

# “Oxygen-pump” measurements of the electron state density at the Fermi level in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Yu. M. Gerbshtein, F. A. Chudnovskii, V. N. Andreev, A. K. Kuz'min, N. E. Timoshchenko, and S. L. Shokhor

*A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad*

(Submitted 19 April 1988)

Pis'ma Zh. Eksp. Teor. Fiz. **47**, No. 12, 625–627 (25 June 1988)

A peak in the electron state density associated with a structural phase transition has been observed near the Fermi level in a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  high-temperature superconductor.

The oxide superconductors of the composition  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  are characterized by a high lattice mobility of oxygen, which accounts for a rapid establishment of an equilibrium at temperatures above 400–500 °C (Refs. 1 and 2). The equilibrium equalizes the chemical potentials of the electrons in the oxide and the gas. There is accordingly a simple relationship between the chemical potential of the electrons in the oxide,  $\mu_e$ , and the oxygen pressure in the gas phase,  $P$  (Ref. 3, for example):

$$\mu_e = \frac{1}{4}\mu_{\text{O}_2} = -\frac{kT}{4}\ln P + C. \quad (1)$$

Here  $\mu_{\text{O}_2}$  is the chemical potential of the oxygen molecule, 4 is the number of free, chemically active electron states in the  $\text{O}_2$  molecule, and  $C$  is a constant.

According to (1), by varying the equilibrium oxygen pressure from  $P_i$  to  $P_{i+1}$  we vary the Fermi energy by an amount

$$\Delta E_F^{(i)} = \Delta\mu_e = -\frac{kT}{4}\ln\frac{P_{i+1}}{P_i}. \quad (2)$$

Expression (2), like all the thermodynamic equalities, is exact. As the equilibrium pressure is varied in the order  $P_1, P_2, \dots, P_i, \dots$  we find corresponding changes in the Fermi energy:

$$E_F^{(i)} = E_F^{(0)} + \sum_{i=1}^i \Delta E_F^{(i)},$$

where  $E_F^{(0)}$  is a constant. In order to bring the sample to equilibrium with gaseous oxygen at a pressure  $P_i$ , we baked it at 500°C for 2.5 h. In order to preserve the value of  $E_F^{(i)}$  which was reached, we quenched the sample by dropping it into a metal chamber.

Guided by relation (2), we changed the Fermi energy of a sample by  $\Delta E_F^{(i)}$ . We then determined the number of oxygen atoms required to make this change,  $\Delta x_i = x_i - x_{i+1}$ , experimentally. We found the electron state density at the Fermi level from

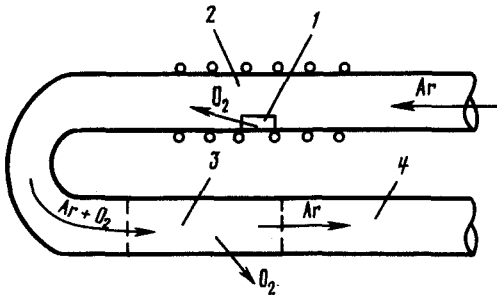


FIG. 1. Apparatus used to determine the amount of oxygen evolved from a sample. 1—Sample; 2— heating chamber; 3,4—superionic oxygen pumps.

$$\tilde{n}(E_F^{(i)}) = \frac{2\Delta x_i}{\Delta E_F^{(i)} \tilde{v}} \quad (3)$$

where  $2\Delta x_i$  is the number of electron states which are contributed by  $\Delta x_i$  oxygen atoms—or the number of holes which float up to the Fermi surface in the process—and  $\tilde{v} = \tilde{m}/D$  is the volume of the sample, calculated from the mass and the density.

The values of  $x_i$  and  $x_{i+1}$  were found with the help of the apparatus shown in Fig. 1. The sample 1, saturated with oxygen at (for example)  $P_i$ , is placed in a quartz heating chamber 2. Two “oxygen pumps” 3 and 4 are connected in succession to the output of this chamber. An “oxygen pump” is a tube of stabilized zirconium dioxide with inner and outer platinum electrodes, to which a potential difference of 0.4 V is applied in this case (the positive terminal was applied to the outer electrode). The oxygen evolved during the heating of the sample was carried off by an argon flow into oxygen pump 3, which was heated to 700°C. At this temperature, the oxygen pump becomes an ion guide and effectively pumps oxygen out of the inner volume. We measured  $J_i(\tilde{t})$ , the ion current through the ion pump, as a function of the time. The area under this curve, expressed in coulombs divided by the charge of the  $O^{2-}$  ion, gives us  $x_i$ : the number of oxygen atoms evolved from the samples. We used oxygen pump 4 to monitor the thoroughness of the pumping achieved in oxygen pump 3.

