Control of the Fermi level and phase transitions in $YBa_2Cu_3O_{7-\delta}$

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(Submitted 23 January 1990; resubmitted 26 March 1990)
Zh. Eksp. Teor. Fiz. **98**, 1375–1381 (October 1990)

The Fermi level of oxide electrons is uniquely related to the magnitude of the equilibrium value of the oxygen pressure above the specimen. The Fermi level dependences of the electron density of states, lattice constants, superconducting transition temperature and other specimen characteristics have been obtained experimentally. A correlation was found between peaks in the electron density of states, anomalously high values of the deformation potential and structural phase transitions. On the free-energy axis these phase transitions are located very close to the high-temperature superconducting phase, at a distance of several tens of millivolts. It is shown that there is a narrow region in the neighborhood of the structural phase transition with extremal values of the electron and lattice characteristics of the compound. It is just in this region that high-temperature superconductivity appears in $YBa_2Cu_3O_{7-\delta}$.

The influence of structural phase transitions on superconductivity has been studied for a long time; see, for example, Ref. 1. The construction of actual models requires a knowledge of the features of the electron-lattice interaction associated with phase transitions. Control of the Fermi level makes it possible to study various details of the electron-phonon coupling.

The Fermi level of an oxide can be controlled by changing the equilibrium oxygen pressure in the atmosphere above the specimen. When the Fermi level intersects singularities of the electron spectrum, a discontinuous change occurs in the oxygen content in the specimen. This opens up a remarkable possibility of analyzing the fine details of the electron spectrum by the change in specimen weight.

The Fermi level dependences of the following quantities were measured in the present work: specimen mass, electron density of states $\partial N/\partial E_F$, lattice constants, superconducting transition temperature, resistivity and the resistance activation energy. The values of the deformation potential were measured in the superconducting and normal phases. A correlation was found between peaks in the electron density of states and structural phase transitions.

THE EXPERIMENTS

Heating of a $YBa_2Cu_3O_{7-\delta}$ specimen in oxygen at temperatures above 450–500 °C leads relatively rapidly to the establishment of equilibrium, which in the present case implies equality in the chemical potentials of the particles by means of which the specimen exchanges with the gaseous oxygen. Such particles are oxygen molecules, atoms and ions and also, of course, electrons. Thus when equilibrium is attained the chemical potentials of the specimen electrons and the electrons of the gaseous oxygen are also equal:

$$\mu_e^{spec}=\mu_e^{gas}. \tag{1}$$

In the ideal gas approximation the electron chemical potential is determined by the usual formula

$$\mu_e^{gas}=-kT\ln n_e+C, \tag{2}$$

where n_e is the electron density. On the basis of the law of mass action, applied successively for the processes $O_2 \rightleftarrows O+O$ and $O \rightleftarrows O^+ + e$, we can write $n_e \sim P^{1/2}$, where P is the oxygen pressure. The expression

$$\mu_e^{gas}=-{}^1/_4 kT\ln P+C \tag{3}$$

follows from this. A change in oxygen pressure from P_i to P_{i+1} leads to a change in the chemical potential of electrons in the gas by an amount

$$\Delta\mu_e^{gas}=-\frac{kT}{4}\ln\frac{P_{i+1}}{P_i}. \tag{4}$$

[Equation (4) is used to determine partial pressures of oxygen with the help of electrochemical probes.]

