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ORBITALS, CORRELATION, VALENCIES IN HIGH–Tc SUPERCONDUCTORS *

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ABSTRACT

The survey is given of certain properties of high–Tc superconductors connected with the details of their electronic structure such as the kind of orbitals involved and the degree of correlation. Special attention is paid to the properties of cuprates at high doping level. The problem whether there exists a "Mott transition" at high electron or a hole concentration is discussed. We also discuss physical factors (d–p Coulomb interaction, orbital mixing) leading to the partial occupation of copper d_{x^2}–orbital. In particular we show that in localized picture $(x^2 - y^2)$ and z^2–levels in $La_{2-x}Sr_xCuO_4$ may cross at $x \approx 0.4$ which may be responsible for a marked change of many properties at this doping. The possible role of z^2–electrons in pairing is discussed in connection with some recent experiments.

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1. Introduction

The common point of view nowdays is that the clue to the understanding of high-Tc superconductivity lies in the normal properties of these systems which display many anomalies whereas their superconducting behaviour is more or less ordinary [1,2].Thus the question of the electronic structure of HTSC's in normal state is of primary importance. There are in general two competing approaches to this problem. The first one treats cuprates on the same footing as ordinary metals or superconductors using standard band theory and usual Fermi -liquid picture. In the second large group of theories main attention is paid to the strong electron correlations and a starting point is usually the Hubbard model or its generalizations e.g. d-p, or Emery model.

Two important questions arise in this connection. The first is to what extent are the correlations really important especially for metallic and superconducting compositions. And the second- which particular valence states and electronic orbitals are involved. We shall address these questions in this report not trying of course to cover all this enormous field but rather paying main attention to some of the recent experimental results and theoretical attempts to explain them which seem to be rather informative and which hopefully will help us to get a deeper insight into the nature of HTSC. To a large extent we shall concentrate on the properties of cuprates at high doping level having in mind mostly the "prototype" systems $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$.

We shall often use below an atomic or "chemical" picture [3] although the band aspects will also be touched upon.

2. Electron correlations in heavily doped cuprates:"Mott transition" under doping?

It is well established that at low carrier concentration (in undoped $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ in $YBa_2Cu_3O_6$) the copper d-electrons should be treated as strongly correlated (localized). This is responsible for insulating nature of these compounds and for their antiferromagnetism. The question arises:what would be the electronic structure of these compounds when doped. As said above there exist in principle several possibilities. From the first point of view the electrons remain largely correlated even in metallic phase (the approach initiated by P.W.Anderson and very popular now among theoreticians). The alternative concept is that these systems should be described by the usual band picture so that correlations, even if important, do not break the applicability of a more or less standard approach. The "intermediate" point of view is that one should treat these systems as essentially two-component ones consisting of correlated d-electrons of copper and nearly free-electron-like p-states of oxygen. With the inclusion of p-d hybridization these systems would then resemble to a large extent mixed valence or heavy fermion materials.

Recent experiments however disclosed yet another possibility: that the character of electronic states may change significantly with doping from correlated to a more or less band-like. The main indication that it may be the case comes from the results of the study of Hall effect in $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ [4]. In fig. 1 we qualitatively show the phase diagram of $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ together with the behaviour of the Hall constant R_H across the series of these compounds [4] (fig. 1). Note the sign of R_H and a change of it at large x.

One can interpret these data as follows: In the standard band approach in the tight-binding approximation the relevant d-p antibonding band of the CuO_2 plane would be half-filled for undoped system (fig. 2a), and it will be less than half-filled for $x \neq 0$ for $La_{2-x}Sr_xCuO_4$ and more than half-filled for $Nd_{2-x}Ce_xCuO_4$

Consequently one may expect in this approach the electron-like Fermi-surface for LaSr case ($m^* > 0$, Hall constant $R_H < 0$) and hole-like behaviour ($R_H > 0$) for NdCe system.

Experimentally at low doping the situation is just the opposite: $R_H > 0$ for Nd-Ce (at small x). The accepted explanation of this fact is that one should treat electrons in this case as strongly correlated. The conduction band then will be split into two Hubbard subbands (fig. 2b) so that the carriers introduced by doping will be holes near the top of the lower Hubbard subband in case of La-Sr system and electrons near the bottom of the upper Hubbard band in Nd-Ce.

This picture is of course rather qualitative and needs a detailed confirmation especially in view of recent XPS results (see e.q.[5]) which seem to show that this simple semiconducting-like picture should probably be modified. However qualitatively it correctly describes kinetic properties including also Hall effect [6,7].

Now, if by some reason with increasing doping we go from the correlated state (split Hubbard bands, fig. 2b) to a band-like situation (fig. 2a) we may expect the change of sign of the Hall constant which is observed experimentally. Thus one could interpret such a behaviour of R_H as a signature of a "Mott transition" (effective decrease of correlations) occurring with increasing doping.

There are several indications that it may be really the case. Some studies show that for overdoped systems when Tc goes down the samples become "more metallic" - the resistivity is lower by absolute magnitude and it loses this strange linear T-dependence which some people attribute to the effect of correlations. But probably more significant is an observation (see e.q. [8]) that Cu NMR in $La_{2-x}Sr_xCuO_4$ acquires Korringa behaviour for $x \geq 0.3$ (with a much smaller value of T_1^{-1}). All these results may be taken as a confirmation that something like "Mott transition" does indeed take place in cuprates at high doping level.

