

## Electronic structure of high-temperature superconductors in the normal state

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 Usp. Fiz. Nauk **158**, 155–161 (May 1989)

During the two years since the discovery of high-temperature superconductors<sup>1</sup> it has become clear that we do not understand the mechanism responsible for superconductivity in these systems, and that the nature of the normal state is not clear either.<sup>1)</sup> The key question is: how should we describe the electronic structure of these compounds, i.e., should this be done in the spirit of traditional band theory and the theory of Fermi liquids or in the spirit of the Hubbard model based on the concept of localized electrons.

The latter assumption was first put forward by Anderson<sup>2</sup> and has frequently been repeated in a more or less categorical form by both theoreticians and experimenters (see Refs. 3–6 elsewhere). At the same time, much recent research takes us back to the theory of the Fermi liquid either completely or partially. In this paper, we provide a brief outline of published descriptions of the electronic structure of the superconducting metallic oxides of copper.

There are now four known groups of high temperature superconductors that contain copper. These are the LCO compounds of the form  $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ , where A is an alkaline earth metal, the YBCO compounds of the form  $\text{RBa}_2\text{Cu}_3\text{O}_{7-y}$  (these include compounds with different rare earth elements R and also some compounds with similar crystal structure), the BSCCO compounds of the form  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ , and, finally, compounds of the form  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ . For most of these compounds, we have band structure calculations, performed by traditional methods, and for some of them there are different spectroscopic data. We shall mostly confine our attention to the LCO compounds in view of the fact that all or almost all the conclusions will be valid for the other classes as well.

Classical band theory assumes that the outer-shell electrons of atoms are completely collectivized and that their spectrum can be described by an effective one-electron Hamiltonian for electrons moving in the mean potential, which, in turn, itself depends on the spectrum of electron states and the degree to which they are filled. The effect of the interaction between electrons (exchange and correlation effects) is then assumed to be almost completely included in the effective potential. Non-one-electron manifestations of exchange and correlation effects are assumed to be so small that they can be regarded as corrections to the band picture.

Naturally, in this approach, most of the effort is invested in finding the dependence of the effective potential on the electron spectrum. The generally adopted approach is now based on the so-called density functional (see Ref. 7). In this approach, the effective potential is different for electrons with different spins and depends only on the electron and spin densities at the given point (plus the electrostatic potential). This approximation is very successful when used to describe the electron structure of simple and transition met-

als, superconductors, and insulators. There are, however, several cases in which this simple approximation is inadequate. For example, the valence and conduction bands of semiconductors and insulators are described reasonably well, but the band gap is several times too small. Moreover, in one case (Ni) the spin splitting of *d*-electron bands is too small by a factor of two. Again, whereas the description of the Fermi surface of compounds with intermediate valence is correct, the description of the emission properties is completely wrong. In compounds with a narrow fully filled *d*-band (Cd, Zn, Cu, Ag, and so on), the position of the *d*-band is too high in comparison with the experimental photoemission data. For example, in copper, it is too high by 0.5 eV. Finally, the narrow-band oxides of *d*-metals (MnO, NiO, etc.) are not satisfactorily described by traditional band theory. This is probably a complete list of the failures of this approach. It is clear that narrow bands present a particular "danger." Calculations of the band structure of the new superconductors, performed immediately after their discovery, have not revealed the presence of such bands. At first sight, this suggested that the band approach might be valid.

Figure 1 shows the calculated structure of LCO for  $x = 0$ . Its typical properties have been found in all HTSC and include the broad complex of hybridized bands of *d*-orbitals of copper and *p*-orbitals of oxygen in which the upper band (conduction band) is formed by the  $d_{x^2-y^2}$  orbitals lying in the  $\text{CuO}_2$  plane and the *p*-orbitals of oxygen lying in the same plane (we are assuming that the reader is familiar with the crystal structure of the HTSC). This band has a particularly strong dispersion in the  $x,y$  plane ( $\text{CuO}_2$ ), which is largely due to the fact that the calculated positions of the  $d_{x^2-y^2}$  level of copper and the *p* level of oxygen are exceedingly close to one another. The result is that the calculated width of this band is found to be of the order of 4 eV. On the other hand, in the *z* direction, i.e., at right angles to the plane, the bands are almost dispersion free.

