Possible temporal mechanism for the suppression of superconductivity in the system YPrBaCuO

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The objective of this work was to determine the mechanism of the suppression of superconductivity in the system YPrBaCuO. It is concluded on the basis of structural data obtained by different methods that in this system praseodymium is in a mixed-valence type state in which the phases resonant with period $\sim 10^{-13}$ s, which is equal to or even less than the lifetime of a Cooper pair. Therefore it is hypothesized that in such systems the main mechanism could be temporal. © *1996 American Institute of Physics.* [S1063-7761(96)01612-5]

1. INTRODUCTION

A surprising property of the $YBa_2Cu_3O_7$ ceramic—superconductivity—is accompanied by other characteristics, not as pronounced but nonetheless incomprehensible. For example, it was expected that replacing yttrium (even partially) with rare-earth ions (RE) with large magnetic moments would result in the suppression of superconductivity. However, this did not happen. This could be explained by the very weak interaction of the magnetic and superconducting subsystems. But it was soon found that praseodymium, which seems not to be distinguished in any way from the other rare earths, dependably quenches superconductivity in the system $Y_{1-x}Pr_xBa_2Cu_3O_7$.

In the present paper these characteristics are analyzed on the basis of models obtained from modern structural data[1,2] and a modified Thomas–Fermi theory.[3] The data of Ref. 1 were obtained by the method of low-temperature (10 K) neutron diffraction (LTND) and are presented in Table I.

One can see from these data that a RE ion is surrounded by eight oxygen ions, and the eight RE–O distances, specifically, for praseodymium, are almost equal to one another (≈ 2.45 Å). At the same time, the data of Ref. 2, which were obtained by analyzing the fine structure of the x-ray absorption spectra (XAFS), indicate that only some Pr–O distances equal 2.45 Å and that the other distances are much shorter (on the average 2.27 Å). Besides the surprising inconsistency of these data, it should be noted that the difference between 2.45 Å and 2.27 Å is not only quantitative. In Ref. 4 it was shown experimentally that for Pr–O=2.38 Å there occurs a phase transition which can be attributed to a transition from separate electronic and nuclear motions to motion of a single vibron.

A modified Thomas–Fermi theory[3] makes it possible to introduce into the calculation the maximum number of outer electrons possible at the present time: two for Ba, eleven for Cu, six for O, and $10+n$ for RE (n is the number of electrons in the $4f$ configuration: $n=3$ for praseodymium and 4 for neodymium).

It is therefore possible to calculate the electron density at virtually any point in a unit cell, and then a diagram of the electron density distribution in any section. One would think that given these data it would be possible to distribute all electrons in a unit cell among the separate ions and calculate the charges of these ions and the radii of the spheres containing these electrons. However, because of the strong overlapping of the wave functions of many ions and the different character of these ions, this cannot be done correctly.

Nonetheless, the calculation makes it possible to divide the entire volume of a unit cell into ionic cells as follows. The entire volume is divided into small volumes (small enough so that the electron density can be assumed to be the same over the entire microvolume), and each such microvolume can be assigned to an ion whose distance from the center of this microvolume is shorter than the corresponding distance of any other ion. It is obvious that the electrons contained in these ionic cells will together give the total number of electrons participating in the calculation. The difference of the number of electrons of a given ion which participate in the calculation and the number of electrons contained in an ionic cell will give the charge of the cell. Moreover, the calculation makes it possible to calculate the spherically averaged electronic density for a sphere of any radius centered on the nucleus of a selected ion. This makes sense when the selected ion is sufficiently isolated from other ions. Then the surfaces with the same density will also be close to spheres, and the region of high electron density belonging to a given ion will be separated by a region of low background electron density from the region of high density belonging to the surrounding ions.

2. RESULTS

As an example of a RE ion which when replacing yttrium does not influence the superconductivity of the system $REBa_2Cu_3O_7$, we give neodymium. Figure 1 displays a diagram of the electron density distribution in a plane containing the neodymium atom and bounded by oxygen ions O2.