If true, this conclusion would have important implications. One should stress that according to experimental results [4] the change of sign of R_H which may be a signature of "Mott transition" coincides more or less with the disappearance of superconductivity. One may conclude that high-Tc superconductivity is somehow tied up to strong correlations; when the latter decrease we simultaneously lose superconductivity.

Two questions arise in this connection. The first is what could be the reason for a transition to a band-like behaviour. And the second- is it really the only possible explanation of the observed behaviour?

As concerning the first question one may argue as follows. In the usual one-band Hubbard model

$$H = \sum t\, a^{\dagger}_{i\sigma} + U n_{i\uparrow}\, n_{i\downarrow} \qquad (1)$$

the relevant parameter is the ratio of effective interaction U to the hopping matrix element t: for $U/t \gg 1$ the electrons are strongly correlated but for $U/t < 1$ we are back to an ordinary metal (at least in 3d-case). So to get a "Mott transition" we need that effective U/t decreases with doping. Why should it be the case?

One may think that the effective interaction U may diminish with x due to screening by extra charge carriers. It is in principle feasible for hole superconductors in which holes mostly occupy oxygen p-states. Following Zhang and Rice [9] one may argue that one-band Hubbard model (1) is still applicable in this case but with CuO_4 cluster playing role of a "site". In this case there can be some screening of the effective interaction of two p-holes on this plaquette. However it is difficult to imagine that the screening would be efficient for Nd-Ce system where the relevant carriers (extra electrons) are located on Cu and the effective U is that on copper.

Another possibility is that the effective bandwith t may increase with x. One of the reasons for this may be the dependence of the effective hopping matrix element on short range magnetic correlations e.q. in the form [10]

$$t = t_0(\frac{1}{2} + 2\langle \vec{S}_0 \vec{S}_1 \rangle) \qquad (2)$$

With the suppression of antiferromagnetic correlations with doping the effective t may increase giving rise to something like "Mott transition" (corresponding mechanism of insulator-metal transition in antiferromagnetic oxides like V_2O_3 was first discussed in [11], see also review article [12]).

However experimentally there are only indirect indications that bandwidth in $La_{2-x}Sr_xCuO_4$ increases (effective mass decreases) with doping. There exist also some experimental results which seem to contradict the picture of " Mott transition", e.g. the magnetic susceptibility increases rather than decreases with doping and becomes more Curie-like [4]. Thus summing up one still has no definite proof that correlations are strongly suppressed

Table 1

U/t	0	0.5	1	2	5	50
x_c	0	0.1	0.16	0.24	0.35	0.48

by doping. So one should ask whether there exists a possibility to explain the observed behaviour without invoking the concept of Mott transition.

Going back to fig.2 one may note that there exists a possibility of the change of sign of R_H with doping even in the limit $U/t \gg 1$: if the lower subband becomes less than half-filled, effective mass at the Fermi level would become positive and R_H <0. The calculations[7] confirm this qualitative conclusion. However R_H would change sign at $x_c = 0.5$ and not at $x_c \approx 0.35$ as in La-Sr or at even smaller value $x_c \approx 0.2$ for Nd-Ce system. One may argue however that for intermediate correlations $U/t \geq 1$ the corresponding critical value of doping may become less than 0.5. Indeed for U=0 R_H changes sign just at $x = 0$; for $U/t \to \infty$ $x_c = 0.5$. Thus one may expect that x_c would have an intermediate value for intermediate U/t (if, of course, corresponding "Mott transition" is continuous). The calculations carried out in [13] using simple Hubbard-I decoupling scheme confirm this point of view. In this approach one-electron Green functions take the form

$$G(\omega, k) = \frac{1}{2\pi}\left[\frac{A_+}{\omega - \epsilon_+(k)} + \frac{A_-}{\omega - \epsilon_-(k)}\right] \qquad (3)$$

where the spectrum of Hubbard subbands for spin σ is

$$\epsilon_\pm(k) = \frac{1}{2}(t(k) + U) \pm \frac{1}{2}\left[(t(k) + U)^2 - 4t(k)U(1 - n_{-\sigma})\right]^{1/2} \qquad (4)$$

and the residues

$$A_\pm = \pm\frac{\epsilon_\pm(k) - U(1 - n_{-\sigma})}{\epsilon_+(k) - \epsilon_-(k)} \qquad (5)$$

The critical value of doping x_c for which the effective mass at the Fermi-level ε_{FC} would change sign is given by the equation

$$x_c = \frac{1}{2\pi^2}\int_{\epsilon_-(k)<\epsilon_F} dk_x dk_y\, A_-(k_x, k_y) \qquad (6)$$

and one indeed obtains that x_c depends on U/t ; some representative results are given in table 1.

We see that the critical value $x_c \approx 0.3$ would correspond to a relatively strong albeit not infinite correlations, $U/t \approx 5$.Thus one can in principle explain the change of sign of R_H for still rather strong correlations without involving the concept of Mott transition. We may say that the question of suppression of correlations by doping remains still open. One general

conclusion however remains valid in both cases: it is clear that high-T_c superconductivity does exist in systems with correlated electrons (either just before the" Mott transition" to an ordinary metal or at still moderately correlated state). It does not tell us of course whether it is just these correlations which are responsible for superconductivity but we see at least that they are somehow very important.

