Lattice Distortions and Charge Carriers in Cuprates

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A phenomenological model with itinerant bands and local states trapped by the lattice on the Cu-sites, is discussed to describe global features of cuprates. Relative energy positions of localized and itinerant states being tuned (thermodynamically or by doping), the system must undergo 1st order Mott metal-insulator transition. Decreasing the local level (from the metallic end of a stoichiometric compound), charge separation instability occurs first before the Mott transition. Crossing and hybridization between local (flat) and itinerant bands introduce a structure in density of states which may account for “pseudogap” features in cuprates. Model results in polaronic lattice effects and is rich enough to serve as a phenomenology of cuprates.

1. INTRODUCTION

More than 10 years of intense studies of HTS after the seminal discovery by G. Bednorz and A. Müller have led to unprecedented amount of experimental results. Numerous theoretical views have been developed. In that follows, an attempt is undertaken to unify physical trends and theoretical ideas in a sort of “coarse-grained” description, mixing together microscopic statements and a phenomenological interpretation.

Vast efforts are currently concentrated on interpretation of the pseudogap phenomenon seen in the so-called underdoped regime in numerous NMR-, transport-, and magnetization-experiments, and, more recently, in the ARPES studies.

As for the “overdoped” regime, a consensus is currently growing [1,2] that the farther one goes away from the “optimal” point, the clearer is the trend to a restoration of the Fermi liquid (FL) state, judging at least, by superconducting properties.

Let us take this view seriously. In the stoichiometric compound YBa$_2$Cu$_4$O$_8$, for instance, the underdoped-to-overdoped-transition may be accessed by external pressure. The 123 compound with $O_{\delta}$, although it suffers from some structural instability [3], would be another example of the material with the stoichiometric composition. If the FL views were correct, the latter, in accordance to the Luttinger’s counting theorem, should be a compensated metal, while the former- a metal with the excess of one electron per unit cell. The most popular compound, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, viewed in the FL-terms at $\delta = 0$, would provide another case of compensated metal. These differences experimentally seem to be of no large importance, henceforth, we conclude that bands or pieces of the Fermi surface (FS) involved into phenomena discussed below, in all cases are of the same origin. The usual assumption is that the conduction bands in the CuO$_2$-plane are of the utmost importance, but this detail will not be essential below.

Note that there is no signature of any presence of localized spins in these (stoichiometric) materials. On the other hand, in case of La$_2$CuO$_4$ or YBa$_2$CuO$_6$ one meets the limit of the Mott insulator. It is also known that the doping process e.g., in La$_{2-x}$Sr$_x$CuO$_4$, above $x > 0.08$ results in the metallic regime, corresponding to a large FS (with the area proportional to $1-x$, not to $x$) with rather ordinary density of states (DOS). We conclude, hence, that doping by Sr realizes the Mott insulator-to-metal transition. We expect that such the transition may occur even in stoichiometric case, provided a thermodynamical variable (such as pressure) could be found to tune the transition.

Mott himself gave theoretical arguments that such a transition for a perfect lattice must be of the $I^{st}$ order. The symmetry arguments allow to liken it to sort of a liquid-to-solid transition.

Driving the Mott transition by a doping process is not a thermodynamical procedure: dopants change the chemical composition and introduce disorder, in addition, which would mask physical phase transition.

There are currently numerous theoretical models under discussion (for a review see [4]). Many of them accept the lattice’s involvement into properties of cuprates as a key ingredient, by using the polaron-bipolaron’s concepts. Equally, there are theories exclusively based on a single band model and strong electron-electron correlations. There are also attempts to mix different views together. Remarkably enough, numerous experimental trends quite often can be equally well explained from apparently opposite points of view. It seems to the author that main difficulties with each of these theories lie in pursuing the underlying models to the extreme, where new qualitative features begin to be important. It seems that a more global view based on mixing microscopic features with a phenomenological approach could be helpful.

Such an attempt is suggested below. Note, however, that we assume importance of the lattice effects to be out of the question. Thus, the isotopic effect is seen in cuprates, although, and it is especially remarkable, on the so-called “underdoped” side. There is convincing experimental evidence for presence of lattice effects both in the normal and superconducting states (for the excellent summary see [5]). It is our hope to show that other theoretical views may stem out of these notions.
2. MODEL

We distract ourselves from the disorder introduced by dopants, and address the metal-to-insulator-transition issue as if it could have occurred in a stoichiometric material. The presence of localized Cu$^{2+}$ states in a stoichiometric material is considered as a hallmark of the insulator phase. To describe the Mott transition, we consider the model first suggested in [6]. This model has been an extension of the intuitive notions which have led Bednorz and Müller to their discovery. It is a “two component” model. It has been shown in [6] for the first time that the Mott phase transition must be preceded by the charge phase separation instability, which plays a key role below.