We studied a polycrystalline sample with microcrystals  $\lesssim 10 \mu\text{m}$  in size. After saturation of the sample with oxygen at a pressure  $P_1 = 12.8 \text{ atm}$  we recorded the  $J_1(t)$  curve shown as curve 1 in Fig. 2. An integration of this curve yields  $x_1$

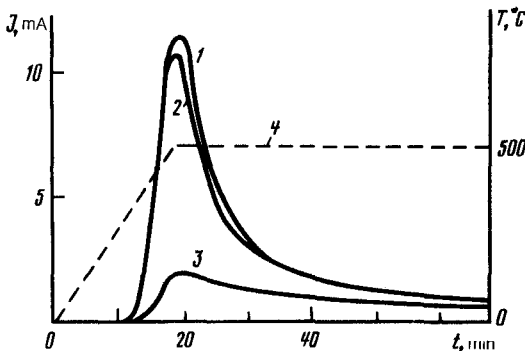


FIG. 2. Time evolution of the current of  $O^{2-}$  ions through the oxygen pump resulting from the thermally stimulated evolution of oxygen from a sample which had been saturated beforehand by oxygen at one of several pressures: 1—12.8 atm; 2—6.4 atm; 3—0.0125 atm. Line 4 shows the time dependence of the sample temperature.

$= 4.04 \times 10^{19}$ . This amount of evolved oxygen changed the composition of the sample by 0.52 of an oxygen atom per unit cell. Curve 2 shows the  $J_2(\bar{i})$  dependence found for the same sample after a subsequent baking in oxygen at  $P_2 = 6.4$  atm. In this case, the number of oxygen atoms evolved from the sample was  $x_2 = 3.89 \times 10^{19}$ . Substituting  $\Delta x_1 = x_1 = x_2 = 0.15 \times 10^{19}$ ,  $\bar{m} = 85.6$  mg,  $D = 6.19$  g/cm<sup>3</sup>, and also the value  $\Delta E_F^{(1)} = 11.7$  mV found from (2) into (3), we find the value  $\bar{n}(E_F^{(1)}) = 1.8 \times 10^{22}$  cm<sup>-3</sup> · eV<sup>-1</sup> for the electron state density. We carried out eleven such measurements, increasing  $E_F$  by 11.7 mV in each case. Curve 3 shows the last dependence of this series,  $J_{11}(t)$ , which was recorded after the sample was baked in oxygen at  $P_{11} = 0.0125$  atm.

In this manner we found several values of the state density,  $\bar{n}(E_F^{(1)})$ , ... ..,  $\bar{n}(E_F^{(11)})$ , which are shown by the points in Fig. 3 (curve 1). We see that this function increases sharply toward the point  $E_F = 100$  mV ( $E_F^{(1)}$  is adopted as the origin for the scale). According to (3), a sharp growth of  $\bar{n}(E_F)$  implies a sharp evolution of oxygen atoms from the sample, in a number which can be determined from the difference between the areas under curves 1 and 3 in Fig. 2. This number turns out to be  $2.3 \times 10^{21}$  cm<sup>-3</sup> or 0.4 of an atom per unit cell. According to Ref. 4, this change in the chemical composition is associated with a structural phase transition from an orthorhombic-1 phase to an orthorhombic-2 phase.

Curve 2 in Fig. 3 shows the superconducting transition temperature as a function of the Fermi energy,  $T_c(E_F^{(i)})$ . The values of  $T_c$  were found from measurements of the magnetic susceptibility  $\chi(T)$  and correspond to the level of 50% of the maximum value of  $\chi(T)$ . There is an obvious correlation between curves 1 and 2, which confirms the transition of the sample to the orthorhombic-2 "50%" phase.

We would like to call attention to the interrelationship between the functions  $\bar{n}(E_F^{(i)})$  and  $\bar{n}(E)_{E_F = \text{const}}$  which stems from the renormalization of the electron spec-

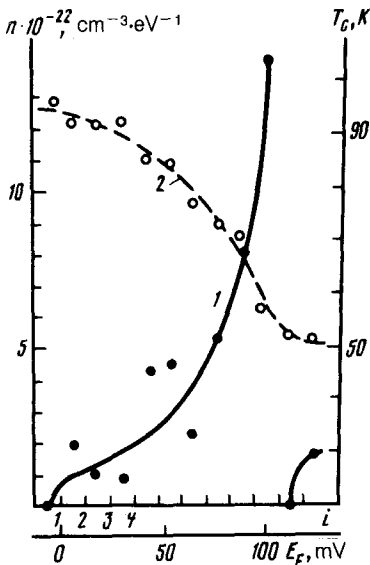


FIG. 3. The electron state density (1) and the superconducting transition temperature (2) as functions of the Fermi energy.

trum as a result of the electron-phonon interaction. In other words, electrons which are excited to energies corresponding to the  $\tilde{n}(E_F)$  peak “pull” the lattice into the orthorhombic-2 phase, exciting corresponding vibrational modes. This circumstance may prove to be of more than trivial importance to the formation of the high-temperature superconductivity of oxides.

We wish to thank A. G. Aronov, M. S. Bresler, and B. P. Zakharchenya for interest in this study and for useful discussions.

<sup>1</sup>P. Monod, M. Ribault, F. D'Yvoire *et al.*, *J. Phys. (Paris)* **48**, 1369 (1987).

<sup>2</sup>K. Fueki, K. Kitazawa, K. Kishio *et al.*, in: *ACS Symposium Series 351: Chemistry of High-Temperature Superconductors* (D. L. Nelson, M. S. Wittingham, and T. F. George, editors), Washington, 1987, p. 38.

<sup>3</sup>R. Hartung, *Z. Phys. Chem.* **254**, 393 (1973).

<sup>4</sup>Y. Nakazawa, R. Ishikawa, T. Takabatake *et al.*, *Jpn. J. Appl. Phys.* **26(5)**, L796 (1987), Part 2.

Translated by Dave Parsons