The previous discussion was based on the simplest model of electronic structure of CuO_2 plane- i.e. one-band Hubbard model.In reality there may exist some important complications. The first is the apparent inclusion of both copper d- and oxygen p-orbitals [13]. However when discussing the behaviour of real systems one may think that the rich orbital structure of 3d-ions may be also significant. In particular when one looks at a crystal field level scheme of Cu (see fig. 6b below) one may expect the contribution of not only the highest $d_{x^2-y^2}$-orbitals but also of the other d-orbitals notably d_{z^2} (it becomes especially important if for doped systems Cu^{3+} valence state starts to become occupied).

One may see that z^2-orbital should be taken into account by looking at the form of corresponding wave functions, see fig.3. One sees that σ -orbitals of oxygen have a strong overlap not only with $d_{x^2-y^2}$, but also with d_{z^2} one; the corresponding matrix element is only $\sqrt{3}$ smaller, $t' = t''/\sqrt{3}$.

Thus there should be an admixture of z^2 orbitals to the states of the conduction band. One may also expect that the admixture of z^2 -states may increase with doping (see below) so that there may exist yet another possibility to explain the behaviour of the Hall effect:there may be a sort of a transition from a single-band to many -band situation under doping (see also a short remark in [1])

3.Orbital structure of copper and its change with doping

The orbital structure of cuprates was studied recently by polarized X-Ray absorption [14-16]. The L_{III} absorption - the transition $2p + h\nu \to 3d$ on copper- -is sensitive to the polarization of incident light and to the type of 3d-states occupied by holes and available for such a transition . The results show that typically there is an admixture of d_{z^2}-states of the order of 10 % in Bi 2212 systems [15,16] but it is much stronger for Bi 2223[15,17]. Bianconi noticed also an interesting and potentially important correlation between the intensity of z^2 -signal in X-Ray absorption and T_c, see fig.4. Usually T_c increases with the concentration of holes n_h (up to a certain maximum level) so one may say that n_{z^2} also scales with n_h (increases with doping) One may think in principle of three possible reasons for admixture of z^2 -orbitals. Let us discuss them consecutively.

1)Distortion of crystal structure. The standard CF level scheme (fig.6b) is valid for tetragonal coordination. However quite often the detailed symmetry of cuprates is lower than tetragonal. Thus e.g. La_2CuO_4 at room temperature is orthorhombic due to rotation of CuO_6 octahedra along [110]

axis. The local axes of CuO_6 octahedra do not coincide with the crystal axes which would mean that wrt crystal axes these will be some admixture of d_{z^2}-states.However the corresponding admixture will be small ,of the order of the distortion, i.e. < 4 % .Besides the orthorombicity in La_2CuO_4 decreases with doping whereas the admixture of z^2 -orbitals (intensity I_{z^2} of the absorption for E||c) in $La_{2-x}Sr_xCuO_4$ increases with x [15]. So the lattice distortion hardly plays main role in $La_{2-x}Sr_xCuO_4$.

Similarly the orthorhombic distortion exists in 123 systems.The O_4-plaquette around Cu in CuO_2 -plane is not a square, but is a rombus elongated along b-direction. This would also produce some mixing of $d_{z^2}$and $d_{x^2-y^2}$orbitals (cf. the situation in K_2CuF_4 [18]) However again this mixing may be shown to be small.

Finally , the most well studied in this respect Bi compounds also have rather complicated structure of CuO_2 - plane[19,17] with at least two rather different Cu-O distances [17,20] differing by 0.115 Åin 2212 and by 0.105 Åin 2223 systems . One may possibly interpret it as a consequence of pseudo Jahn -Teller distortion superimposed on the initial orbital structure dictated by the existence of 5-fold coordinated Cu. The corresponding effect in Bi systems seems to be larger than in La-Sr or in 123 but it is also hardly enough to explain large values of z^2 -occupations $\approx$ 40 % observed in Bi 2223 [15,17]

2) The second physical factors which can provide some mixing of $d_{z^2}$and $d_{x^2-y^2}$-orbitals is just the standard d-p overlap responsible for band formation. As noted above due to nonzero (and rather strong) overlap of p_σ -orbitals not only with $d_{x^2-y^2}$, but also with d_{z^2}-orbitals one should include all three of them in constructing the corresponding bands. One should also take into account possible influence of d-d correlations on the resulting form of the bands. The corresponding calculations were carried out in the mean field (LDA) approximation in [21] and with a more detailed treatment of electron correlations in [22]. The results show that one does really get some contribution of z^2 -orbitals to the conduction band states but for realistic values of parameters it is rather small, < 10 % , and it becomes even smaller with increasing Hubbard U . Thus in fig.5 we show the results of corresponding calculations for a generalized d-p model

$$H = \sum \varepsilon_z d_{zi}\dagger d_{zi} + \varepsilon_x d_{xi}\dagger dxi + \varepsilon_p p_j\dagger p_\beta + (t^\alpha_{ij} d_{\alpha i}\dagger p_j + h.c.) + U n_{i\alpha\sigma} n_{i\beta\sigma'} \quad (7)$$