It is evident that when equilibrium is reached between specimen and gas, when Eq. (1) is satisfied, the chemical potential of the specimen electrons or the Fermi level changes by the same amount

$$\Delta\mu_e^{spec}=\Delta E_F=-\frac{kT}{4}\ln\frac{P_{i+1}}{P_i}. \tag{5}$$

We consider an example. Suppose the Fermi level is located in some band of allowed states; equilibrium then exists between specimen and gas, i.e., $\mu_e^{gas}=E_F$ (Fig. 1,a). We then bring this system out of equilibrium by sharply increasing the oxygen pressure. This leads to a lowering of μ_e^{gas}, as shown in Fig. 1,b. Relaxation to a new equilibrium state will be associated with the introduction into the specimen of a new supply of oxygen atoms. Each oxygen atom introduces two empty states into the specimen into which electrons are drained from the Fermi surface, thereby reducing its level. This will go on until the Fermi level in the specimen equals the new value of the chemical potential of the electrons in the gas (Fig. 1,c). The possible form of the new band of electron states introduced by oxygen atoms is shown there by the dashed line.

If the oxygen in the specimen is divalent, then the new band will be located below the Fermi level. In that case the number of electron states in the interval ΔE_F is determined by the expression

$$\Delta N=2\Delta x, \tag{6}$$

where Δx is the number of oxygen atoms entering the specimen as a result of the change ΔE_F in the Fermi level.

If the oxygen valency in the specimen is less than two, then part of the band appears above the Fermi level. In that case the number of electron states in the interval ΔE_F corresponds to the expression

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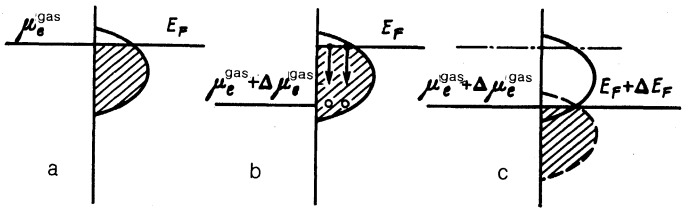

FIG. 1. Scheme of relative position of the chemical potential of electrons in the gas μ_e^{gas} and in the specimen E_F: a) in the initial equilibrium state; b) immediately after increasing the oxygen pressure; c) in the final equilibrium state.

the expression

$$\Delta N = n\Delta x, \tag{6'}$$

where n is the effective oxygen valency which, for example, takes a value in the interval $1 < n < 2$.

Since the amount of oxygen Δx is in principle accessible to measurement, the value of ΔN can be determined experimentally. Afterwards the function

$$D(E_F) = \Delta N / \Delta E_F v, \tag{7}$$

can be calculated, which has the dimensions of the electron density of states.[1)] Here v is the specimen volume.

We determined the amount of oxygen Δx by two methods—by weighing the specimen before and after baking or, as described by Gerbshtein *et al.*,[2] by using a superionic oxygen pump. The corresponding number of electron states ΔN was then found according to Eq. (6), after which the values of the function of Eq. (7) were calculated.

The specimens were baked at 500 °C in oxygen at pressures of 10, 3,..., 10^{-5} atm consecutively in order to obtain values of $D(E_F)$ over a wide range of changes of E_F. Times from 3 to 24 h, as a function of the pressure, were sufficient to establish equilibrium. The oxygen pressure was monitored with the help of a superionic oxygen sensor. According to Eq. (5), each consecutive baking of the specimen raised the Fermi level by 18 mV. Before each baking the specimen was weighed, and lattice constants, superconducting transition temperature, the resistivity at room temperature and also the resistance activation energy at the transition to the dielectric phase were measured.

One of the $D(E_F)$ dependences obtained in this way is shown in Fig. 2. The value of the oxygen pressure at which the specimen was heated is plotted along the vertical axis with the values of the Fermi level corresponding to them.

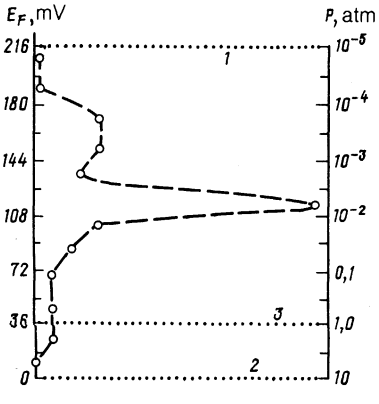

FIG. 2. Dependence of the electron density of states at the Fermi level D on E_F. The dotted straight lines correspond to E_F for 1) $YBa_2Cu_3O_{6.3}$, 2) $YBa_2Cu_3O_7$ and 3) E_F for $T_c = 90$ K.