These facts were discovered in the course of the very first band calculations and provided the basis for the assertion (as of now no one challenges these assertions) that high temperature superconductors are quasi-two-dimensional compounds and that the properties of both normal and superconducting states are largely determined by electrons in the  $\text{CuO}_2$  plane.

The alternative approach to the band structure of high temperature superconductors relies, as already noted, on the Hubbard model. The physical significance of this model is as follows. Outer-shell atomic electrons are assumed to be highly localized and confined to their particular atoms (ions). When the solid is formed, they become completely collectivized and travel through the lattice by "hopping" from one atom to another. This process is controlled by two

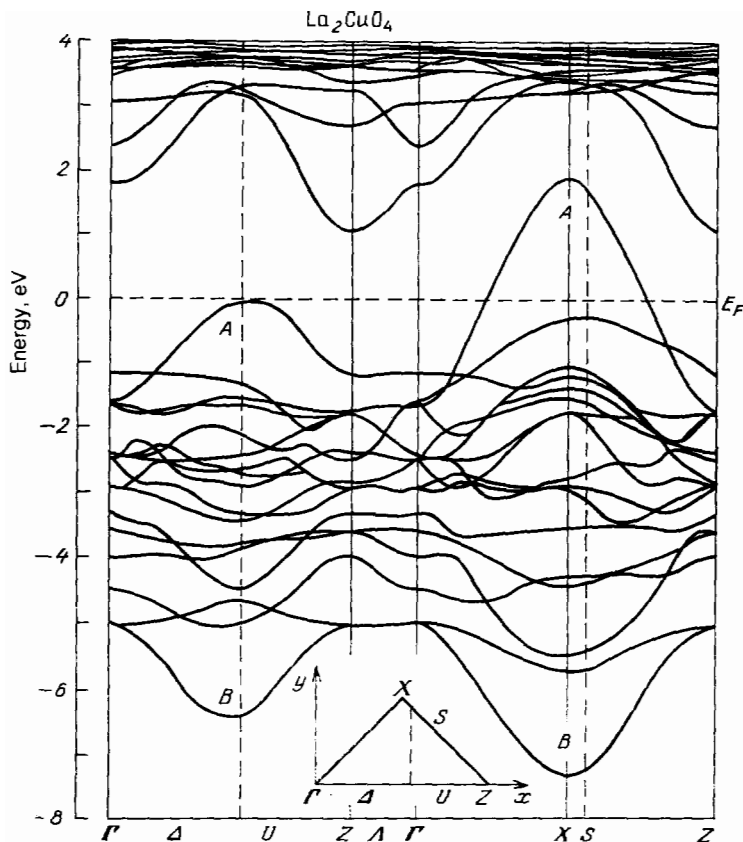


FIG. 1. Band structure of the tetragonal  $\text{La}_2\text{CuO}_4$  taken from Ref. 16: A—hybridized band formed by the  $d_{x^2-y^2}$  states of copper and the  $p$ -states of oxygen.

parameters, namely, the hopping probability, which is determined by the overlap integral  $t$  of wave functions and potentials of neighboring atoms (ions), and the energy  $U$  necessary to transport one electron between neighboring atoms. This energy is determined by the Coulomb repulsion between the "extra electron" and the electrons resident on a given ion, and is therefore usually referred to as the interatomic Coulomb repulsion energy.