where $\alpha = x, z$ and x, z stand for (x^2-y^2) and (z^2) and $t^z = t^z/\sqrt{3}$. The calculations were done for the parameters $(\varepsilon_p - \varepsilon_x) = 2.5eV$,$t^z = 1.2eV$, for different values of $\varepsilon_z - \varepsilon_x$ and U. Coulomb interaction of d-electrons was taken into account in a Hubbard-I decoupling scheme.One sees from fig.5 that the occupation of z^2 -states does really decrease with $(\varepsilon_z - \varepsilon_x)$ and with U and that in this model it would hardly exceed 10 % .(One should note

that ε_z and ε_x the Hamiltonian(7) and in fig.5 are the bare values;due to the same covalent mixind $t^{x,z}$ the actual position of these levels would change so that e.g.even for $\varepsilon_z < \varepsilon_x$ the level sequence may well be $\tilde{\varepsilon}_z > \tilde{\varepsilon}_x$: therefore for instance the situation with $\varepsilon_z = \varepsilon_x$ in fig.5 is not unreasonable. However even then one cannot expect large admixture of z^2 -orbitals due to this effect for reasonable values of U [22]).

3) The last and probably the most important physical factor which may provide rather large admixture of z^2 - states as well as its strong dependence on doping is the Coulomb interaction between d-electrons and extra holes introduced by doping. These holes in CuO_2 -plane predominantly occupy oxygen sites and will eventually change crystal level scheme of copper d-states leading even to the crossing of (x^2-y^2) and z^2 -levels [23]. The physics behind this effect is very simple and is actually similar to the one invoked by Weber [24] in his theory of the origin of pairing in high - T_c superconductors.If we have an extra hole on an oxygen site close to a given Cu, one may decrease the Coulomb repulsion of copper d-hole with a hole on oxygen by promoting d-hole from the $d_{x^2-y^2}$-orbital to a d_{z^2}-one.

The corresponding calculations were carried out in a point charge model of crystal field. We studied CuO_6 -octahedron with Cu-O distances corresponding to those in La_2CuO_4 The effect of doping was modelled by the change of effective charge of in-plane oxygens: $O^{2-} \to O^{(2-x/2)-}$(fig.6a). The decreasing charge compensate for a closer distance of these oxygens to copper so that with increasing x the situation becomes in a sense "less tetragonal": The splitting of x^2-y^2 -orbitals and z^2 -levels decreases and they even cross at $x_c \simeq 0.4$ (fig.6b). Thus we can explain by this mechanism the mixing of z^2 and x^2-y^2 -orbitals and its increase with doping . Experimentally it was noticed [15] that the splitting $\varepsilon_{z^2} - \varepsilon_{x^2-y^2}$ does indeed decrease with n_h and for $La_{2-x}Sr_xCuO_4$ it tends to zero at the compositions with the highest T_c.

The possible meaning of the correlation between z-occupation and T_c will be discussed in the next section; here we shall make a few extra remarks.

If our conclusions are correct one may expect a crossing of x^2-y^2 and z^2 -levels of Cu^{2+} in $La_{2-x}Sr_xCuO_4$ at $x \approx 0.4$. It is known that many properties of $La_{2-x}Sr_xCuO_4$ change just in this region. One is tempted to connect these phenomena. Thus the increasing contribution of z^2 -orbital at $x \approx 0.3-0.4$ may play some role in the behaviour of the Hall constant in this region discussed in the first part of this article. Further on, if there is a crossing of x^2-y^2 and z^2 -levels one would be back to the degenerate situation (one hole on the doubly degenerate (x^2-y^2) and z^2 -orbitals). But due to Jahn-Teller effect this situation is unstable and it usually leads to some structural distortions. It may be that the well known instability of $La_{2-x}Sr_xCuO_4$ for $x \geq 0.3$ is connected just with this fact (note that this system does again exist close to the composition $La_1Sr_1CuO_4$ where either the valence of copper may change or at least the sequence of d-levels may be reversed).

The correlation between T_c and z^2 -orbital occupation n_z mentioned in [15] (see fig.4) resembles somewhat the empirical correlation between T_c and the quadrupolar splitting of Cu NMR lines [8]. One may think that decrease of splitting with increasing T_c noticed in [8] is also connected with z^2 -occupation: the higher T_c - the higher z^2 -occupation i.e. the more spherical becomes d-shell and the smaller is quadrupolar splitting.

One final word concerning numerical estimates of n_{z^2}. As we have seen one may expect quite a significant contribution of z^2 -states in $La_{2-x}Sr_xCuO_4$ for large x. However similar calculations for Bi compounds (Cu in pyramids [23]) show that due to a much higher initial splitting one would need unreasonably large deviations from the standard oxygen state O^{2-}: the crossing of x^2-y^2 and z^2 -levels would occur for $O^{0.8-}$ instead of $O^{1.8-}$ in La-Sr-system. Thus although qualitatively d-p Coulomb interaction may be important in this case too, it is difficult to explain numerically large occupation of z^2 -orbital reaching ≈40% in Bi 2223 [15]. Probably in this system it is due to a simultaneous action of several mechanisms discussed above (d-p Coulomb interaction, lattice distortion).