The dependence shown is of complicated form with peaks at the values $E_F = 120$ and 160 mV.

The value of the function $D(E_F)$ varies weakly in the range $30 < E_F < 60$ mV and equals 2.6 states per eV in the elementary cell. Since the lattice constants and the superconducting transition temperature also change little in this interval (Figs. 3 and 5), it can be expected that the measured $D(E_F)$ relation is roughly the same as the usual electron density of states $D(E)$ at the Fermi level. The corresponding value of $D(E_F)$ averaged over the results of measurements on eight specimens, constituted 2 states per 1 eV in the elementary cell.

The positions of the Fermi level for oxygen concentrations in the specimen corresponding to the formulae $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_{6.3}$ are shown by the dashed lines. It can be seen that the removal of 0.7 oxygen atoms is accompanied by a raising of the Fermi level by about 200 mV.

Values of the specimen mass m and of the coefficient δ (curve 2) are shown in Fig. 3 together with $D(E_F)$ and also values of the difference in lattice constants $b - a$ (curve 3). It can be seen that the peaks of the $D(E_F)$ curve can be associated with the features determined in curves 2 and 3.

The lower peak corresponds to a sharp change in δ and $b - a$. The structure of the specimen before and after this change remains orthorhombic; consequently, a transition from the orthorhombic-1 to the orthorhombic-2 phase takes place. The chemical formula changes here roughly from $YBa_2Cu_3O_{6.8}$ to $YBa_2Cu_3O_{6.5}$. This transition can be associated with doubling of the lattice period which takes place as a result of the removal of half the oxygen atoms from the CuO chains.[3]

The upper peak corresponds to equalizing of the lattice

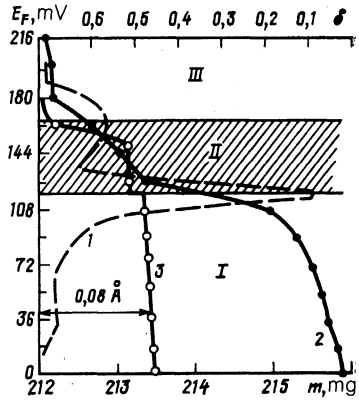

FIG. 3. Location of the phases (I—orthorhombic-1, II—orthorhombic-2, III—tetragonal) and (curve 1) the electron density of states D as a function of E_F; 2) the specimen mass m and the coefficient δ characterizing the specimen composition 3) the difference in lattice constants $b - a$.

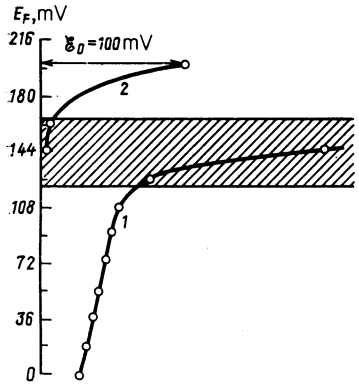

FIG. 4. Location of the phases and the form of the dependence on E_F of 1) the resistance at room temperature R_{300} and 2) the resistance activation energy at the transition to the dielectric phase $\mathscr{E}_0$.

constants and consequently is associated with the transition to the tetragonal phase. The transition is of the order–disorder type and the ordered state, corresponding to the formula $YBa_2Cu_3O_{6.3}$, can be associated with a tripling of the period of oxygen atoms in the chains.[3] The position of the three observed phases relative to the E_F axis is also shown in Fig. 3.