One can see that the contours determining the density above the average value (93) are practically circles, which indicates that the neighboring oxygen ions have no appreciable effect. The attraction of the Nd electrons to these ions is manifested only in a region of low electron density. This is also true of the distribution of the electron density around the oxygen nucleus. Between Nd and O there is a region of very

TABLE I. Coordinates of the atoms in $REBa_2Cu_3O_7$ (RE=Pr, Nd, Y).

Ion	x	y	z(Pr)	z(Nd)	z(Y)
RE	0.0000	0.0000	0.0000	0.0000	0.0000
Ba	0.0000	0.0000	0.3197	0.3191	0.3166
CU1	0.5000	0.5000	0.5000	0.5000	0.5000
CU2	0.5000	0.5000	0.1482	0.1506	0.1446
O4	0.5000	0.5000	0.3406	0.3423	0.3406
O3	0.5000	0.0000	0.1305	0.1263	0.1224
O2	0.0000	0.5000	0.1268	0.1319	0.1230
O1	0.5000	0.0000	0.5000	0.5000	0.5000
a, Å			3.863	3.856	3.817
b, Å			3.918	3.912	3.883
c, Å			11.650	11.719	11.687
Phase 1 O2	0.0000	0.4399	0.1268	-	-
Phase 2 O2	0.0000	−0.4399	0.1268	-	-

TABLE II. Characteristics of ionic cells in $NdBa_2Cu_3O_7$.

Ion	R, a.u.	R, Å	N	Q
Nd	2.747	1.453	13.590	0.41
Ba	3.063	1.620	0.387	1.613
Cu1	2.718	1.438	8.170	2.830
Cu2	2.492	1.318	7.900	3.100
O4	2.899	1.534	7.952	−1.952
O3	2.747	1.453	7.685	−1.685
O2	2.746	1.453	7.738	−1.738
O1	2.883	1.525	7.917	−1.917

Note: N—number of electrons in an ionic cell, Q—ion charge (difference of the number of electrons used in calculation and the number of electrons in the ionic cell), R—radius of a sphere whose volume equals the volume of the ionic cell.

low electron density. This background region is determined by the contributions of practically all ions in the cell.

Data for the ionic cells of $NdBa_2Cu_3O_7$ are given in Table II. According to these data, the copper, oxygen, and barium ions in a cell in $NdBa_2Cu_3O_7$ practically neutralize one another, the charge of the neodymium ion is less than 0.5: $Nd^{+0.41}$ (not Nd^{+3}, as ordinarily assumed), and the copper ions possess an unusually high charge—$Cu^{+2.8}$ and $Cu^{+3.1}$. Allowing for the provisional nature of these numbers, they confirm or at least do not contradict the idea that the interaction of the RE ion and the superconducting planes is weak.

The spherically averaged electron density $\langle \rho_e \rangle$ is presented in Fig. 2 as a function of the radius of the sphere with a Nd nucleus at the center. One can see that the neodymium ion is indeed quite clearly separated from the environment, since the easily distinguishable region of high density, where neodymium electrons undoubtedly predominate, and part of the region of high electron density of the environment (oxygen and copper) are separated from one another by a low background density.

The boundary of the neodymium ion should probably also lie somewhere in this background region. But, to determine the boundary, it would be necessary to perform at least two operations: First, this boundary must be determined quantitatively (for example, a point, where the contribution of the neodymium electrons equals the maximum contribution of some other ion) and, second, which is practically impossible, this point must be found.

The value $R = 1.453$ Å, equal to the radius of a sphere equivalent to the ionic cell of Nd (Table II), is indicated in the figure. A sphere of this radius contains 13.644 electrons, i.e., a number close to the number of electrons contained in the ionic cell of Nd (13.590). This shows that the ionic cell is nearly spherical.