4. Orbital structure and superconductivity

The correlation between the occupation of z^2 -orbitals and T_c noticed in [15] may be rather significant. Of course it does not imply that orbital excitations are responsible for pairing; it may well be that these two phenomena - increase of T_c and the occupation of z^2 -orbitals - are just two independent consequences of one common factor - e.q. increase of hole concentrations. However z^2 -orbital may play a more active role in superconductivity. The corresponding arguments were put forth by Weber [24] and Cox [25]. They suggested that the interatomic orbital excitations e.q. from $d_{x^2-y^2}$ to d_{z^2}-level may play a role of phonons in providing mechanism of pairing. These quadrupolar excitons with an excitation energy Δ would give in a perturbation theory an attraction $\lambda \propto |\langle x^2-y^2|V|z^2\rangle|^2/\Delta$ where V is d-p Coulomb interaction so that we could get $T_c \propto \Delta \exp\{-1/\lambda N(0)\}$ Thus the mechanism suggested in [24,25] is making use of nondiagonal matrix elements of d-p Coulomb interaction V. As discussed in the previous section diagonal matrix elements of the same interaction $\langle x^2-y^2|V|x^2-y^2\rangle, \langle z^2|V|z^2\rangle$ may also play a significant role renormalizing effective d-levels (decreasing $\Delta = \varepsilon_z - \varepsilon_x$) and eventually leading to a crossing of these levels. One may show that these terms by themselves can provide a mechanism of attraction [26].

The arguments of Vekhter go as follows. Let us parametrize the dependence of (x^2-y^2) an z^2 -levels on doping as

$$\varepsilon_{x^2-y^2}(x) = \varepsilon^0_{x^2-y^2} + ax$$
$$\varepsilon_{z^2}(x) = \varepsilon^0_{z^2} + bx \qquad (a > b) \tag{8}$$

Suppose that for one hole near a given Cu site we are still below the crossing of (x^2-y^2) and z^2-levels but close to it. The energy of two separate holes would be

$$E_{sep} = 2(\varepsilon^0_{x^2-y^2} + a) \tag{9}$$

But if both these holes turn out to be close to the same Cu site they may induce level crossing and a change of electronic structure of this site so that its energy becomes $\varepsilon_{z^2} = \varepsilon^0_{z^2} + 2b$ and the total energy is

$$E_{bound} = \varepsilon^0_{z^2} + 2b + \varepsilon^0_{x^2-y^2} \tag{10}$$

(we added the energy $\varepsilon^0_{x^2-y^2}$ of Cu site close to which the transferred p-hole was before)

As we supposed there exist for two holes a crossing of d-levels. It means that $\varepsilon^0_{z^2} + 2b < \varepsilon^0_{x^2-y^2} + 2a$ or $E_{bound} < E_{sep}$. In other words there exists an effective attraction between p-holes (decrease of total energy for bound p-holes due to crossing of d-levels near bound state).

One may easily show [26] that if we include both nondiagonal and diagonal matrix elements of d-p interaction this mechanism will operate for all values of initial splitting $\Delta^0 = \varepsilon^0_{z^2} - \varepsilon^0_{x^2-y^2}$ due to a nonlinear dependence of the lowest d-level on doping. For $\Delta \gg V$ the results coincide with those of [24,25] but here they are naturally extended to a case of arbitary Δ. In the case considered in [24,25] we were dealing with virtual $(x^2-y^2) - z^2$ transitions. Here, for small Δ we have a substantial real admixture of z^2 -states in Cooper-pairs.

One interesting consequence of this treatment is that it predicts an increase of z^2 -admixture in a superconducting state, when the pairs are formed. In a picture described above single (unpaired) p-holes stabilize $d_{x^2-y^2}$-state of copper but pairing of p-holes is accompanied (and is actually induced) by the transition $d_{x^2-y^2} \rightarrow d_{z^2}$. In this respect one should point that experimentally it was established [15] that occupation of z-orbital in Bi 2212 at 10 K is larger than at 300 K (see fig. 5). This result corresponds to a picture described above but does not tell us whether this change occurs mainly at T_c or is gradual over all temperatures. However one may draw some conclusions from the results of recent measurements of the temperature dependence of the distance Cu(2)-O(4) between in-plane copper and apex oxygen. It was shown in [20] that in both Bi 2212 and Bi2223 this distance is nearly constant at $T>T_c$ and decreases markedly below T_c. This experiment may be taken as a confirmation of the picture described above. If the pairing of holes at $T<T_c$ is really accompanied by the increase of z^2 -content one may expect just such a behaviour of Cu(2)-O(4) distance: when n_{z^2} increases apex oxygen would come closer to in-plane copper both because of the increasing Coulomb attraction and due to a strengthening of respective covalent bond.

The important role of the distance between in-plane Cu and apex oxygen and its correlation with T_c was previously noticed several times [27,28]. The recent experiments discussed above show that this correlation not only holds across the series of compounds with different composition but that the interrelation between this distance and superconductivity is more intimate. In my opinion all these general correlations taken together may serve as serious indication that the rich orbital structure of copper d-levels in particular $d_{x^2-y^2}$- d_{z^2}mixing may be an important ingredient in a mechanism of high-temperature superconductivity.