In the model there are two types of electronic (hole) sites. The localized ones are basically associated with the each Cu-sites (in the plane). If a local level with an energy $\varepsilon_f$ was occupied by one hole ($d^2$; Cu$^{2+}$), being well below any “empty conduction” band, this state would correspond to the insulating end. On the other end, in the ideally metallic state itinerant bands are properly filled up. There are no holes on the levels $\varepsilon_f$. Level $\varepsilon_f$ being tuned down, holes may begin to occupy the local states by thermal activation, or, if $\varepsilon_f$ goes below the initial chemical potential, a non-zero concentration of occupied local centers appears even at $T = 0$. The physical idea for charge phase separation was that an occupied center inevitably produces local lattice deformations. Two levels may relieve elastic energy by coming closer to each other. Hence, the tendency to form clusters (the charge-phase separation) would be an immediate consequence of such an attraction which, however, is limited by the electroneutrality condition. Therefore clusters may exist in a virtual form, resulting in a “foggy” state as described in [6]. (If the electroneutrality can be achieved by redistribution of mobile oxygen ions, the actual phase transition may occur as it, in fact, takes place in the oxygen rich La$_2$CuO$_{4+\delta}$.

The charge phase separation instability at small enough $|\varepsilon_f|$ is not to be confused with the Mott transition. Although the lattice energy brings local centers together, the Coulomb repulsion still keeps them apart. The clusters mentioned above are rather loose formation (on the scale of two-four interatomic distances, as judged from the miscibility gap value $\delta = 0.06$ for the phase separation in the oxygen rich La$_2$CuO$_{4+\delta}$). The energy barrier related to the Mott transition, corresponds to the energy cost of bringing local centers close together. For that the level $\varepsilon_f$ must sink deep down into the filled-up band.

The concentration of populated centers, $n_f$, is determined by the obvious relation:

$$n_f + n_h = n_0$$

(1)

where $n_0$ is the total number of holes per unit cell. There is no double occupancy on the local site:

$$n_f = 2e^{-(\varepsilon_f - \mu)/T} \cdot \left(1 + 2e^{-(\varepsilon_f - \mu)/T}\right)^{-1}$$

(1')

The number of the hole-occupied local centers is exponentially small at $\Delta = \varepsilon_f - \mu > 0$ and $T \ll \Delta$. On the other hand, it is easy to see from (1, 1') that at $T \gg |\Delta|$: $n_f \propto (T/\mu_0) \ln (\mu_0/T)$.

Scattering of the band holes by these centers is one of the sources of resistivity at high enough temperatures.

3. HYBRIDIZATION AND FERMI SURFACE

Leaving aside for a while center’s tendency to cluster (which is due to lattice effects and is to be characterized by another energy scale), one may consider the problem of local centers in frameworks of the periodic Anderson model, if a hybridization between localized and itinerant states is present. One should be cautious, however. Our assumption was that local levels if occupied by a hole, produce local deformations and may be due to the latter itself, at least to some extent. In other words, a polaronic aspect is already here. On the other hand, the thermodynamical equilibrium in eq.(1) establishes itself through exchange by holes between itinerant and local states. Therefore, the Anderson model is applicable to the extent that hopping, $V$, is large enough to neglect a slow motion of the lattice degrees of freedom. Hence, the assumption

$$V > \omega_0$$

(2)

where $\omega_0$ is a characteristics phonon frequency scale.

The periodic Anderson model has no exact solution yet. However, the basic physics, sufficient for the discussion here, becomes clear from the mean field solution [7,8]. Namely, let $\varepsilon(k)$ be the initial band spectrum, and write the hybridization Hamiltonian in the form:

$$\sum_k \tilde{V}_k (\hat{c}_{k}^\dagger \hat{d}_k + \hat{d}_{k}^\dagger \hat{c}_k)$$

(3)

where the “bare” hybridization comes together with the factor $(1 - \bar{n}_f)^{1/2}$ accounting for single occupancy of the $\varepsilon_f$-level:

$$\tilde{V}_k = (1 - \bar{n}_f)^{1/2}V_k$$

(4)

($\bar{n}_f$- the average occupancy of the $\varepsilon_f$-level). For the hybridized spectrum one obtains

$$\varepsilon_{\pm}(k) = \varepsilon_f + \frac{1}{2}(\varepsilon(k) - \varepsilon_f) \pm$$

$$\sqrt{(\varepsilon(k) - \varepsilon_f)^2 + 4|\tilde{V}_k|^2}$$

(5)

The chemical potential lies inside the $\varepsilon_-(k)$-“conduction” band ($T = 0$) preserving the total
number of carriers. Hybridization between one flat ($\varepsilon_f$) and one dispersive band results in only minor changes of the FS at $\varepsilon_f > \mu_0$ ($\mu_0$=the bare chemical potential), while the “flattening” of the $\varepsilon_-(\mathbf{k})$ at $\varepsilon_f < \mu_0$ increases rapidly when $\varepsilon_f$ goes deeply enough under $\mu_0$. The new Fermi momenta, $\mathbf{k}_F$, may then lie far apart from the “crossing” points, $\mathbf{k}_0$, defined by $\varepsilon(\mathbf{k}_0) = \varepsilon_f$. Recall that in the mean field approximation the “new” FS is still determined from conservation of the total hole number.