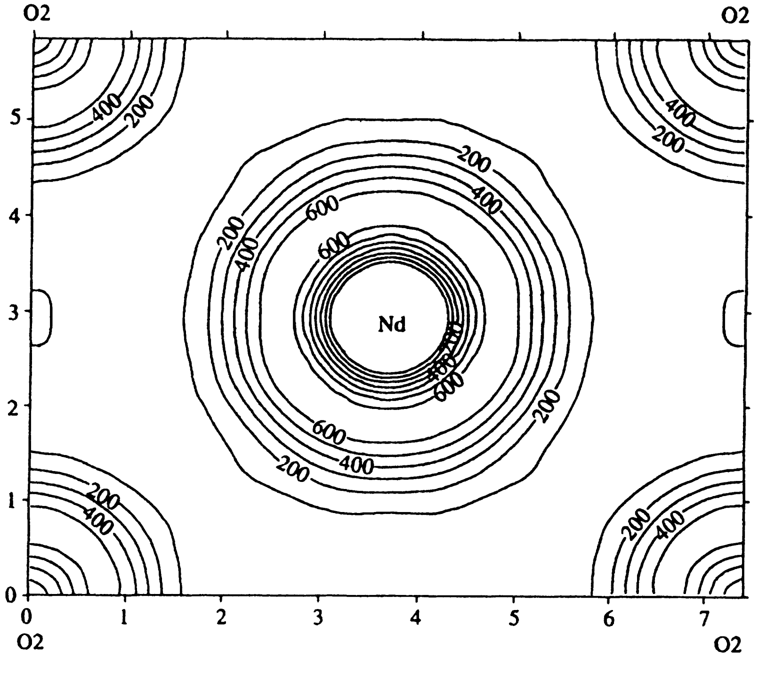

FIG. 1. Diagram of the electron density distribution in a $NdBa_2Cu_3O_7$ cell for a plane containing the neodymium ion and bounded by O2 oxygen ions (the average density for the cell equals 93 and the coordinates are expressed in atomic units).

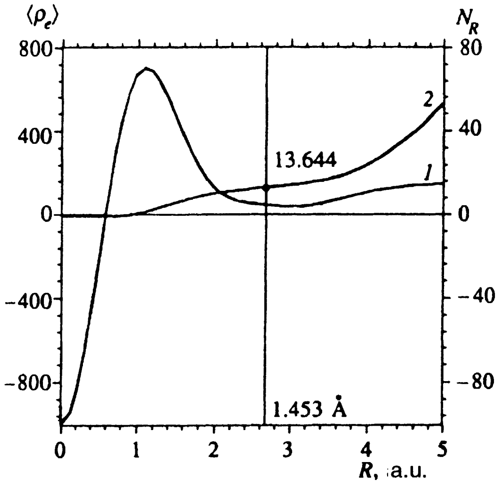

FIG. 2. Spherically averaged electron density (*1*) and the number of electrons in a sphere (*2*) as a function of the radius of the sphere with a Nd nucleus at the center.

Finally, it is necessary to comment on the region in Fig. 2 (near the nucleus) where the density is negative. This is an error of the theory. However, the error introduced into the subsequent calculations is very small (because the radius is small). This is clearly seen in curve 2 in this region. It is obvious that the number of electrons in a sphere of this radius is also negative. But this number is so small that it is unnoticeable on the scale of Fig. 2.

We now consider the compound $PrBa_2Cu_3O_7$. The figures analogous to Figs. 1 and 2 are virtually identical to the latter and are not presented here. The characteristics of the ionic cells of this compound are given in Table III; they likewise differ little from the corresponding characteristics of $NdBa_2Cu_3O_7$. However, $NdBa_2Cu_3O_7$ is a superconductor with $T_c=96$ K and $PrBa_2Cu_3O_7$ is an insulator. There are hundreds of papers devoted to the reason for this difference, but these works all leave a sense of dissatisfaction. There are theoretical works devoted to two mechanisms for the suppression of superconductivity: magnetic breaking of pairs[5] and localization or neutralization of current carriers (in this case, holes).[6] It is entirely legitimate to invoke these mechanisms for analysis of superconductivity suppression in $Y_{1-x}Pr_xBa_2Cu_3O_7$. However, then it becomes incomprehensible why the same mechanisms cannot be invoked for the other $REBa_2Cu_3O_7$ compounds. Up to now there have been no experimental indications of any unusual results that would make it possible to look at this puzzle from an unexpected point of view. We think that the difference of the structural data in Refs. 1 and 2 are such results. Could it be that the eight quantities 2.45 Å determined by one method and the set of quantities 2.45 Å and 2.27 Å obtained by other methods are in fact one and the same thing?