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Figure captions

Fig.1. Qualitative correlation of the phase diagram of $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ and the behaviour of the Hall constant R_H (after[4]) A.f. - antiferromagnetic phase, s.c. - superconducting one.

Fig.2. Qualitative change of the band structure with increasing electron correlations. Dashed line is a position of the Fermi -level for not very high hole doping

Fig.3. Relevant copper and oxygen orbitals in CuO_2 -plane

Fig.4. Correlation between superconducting critical temperature and occupation of d_{x^2}-hole state on Cu[15].

Fig.5. Occupation of d_{x^2}-state in a model (7) for different values of parameters

Fig.6.a) Effective charges of oxygen around Cu in CuO_6 cluster

b) Relative shift of d-levels in CuO_6 cluster with doping (ignoring the center of gravity shift).

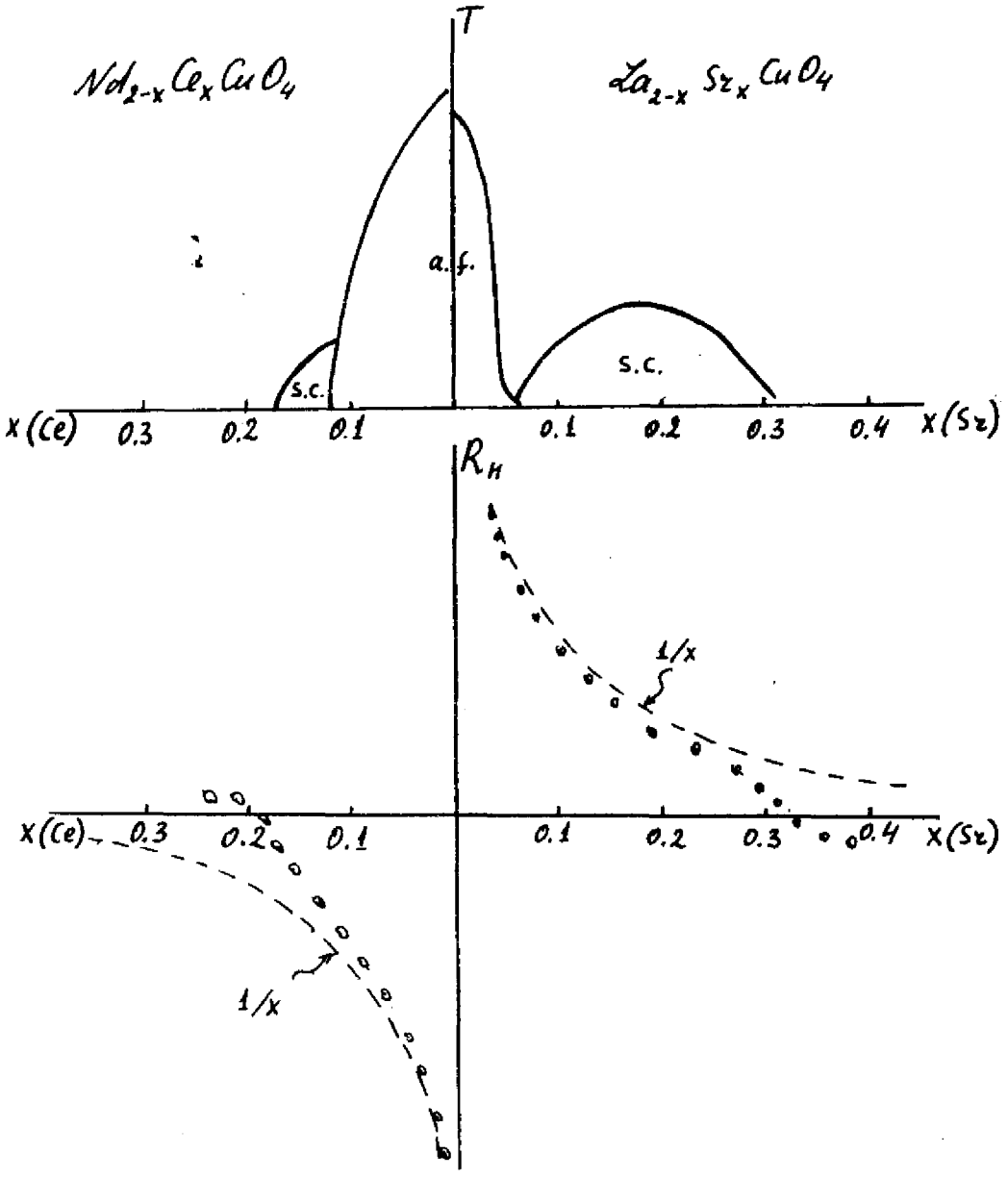

Fig.1

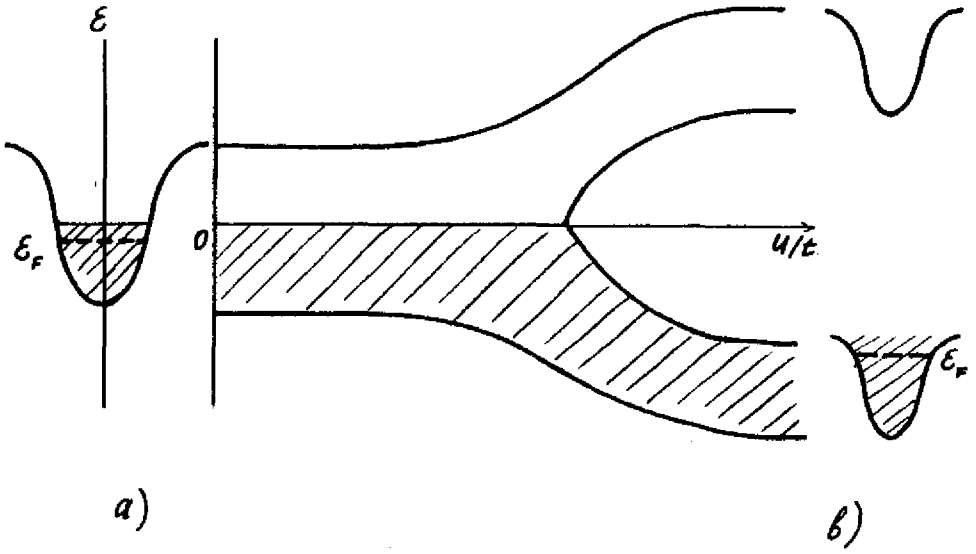

Fig.2

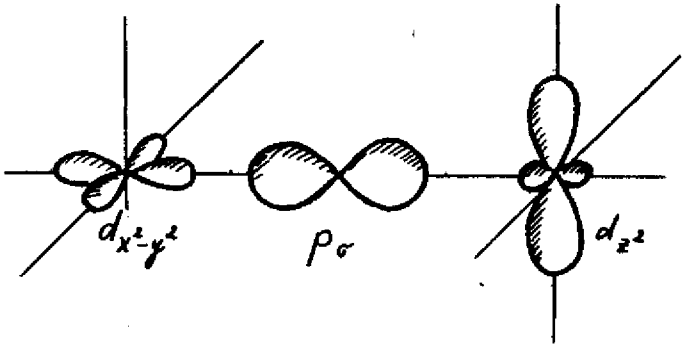

Fig.3

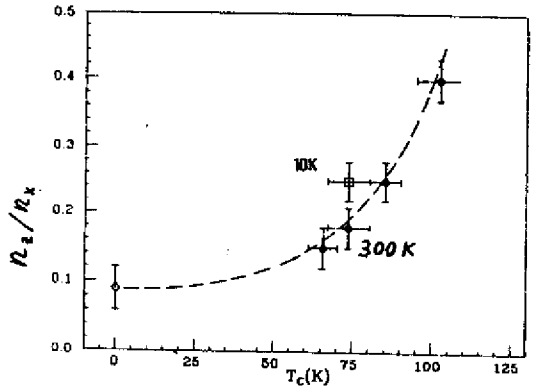
0.5
0.4
0.3
0.2
0.1
0.0
n_z/n_x
10K
300 K
0
25
50
75
100
125
T_c(K)