The additional complexity in the case of high temperature superconductors is that it is essential to take into account the presence of the two types of ion that correspond to the  $d^9$  and  $p^6$  electron configurations, i.e.,  $\text{Cu}^{2+}$  and  $\text{O}^{2-}$ . The electron structure is then determined by the ratio of parameters such as the energy levels  $\epsilon_d$  and  $\epsilon_p$  of  $d$ -electrons in copper and  $p$ -electrons in oxygen, the interatomic repulsion energies  $U_d$  and  $U_p$  of the  $d$ -electron of copper and  $p$ -electron of oxygen, the overlap integral  $t$  of the  $d$ - and  $p$ -electron wave functions for electrons on neighboring lattice sites, and, finally, the charge transfer energy  $\Delta$ , i.e., the energy necessary to transfer one electron from copper to oxygen. Unfortunately, direct estimates of these parameters are relatively difficult. A high degree of utilization has been achieved by values deduced from the satellite structure of photoemission spectra<sup>21</sup> ( $U_d \sim 6-7$  eV,  $U_p \sim 2-3$  eV,  $t \sim \Delta \sim 1-2$  eV). Unfortunately, recent experiments<sup>8</sup> have not confirmed the presence of the satellites. However, indirect theoretical estimates (see for example Ref. 9) have yielded values of more or less the same order. At any rate, although an error by a factor of 2 cannot be completely discounted, we may suppose that  $t$ ,  $\Delta$ , and  $U_p$  are small in comparison with  $U_d$ . Although the exact solution for the Hubbard model is not known, we do know quite a lot about the

behavior of the system in this limiting case.<sup>10</sup> Thus, the presence or absence of a gap in the spectrum is determined by the ratio of  $t$  and  $\Delta$ .<sup>31</sup> The copper sub-bands corresponding to the  $d^9$  and  $d^{10}$  configurations are then highly split, and doping produces holes on oxygen atoms, which are responsible for conductivity. The magnetic properties are determined by the presence of antiferromagnetic superexchange whose magnitude is determined by  $t^2/\Delta$ .

The fact that the Hubbard model, especially its multi-band version, has remained in a virtually primitive theoretical state, has meant that the band approach has for many years remained the basic method in solid state theory. It seemed at first that the situation in high temperature superconductivity will be the same. However, a series of experimental results obtained in the course of the last two years has suggested that the validity of the band approach to high-temperature superconductivity must be in serious doubt. These facts are: the magnetic phase diagram, the metal-dielectric transition, and spectroscopic data. Let us examine them in greater detail.

## 1. MAGNETISM

The LCO phase diagram is shown in Fig. 2 (taken from Ref. 11 etc.). It is clear from this diagram that pure  $\text{La}_2\text{CuO}$  ( $x = 0$ ) exhibits strong antiferromagnetism and an orthorhombic distortion of the characteristic tetragonal structure of layered perovskite. On the other hand, we must not overestimate the precision of this phase diagram, especially in relation to the  $O-T$  transition line for  $x \neq 0$  and the transition between the paramagnetic state and the spin glass. All the same, the diagram is essentially correct, especially in relation to magnetism, which vanishes very rapidly when the

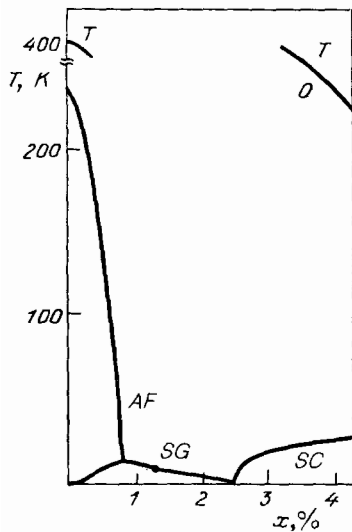


FIG. 2. Phase diagram of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ : O—orthorhombic phase, T—tetragonal phase, AF—antiferromagnet, SC—superconductor, SG—magnetic phase, possibly a spin glass (the boundary of the SG phase is determined by the singularity in the temperature dependence of the NMR relaxation time). When  $x \lesssim 0.02$  and  $T \lesssim 400$  K, the system is a semiconductor, but the metal-semiconductor boundary is not sharply defined.

dopant in the form of the alkaline earth metal is introduced, and to the existence of the orthorhombic distortion at moderate temperatures and moderate dopant concentrations. Strong antiferromagnetic correlations are also found above the Néel point. On the other hand, band structure calculations performed in the effective potential approximation mentioned above, predict a zero magnetic moment for copper even when  $x = 0$ . It is important to note that this fact is not in itself unique: for the great majority of materials for which these calculations have been carried out, the magnetic structure is reproduced correctly. Even in strongly magnetic materials such as Fe, Co, and Ni (magnetic moment in the range 0.7–2 Bohr magnetons), the magnetic moment is predicted correctly to within a few percent. Moreover, the magnetic moment is not small ( $0.5\mu_B$  per copper atom, i.e., one-half of the maximum possible value for a spin-half particle), but direct calculations do not reveal the presence of magnetic instability!<sup>4</sup> Moreover, the calculated paramagnetic ground state is found to be metallic whereas experiment indicates that the orthorhombic phase is a semiconductor for  $x = 0$ .

