature of the resistance of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBaCuO) samples on heating above room temperature. The effect can be due to variations in the transport mechanism and/or in the carrier concentration. In a previous publication from our laboratory [1], emphasis was put on the role of the transport mechanism, because of the correlation that was found between the temperature dependences of the resistivity and the thermal expansion measured at high temperatures.

It is by now well known [4] that the oxygen content of the material determines the normal-state conductivity of YBaCuO below room temperature, and its superconducting (SC) transition temperature. We wanted to investigate the dependence of the carrier concentration on the oxygen content of the sample. In this report we address the problem of the carrier
concentration in this material, and its variation with oxygen pressure and temperature up to 950°C.

The carrier concentration in YBaCuO at low temperatures has been estimated by Hall-effect measurements [5]. Such measurements at high temperatures are difficult to perform. Thermoelectric power (TEP), which is easier for measurement at high temperatures, is a very sensitive tool to probe the carriers participating in the transport.

We report here on simultaneous measurements of the resistance and TEP of a ceramic sample of YBaCuO up to 950°C in oxygen at 1 bar pressure and in air. The sample was a bar of 4.0 cm length and 0.75 cm diameter. It was prepared by the standard procedure, and shaped by isostatic pressure. The measurements were carried out after sintering in an oxygen atmosphere. Four-probe resistance measurements were carried out using as probes gold wires implanted in little holes in the sample. The current leads were also used for the TEP measurements; two Chromel-Alumel thermocouples were also implanted into current lead holes. The small TEP of the gold leads was taken into account in the analysis of the results.

The measurements were taken over a long period of time, typically about 2 days for heating from room temperature to 950°C at constant oxygen pressure. Some measurements at constant temperature and pressure were repeated until no significant changes were observed. We assumed then that the material reached equilibrium. To our surprise, even at high temperatures the kinetics were relatively slow. The changeover from pure oxygen at 1 bar pressure to air was done at 950°C. It took several hours to extract oxygen from the sample and to reach equilibrium. Prior to each TEP measurement, the resistance of the sample was measured.

Figure 1a represents the temperature (T) dependence of the absolute TEP (S) of a sample of YBaCuO in air and in oxygen at 1 bar. In Fig. 1b we have plotted the resistivity ρ on a semilog scale. The resistivity results agree remarkably well with the corresponding results reported previously [1]. This confirms the reproducibility of our samples.

Inspection of the TEP results, at fixed oxygen pressure, shows that while S remains very low between room temperature and 700 K, it increases steeply with temperature above 700 K up to about +120 μV/K in oxygen and to +140 μV/K in air at 1200 K. The turning temperature point, 700 K, is also the temperature where the slope of log ρ vs. T, in Fig. 1b, changes considerably.

The effect of the orthorhombic to tetragonal transition, at about [6] 950 K, on our measured transport properties seems to be minor (a small change in the slope of log ρ vs. T in Fig. 1b is observed around 950 K). Neutron diffraction measurements [6] indicate that at 700 K the crystal structure remains orthorhombic. However, from thermogravimetric measurements [7] it was shown that at constant oxygen pressure $P_{O_2}$, the