The dependence of two quantities on E_F is shown in Fig. 4: R_{300} is the resistance of the specimen at room temperature (curve 1) and $\mathscr{E}_0$ is the average value of the resistance activation energy, characterizing the transition of the specimen to the dielectric state (curve 2). These dependences look different in each of the three phases. In the orthorhombic-1 phase R_{300} increases linearly with E_F. In the orthorhombic-2 phase this dependence becomes exponential. At a temperature below 1–2 K such a specimen goes into the dielectric state with resistance activation energy $\mathscr{E}_0$ dependent on temperature as in Anderson localization, as was noted by Moshchalkov *et al.*[4]

The activation energy $\mathscr{E}_0$ grows rapidly in the tetragonal phase, reaching a value of 100 mV. The dependence of the superconducting transition temperature $T_c(E_F)$ is shown in Fig. 5 on the background of the function $D(E_F)$. As E_F is increased a transition from 90 degree superconductivity to 60 degree superconductivity takes place. Superconductivity disappears in about the middle of the orthorhombic-2 phase.

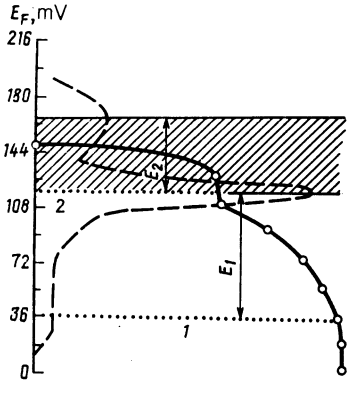

FIG. 5. Comparison of the dependences $T_c(E_F)$ (full line) and $D(E_F)$ (dashed). The values $E_1 = 70$ mV and $E_2 = 40$ mV indicate the distance from the Fermi level to the peaks in the electron density of states for (trace 1) 90- and (trace 2) 60-degree superconductivity.

The lower dotted line shows the position of the Fermi level in a specimen when its oxygen content corresponds to $T_c = 90$ K. It can be seen that 70 mV above the Fermi level there is a strong peak in $D(E_F)$. The upper dashed line shows the position of the Fermi level for $T_c = 60$ K. In this case there is a peak in $D(E_F)$ at a somewhat smaller distance of 40–50 mV above the Fermi level. The tendency for the formation of peaks in the electron density of states may be essential for high-temperature superconductivity.

We give, finally, the experimental values of the deformation potential $\nu = \Delta E_F/(\Delta v/v)$, where $v = abc$ is the x-ray volume of the elementary cell and Δv the change in this volume arising on changing the Fermi level by ΔE_F. In the orthorhombic-1 phase $\nu_{01} \approx 30$ eV, in the orthorhombic-2 phase $\nu_{02} \approx 4$ eV and in the tetragonal phase $\nu_T \approx 30$ eV. It can be seen that in the superconducting orthorhombic-1 phase the deformation potential is an order of magnitude greater than in ordinary metals and superconductors, while in the orthorhombic-2 phase it is the same as in ordinary metals. Although the quantity $\Delta v/v$ is not a "good" description of the deformation of an anisotropic material, the values obtained for the deformation potential carry important information, which we discuss below.

DISCUSSION

Conductivity in $YBa_2Cu_3O_{7-\delta}$ is mainly determined by the CuO_2 planes. The sharp increase in R_{300} (see Fig. 4) at the transition from the orthorhombic-1 to the orthorhombic-2 phase is therefore evidence of a radical rearrangement in the electron spectrum of the planes. The transition to the dielectric state observed for $T < 1$–2 K, which is characteristic of Anderson localization, also indicates a rearrangement of the electron spectrum of the planes. A rapid increase in $\mathscr{E}_0$ takes place at the transition to the tetragonal phase, which is evidence of further rearrangement of the electron spectrum of the planes.

As can be seen from the experiment, the sequence of transitions from the conducting state to Anderson localization and then to the usual dielectric state is a result of successive raising of the Fermi level. The simplest explanation of the transition to Anderson localization and then to the dielectric state is the approach of the Fermi level to the top of the valence band (below the percolation threshold of holes) and then its (the Fermi level) emergence into the forbidden band.