## 2. SPECTROSCOPIC EXPERIMENTS

The majority of photoemission experiments were performed with YBCO. The first experiments revealed the practically complete absence of the  $d$ -electrons of copper at the Fermi level. The density of states of oxygen electrons was also low. The overall structure of the valence band was satisfactorily reproduced by band calculations, but was shifted downward relative to the experimental value by about 1 eV. Several satellites were observed and gave rise to a variety of interpretations (see Ref. 12 and elsewhere). The photoemission experiments have been regarded as a powerful argument against the validity of the band theory. On the other hand, recent and more accurate experiments,<sup>8</sup> performed with freshly cleaved single crystals, have not confirmed the absence of  $d_{Cu}$  and (particularly)  $p_O$  electrons at the Fermi

level. As far as the satellite structure is concerned, powerful arguments were put forward in Ref. 8 in support of the conclusion that this structure was connected with the poor quality surface of the high-temperature superconductor and did not represent bulk properties. On the other hand, the 1 eV discrepancy was confirmed.

A considerable stir was produced by experiments on the characteristic losses of fast electrons whose energy corresponded to transitions from the atomic core to the conduction band.<sup>6</sup> These experiments also showed that electrons at the Fermi level belonged mostly to oxygen.

Finally, measurements of the frequency dependence of the reflection coefficient must also be assigned to this group of experiments. Once again, the interpretation of the early experiments in this area turned out to be erroneous (see Ref. 13 and elsewhere). For example, an exciton peak was thought to be present in absorption at a frequency of the order of 0.3–0.6 eV in LCO and YBCO. If this were true, it would undoubtedly be in conflict with the calculated band structure of these compounds, but it eventually became clear that the appearance of the peak was due to the incorrect processing of experimental data on polycrystalline samples. Other features of HTSC optics, including the anomalously low plasma frequency, which depends on the dopant concentration in LCO, can be satisfactorily explained in terms of the band approach.<sup>14</sup> At the same time the calculated plasma frequency (at any rate for LCO) is probably too high by about 20%.

3. The fact that the calculated ground state of  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  turns out to be metallic is a strong argument against the validity of the band theory as a means of describing the electron structure of the new superconductors (experiment shows that both compounds are semiconductors). At the same time, this fact is closely related to the absence of antiferromagnetism in these compounds. For example, the application of an external magnetic field of constant strength, but alternating sign, in accordance with the observed antiferromagnetic ordering, produces a significant change in the electron structure. If the field strength is chosen so that the induced magnetic moment of copper is equal to the observed magnetic moment ( $\sim 0.5\mu_B$ ), a gap at the Fermi levels appears in the electron spectrum.<sup>15</sup> It is therefore very probable that the failure of the band approach in this case is a consequence of the absence of magnetism<sup>5</sup> in these calculations (see Section 1 above).

It is therefore clear that there are now two reasonably reliable facts that are in conflict with the calculated band structure of high-temperature superconductors. They are: (1) the absence of antiferromagnetism in the calculated ground state of  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and (2) the shift of the photoemission curves by about 1 eV as compared with the experimental result.

The first of these two facts finds a simple and natural explanation in the Hubbard model. Actually, if the  $d$ -band of copper is split into two Hubbard bands that correspond to the  $d^9$  and  $d^{10}$  configurations, the number of electrons remaining in the calculation is even, so that the semiconducting character of the compound is easy to understand. [We note that, in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , we must then assume that the "chain copper" is radically different from the planar copper because it has a fully filled  $d$ -band ( $d^{10}$ ). Since the  $d^9$  configuration corresponds to a magnetic ion, the presence

of magnetism presents no difficulties either. However, there is some difficulty with the non-integer magnetic moment of copper. We may assume, on the other hand, that quantum fluctuations and shielding by other electrons can reduce the observed magnetic moment by the required amount, i.e., about 50%.