TABLE III. Characteristics of ionic cells in $PrBa_2Cu_3O_7$ with structure according to Ref. 1.

Ion	R, a.u.	R, Å	N	Q
Pr	2.739	1.449	12.150	0.850
Ba	3.064	1.621	0.398	1.602
Cu1	2.721	1.439	8.126	2.784
Cu2	2.485	1.315	7.902	3.098
O4	2.898	1.533	7.993	−1.993
O3	2.748	1.454	7.790	−1.790
O2	2.740	1.449	7.763	−1.763
O1	2.877	1.522	7.941	−1.941

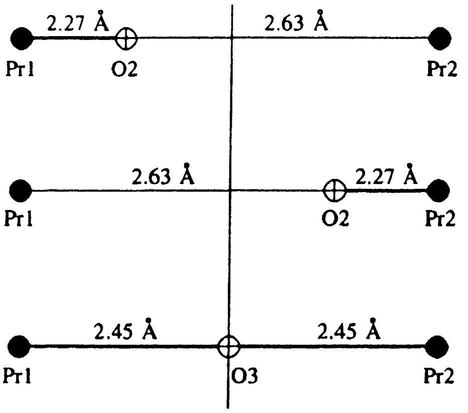

FIG. 3. Positions of the O2 oxygen ions with respect to the central ions of two neighboring cells in the phases 1 and 2 (top two) with the same position of the O3 oxygen ions (according to the provisionally adopted model).

If it is assumed that some Pr–O distances can vary rapidly, taking on two values with a period from 10^{-13} down to 10^{-15} s, then the method for analyzing the fine structure of the x-ray absorption spectra will give two true values (the transition lifetimes in the region of the x-ray levels $\tau_X\sim 10^{-16}$ s) and the low-temperature neutron diffraction method will give only one, average value.

The mechanism leading to such processes could be similar to the mixed-valence mechanism (see, for example, Ref. 7). This is either a resonance of the $4f^1$ and $4f^2$ configurations or a resonance between a state of the $4f^2$ electronic configuration of praseodymium and a vibronic state of the PrO_6 complex.

The first case is $4f^2+L\leftrightarrow 4f^2L=4f^1$. This mechanism was invoked to explain the suppression of superconductivity as a result of the absorption of free carriers by the $4f^2$ configuration (L—ligand hole).[6]

The second case is $4f^2+\nu\leftrightarrow 4f^2\nu$, where ν is the sum of the frequencies of the quanta interacting with local $4f$ electrons accompanied by the formation of a $4f^2\nu$ vibronic state.

In deriving their theorem,[8] Jahn and Teller ruled out rare earths because the $4f$ electrons are practically isolated. In the case at hand, however, and also at high pressure, this isolation breaks down and the Jahn–Teller theorem, together with all of its consequences,[9] extends also to the $4f$ configuration. In these cases, a vibronic motion is formed.[4]

A vibronic motion is a motion from which the electronic and nuclear motions cannot be individually separated. The "dissolution" of some vibrations in the vibronic motion will undoubtedly influence the transition into the superconducting state. But this can have both a positive and negative effect, depending on the characteristics of the vibrations.