The conclusion can be drawn from an analysis of the geometry of the elementary cell of $YBa_2Cu_3O_{7-\delta}$ that for $T \gtrsim 500$ °C there is an effective exchange by oxygen atoms between CuO chains and CuO_2 planes. This conclusion follows from experiments on isotopic oxygen exchange.[6]

This indicates that in the process of establishing equilibrium the oxygen content changes not only in the chains but also in the planes. We will evaluate the change in the oxygen content in the planes. According to Eqs. (7) and (6) we can write for $v = 1$ the expression

$$\Delta x = {}^1/_2 D(E_F)\,\Delta E_F, \qquad (8)$$

which represents a peculiar conservation law: one must "pay for" the change in Fermi level by a change in oxygen content,

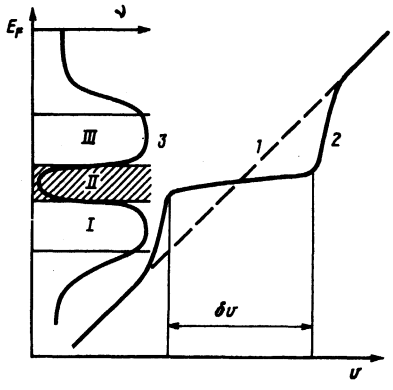

FIG. 6. Schematic of the location of the phases (I—orthorhombic-1, II—orthorhombic-2, III—tetragonal) and the form of the dependence of E_F on 1) the specimen volume v in the absence of a structural phase transition 2) on specimen volume v, and 3) on deformation potential $\nu \sim \partial E_F/\partial v$ when a structural phase transition occurs.

and the "price" is determined by the electron density of states. Let us suppose that for the CuO_2 chains $D(E_F) \approx 1$, then we obtain the result that a change in Fermi level by 200 mV gives rise to a change in the number of oxygen atoms in the elementary cell by 0.1 atom, i.e., in each tenth elementary cell there will be a lack of one oxygen atom.[2)] When these defects are distributed along the planes, the distance between them is approximately three lattice constants, or 12 Å. Under corresponding conditions the ordering of defects can occur, such as in essence, Jahn-Teller phase transitions in the chains, which illustrates the rich possibilities for realizing different superstructures, not only in the chains, but also in the planes.

Finally, we show that the anomalously high value of the deformation potential in the superconducting, orthorhombic-1 and the tetragonal phases is associated with the nearness of structural phase transitions.

Suppose trace 1 in Fig. 6 describes the dependence of specimen volume on the electron chemical potential $v(E_F)$ in the absence of a phase transition. If there exists a region of "forbidden" values of the volume δv through which the specimen passes discontinuously, i.e., if a structural phase transition occurs, then the $v(E_F)$ dependence acquires the form shown in curve 3, on which there are two peaks on both sides of the orthorhombic-2 phase region. The position of the phase shown in the figure corresponds to the experimental values of the deformation potential. We point out that the high value of the deformation potential only occurs for a deformation which accompanies a structural phase transition.

Apparently, near such a structural phase transition, not only the deformation potential but also other electronic and lattice characteristics should have extremal values, an example of which is the peaks in the electron density of states $D(E_F)$. In our opinion this fact can have a key role in the mechanism of high-temperature superconductivity.

The authors thank M. S. Bresler and B. P. Zakharchenya for their interest in the work and for valuable discussions.

[1)] Unlike the usual electron density of states $D(E) = \partial N/\partial E$, the proposed function $D(E_F) = \partial N/\partial E_F$ reflects the response of the electron spectrum to a rearrangement of the lattice. Under conditions of strong electron-phonon interaction, this function carries information important for elucidating the nature of high-temperature superconductivity.

[2)] The calculation is valid if a phase transition does not occur in the plane for a change in Fermi level. This value grows appreciably in the opposite case.

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Translated by Robert Berman