The weak point of the Hubbard model is that it cannot readily explain why optical and, especially, photoemission spectra are satisfactorily described by the band theory. One would expect to see splitting of the Hubbard bands in spectroscopic experiments. (Strictly speaking, in early experiments, the satellites at 9–12 eV and certain other features were identified with precisely such manifestations. As we have already noted, the presence of these features subsequently became doubtful.)

This refers in the first instance to samples having the superconducting composition, i.e.,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{La}_{1.5}\text{A}_{0.15}\text{CuO}_4$ , etc. It may well be that in their semiconducting analogs  $\text{La}_2\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$ , and so on, interatomic correlations are strong enough to produce Hubbard splitting on copper. At the same time, it is possible that, for the latter, the band theory is qualitatively correct, but the approximations employed for the effective potential in traditional band calculations are not accurate enough. If this is so, it means that the use of a more accurate approximation would lead to the appearance of antiferromagnetism in the ground state and, as a consequence, to the discovery of a gap in the spectrum. As far as metallic compounds such as LCO, YBCO, and, probably, bismuth-thallium HTSC are concerned, interatomic repulsion on the copper atom is probably reduced by shielding, and there is no Hubbard splitting. However, strong interelectron correlations that remain give rise to a distortion of the band structure as compared with calculations based on the traditional theory of the density functional. At this point, we note that, even in pure copper, band-structure calculations tend to overestimate the position of the  $d$ -band by approximately 0.5 eV. It is very likely that this effect is even greater in superconducting cuprates. If this is so, we can readily explain the shift of the photoemission curves as compared with calculations, and also the absence of antiferromagnetism in these calculations. The latter is related to the fact that the position of the copper  $d$ -band predicted by the calculations is the same as the position of the oxygen  $p$ -band, which sharply enhances  $p$ - $d$  hybridization and suppresses the tendency to magnetism. A shift of the  $d$ -band by about 1 eV would substantially reduce this hybridization.

The foregoing considerations enable us to formulate the following working hypothesis on the electron structure of high-temperature metallic oxides of copper: the copper electrons on the  $\text{CuO}_2$  planes experience appreciably interatomic repulsion which, however, is significantly suppressed

due to shielding by conduction electrons in the metallic compounds  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , etc.

As far as the semiconducting analogs of high-temperature superconductors are concerned, the presence of Hubbard splitting on copper (but not on oxygen) is more probable although even this fact cannot be regarded as firmly established experimentally.

The final resolution of the problem of the character of the electron structure of high-temperature superconductors in the normal state will have to wait until reliable experimental data become available, especially spectroscopic data (with particular attention being paid to the quality of sample surfaces).

The author is indebted to D. A. Kirzhnits and members of the Theoretical Superconductivity Group at the Physics Institute of the Academy of Sciences of the USSR for numerous useful discussions.

- <sup>1</sup> Here and henceforth we shall not be able to provide exhaustive references; we shall confine ourselves to citing examples of papers containing a particular proposition. These publications were chosen as examples more or less at random.
- <sup>2</sup> It is important to note that the discrepancy between the estimated values of  $U_d$  etc., can be quite substantial. For example, the estimates reported for  $U_d$  range from 4 to 12 eV.
- <sup>3</sup> When  $T \ll \Delta$ , the system is a dielectric with a gap of the order of  $\Delta$ , whereas for  $T \gg \Delta$  it is a  $p$ -metal.
- <sup>4</sup> It is sometimes suggested that strong magnetism is by itself an indication that there are large correlation effects, so that the single-electron (band) approach is invalid. This is not the case. Even very strong correlations producing a magnetic moment of about  $2\mu_B$  (in iron) can be reduced to merely a renormalization of the (strong) effective single-electron potential, and are therefore not inconsistent with the band approach.
- <sup>5</sup> We note that the antiferromagnetic transition line shown in Fig. 2 corresponds to the establishment of three-dimensional long-range order in the system; the antiferromagnetic correlation length remains very long even above the transition and up to the transition to the metallic state.

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Translated by S. Chomet