To choose between these mechanisms, we shall attempt

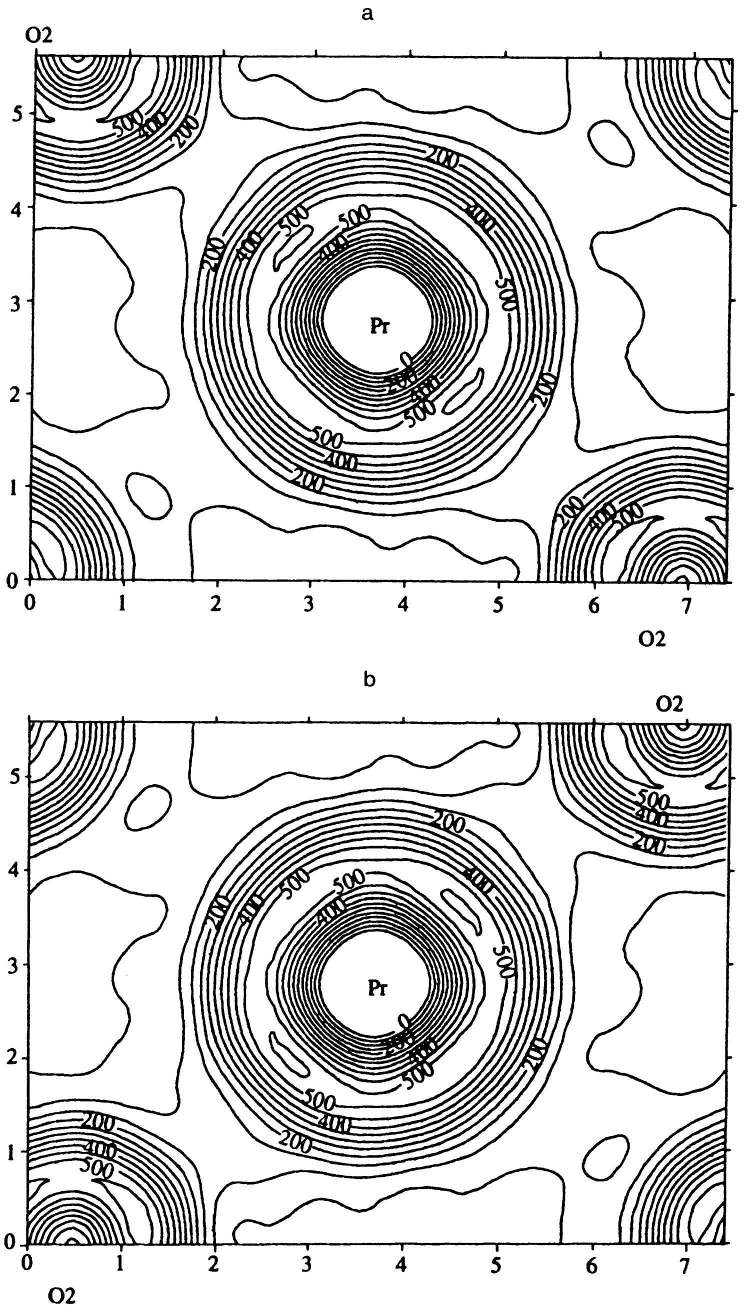

FIG. 4. Diagrams of the electron density distribution in a cell for the plane containing the praseodymium ion and bounded by O2 oxygen ions for the phases 1 (a) and 2 (b).

to estimate the state of the two supposed phases. One model that makes it possible to match the structural data obtained by the methods of low-temperature neutron diffraction and analysis of the fine structure of x-ray spectra is as follows (Table I, bottom rows).

According to Ref. 2, the coordinates of all ions except oxygen are the same as the coordinates of the ions in a cell in $YBa_2Cu_3O_7$. In the model adopted the coordinates of the O3 oxygen ions also remain unchanged. For the O2 oxygen ions in the phase 1 the coordinate z is constant and the coordinate x changes so that two ions approach to within 2.27 Å from the Br ion and the two other O2 ions leave the cell and approach to within 2.27 Å from the central atoms of the neighboring cells. In the phase 2 these pairs undergo the opposite motions. Phase 2 is the reflected phase 1 (Fig. 3). These phases are characterized by the same energy.

So, the data obtained by the method of analyzing the fine structure of the x-ray spectra should correspond to a six-fold oxygen environment of praseodymium (four distances Pr–O3=2.45 Å and two distances Pr–O2=2.27 Å). The data obtained by the low-temperature neutron diffraction method should correspond to adding the positions of the phases 1 and 2 with the average positions of the O2 ion on the faces of the unit cell and a Pr ion surrounded by eight oxygen ions with Pr–O=2.45 Å. The diagrams in Figs. 4a and 4b give, respectively, the electron density distribution for phases 1