Fig.4

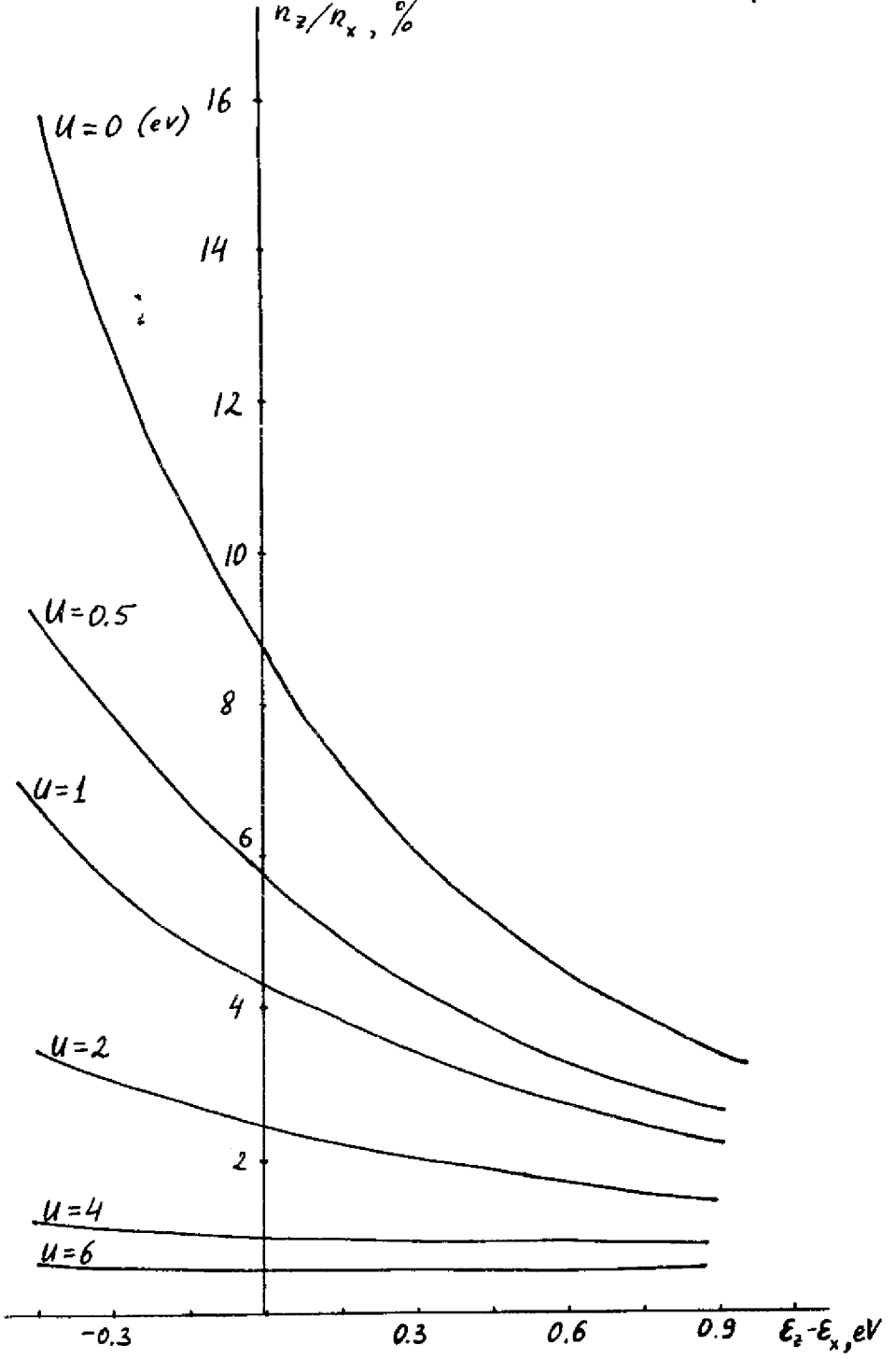
n_z/n_x, %
U=0 (ev)
U=0.5
U=1
U=2
U=4
U=6
16
14
12
10
8
6
4
2
-0.3
0.3
0.6
0.9
$\varepsilon_z-\varepsilon_x$, eV

Fig.5

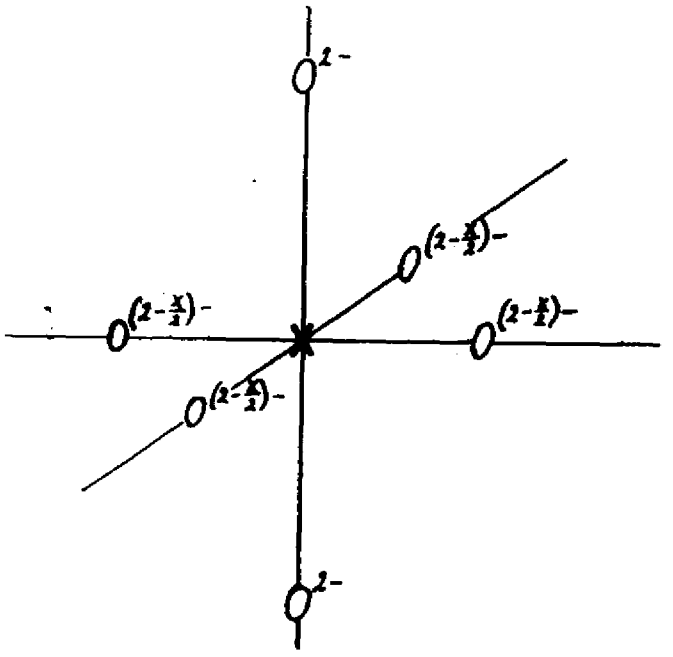
2-
(2-x/2)-
(2-x/2)-
(2-x/2)-
(2-x/2)-
2-

Fig.6a

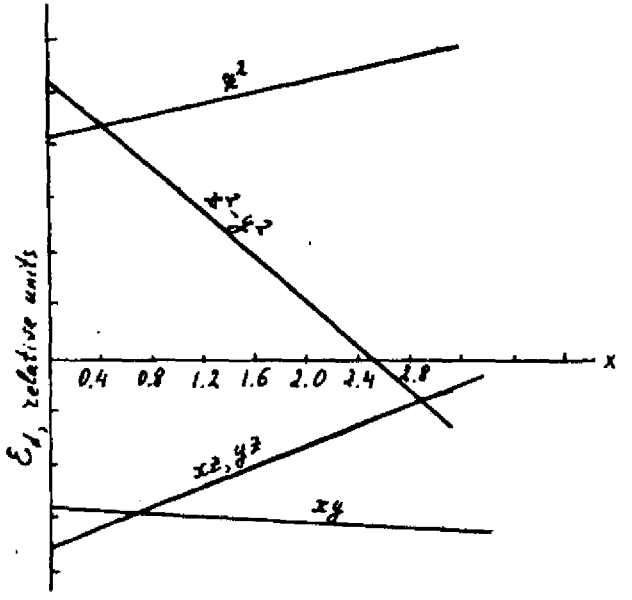
x²
x³, x⁴
x², y²
xy
0.4
0.8
1.2
1.6
2.0
2.4
2.8
x
ε_d, relative units

Fig.6b

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