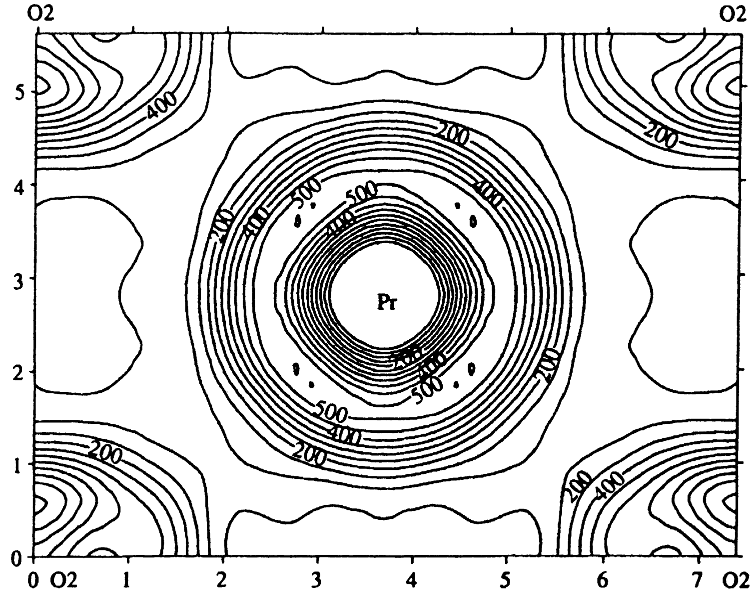

FIG. 5. Diagram of the total electron density distribution, divided in half, for phases 1 and 2 (the average over the cell equals 92 and the coordinates are expressed in atomic units).

and 2 and the diagram in Fig. 5 gives their sum.

As one can see by comparing Tables III, IV and V, to pass from phase 1 to phase 2 the system must overcome an energy barrier equal to 0.03 a.u. = 6582 cm^{-1}. The difference of the charges of the ionic cell of praseodymium in the virtual phase and in the true phases is 0.07. It is obvious that neither changes in the energy nor changes in the charge correspond to a $4f^2 \leftrightarrow 4f^1$ resonance, but they do fit in the scheme of an electron–vibronic transition. The electronic motion mixes with the vibrational motion and the latter motion apparently determines the lifetime of these phases. If the mixing of the motions is limited by the frequency 300 cm^{-1}, then this corresponds to a frequency of $300 \cdot 10^{10}$ Hz.

TABLE IV. Characteristics of ionic cells of phase 1 or 2 in $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

Ion	R, a.u.	R, Å	N	Q
Pr	2.734	1.446	12.080	0.920
Ba	3.065	1.621	0.446	1.554
Cu1	2.721	1.439	8.122	2.878
Cu2	2.497	1.321	8.001	2.999
O4	2.898	1.533	7.952	−1.952
O3	2.747	1.453	7.843	−1.843
O2	2.732	1.445	7.717	−1.717
O1	2.872	1.519	7.877	−1.877

TABLE V. Energies of the substances studied.

Substance	$E_e + E_e^{\text{core}}$, a.u.	$E_{\text{core}}^{\text{core}}$, a.u.	E_{total}, a.u.
Nd-123	−77.46	−177.55	−255.01
Pr-123 (Ref. 1)	−71.34	−174.09	−245.43
Pr-123 (Phase 1)	−71.48	−173.98	−245.46

Note: E_e — interaction energy of all electrons used in the calculation; E_e^{core}—energy of interaction of these electrons with the cores; $E_{\text{core}}^{\text{core}}$—interaction energy of all cores; E_{total}—total energy.

There arises the question of whether the formation of a complex PrO_8 partially as a result of a bond with the participation of $4f$ electrons, which facilitates absorption of holes, and delocalization of the magnetic moment of the $4f^2$ configuration, which can stimulate magnetic breaking of pairs allow, a Cooper pair to form over a time $\tau_p \simeq 10^{-13}$ s and establish coherence over the entire volume of the sample. It is obvious that for an energy gap $\Delta \cong 200\ \text{cm}^{-1}$ the time τ_p will be of the same order of magnitude and even somewhat longer. Therefore we must advance the following hypothesis.

Irrespective of other conditions, for a transition into the superconducting state the lifetime τ_p of a phase must be longer than the lifetime τ_C of a Cooper pair. If $\tau_p \leqslant \tau_C$ holds, then the probability of a transition into the superconducting state equals zero, which apparently is also valid in the case of $\text{PrBa}_2\text{Cu}_3\text{O}_7$.

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