The Green function for the conduction band is of the form [8]:

$$G_c(\mathbf{k}, \omega) = \frac{\nu_k^2}{\omega - \varepsilon_-(\mathbf{k})} + \frac{\nu_k^2}{\omega - \varepsilon_+(\mathbf{k})}$$  \hspace{1cm} (6)

where the factors, $\nu_k$, are, as usual:

$$\nu_k^2 = \frac{1}{2} \{ 1 - (\varepsilon(\mathbf{k}) - \varepsilon_f)/E(\mathbf{k}) \}$$  \hspace{1cm} \text{(here $E(\mathbf{k})$ stands for the square root in (5)).}

Allusions to recent low temperature ARPES-results [1,2,9] are self evident. First of all, factor $\nu_k^2$ smears away the sharpness of $\mathrm{Im}G_c(\mathbf{k}, \omega)$ at the Fermi surface on distances $|\varepsilon(\mathbf{k}) - \varepsilon_f| \sim |V_k|$. Secondly, one may have chosen an anisotropic $V_k$, say:

$$V_k = V_0 (\cos k_x a - \cos k_y a)$$  \hspace{1cm} (8)

Under assumption (8) most profound effects are expected to take place in a vicinity of the point $(0, \pi)$ of the Brillouin zone. Changes in the shape of FS certainly depend on the “bare” spectrum, $\varepsilon(\mathbf{k})$, near $(0, \pi)$. A more detailed discussion will be published elsewhere. Here we content ourselves with the remark that the decrease of the residue, $\nu_k^2$, in eq. (6) at approaching $\mathbf{k}_F$ across the intersection point, $\mathbf{k}_0$ ($\varepsilon(\mathbf{k}_0) = \varepsilon_f$), qualitatively accounts for smearing of the normal state excitation peak and appearance of the “leading edge” feature seen in the ARPES-experiments [1,2] for the 2212-compound along the X-M-direction. If the above is indeed related to phenomena seen in [1,2,9], one may expect $V$ of order of 10-40 meV, depending on the material.

Further “heaviness” (flatness of the $\varepsilon_-(\mathbf{k})$-band at $\mathbf{k}_F$) would proceed with the further sinking of the local level into the broad band resulting in the increase of the density of states and other Kondo-like features well known from the Heavy Fermions (HF) physics. It suppresses charge fluctuations by reducing $V_k$ and breaking down (2). The Born approximation ceases to be valid, and non-adiabaticity results in the polaronic factors of the form

$$\exp(-W/\omega_0)$$  \hspace{1cm} (9)

(with $W$ being on the bandwidth scale) weakening the rate of transitions between localized and itinerant states.

The physics of mixed valency would not work anymore because transitions between occupied and unoccupied states for the local center now involve inelastic lattice processes. The structure of the conduction bands of eq. (5) around $\mathbf{k}_F$ gets “saturated” at $V_k \sim \omega_0$. The flat incoherent portions correspond to polarons which may be thermally activated to form an “occupied site” in a vicinity of the Cu-ions. Quantum-mechanically, their evolution is slow (i.e., is on the $\omega_0$-scale).

4. CLUSTERS

As mentioned above, there is a tendency for the occupied local centers to cluster gaining in the elastic (lattice) energy. On the other hand, the Coulomb energy prevents occupation of local centers on adjacent Cu-sites. Therefore, such a cluster being a nucleation center of a new phase, is actually a rather complicated object which may live on a time scale even longer than $\sim \hbar/\omega_0$. Lattice and charge degrees of freedom are strongly coupled in it. However, it is important to emphasize that such an object cannot reach a macroscopic scale without causing a violation of the electroneutrality in underlying lattice [6,10]. Here lies the major difference with notions regarding formation of self-trapped polarons or bipolarons. The cluster may be comprised of a large number of occupied local centers but still has a finite life time for its existence.

There is no shortage in theoretical studies of “negative-U” centers, or superconductivity based on mixed valence or bipolaronic mechanisms [5,11]. In our view, they all suffer from too specific assumptions. In particular, they do not include the interplay between lattice and the physics of the periodic Anderson model.

It seems that ideas used for treatment of nuclear reactions in heavy nuclei may provide us with a helpful phenomenological approach. The Bohr’s concept of a compound (composite) nucleus assumes that a scattering or a nuclear reaction, (i), passes through the initial stage at which an incident particle colliding with a nucleus, is first trapped by it, exchanging by energy with other particles inside. At the final stage (f) the compound nucleus emits a few over particle, or the same particle. For a specific channel (i, f) the partial amplitudes, $f_{if}(\omega)$, may be written in the form [12]:

$$f_{if}(\omega) = \frac{\Gamma(\gamma_{if}/k_F)}{\omega - E_0 + \Gamma}$$  \hspace{1cm} (10)

where $\gamma_{if}$ is a matrix element for a specific “reaction”, while $\Gamma$ represents the total width of the resonance at some $E_0$. The contribution from scattering on clusters into the imaginary part of the self-energy is then

$$\sum_{(\omega, \mathbf{k})} \propto \sum_{f} \int d\omega' d\mathbf{k}' |f_{if}(\omega - \omega')|^2.$$ \hspace{1cm} (11)
Summation (over $f$) in (11) corresponds to all possible processes at interaction of an electron, $\mathbf{k}$, with a cluster. At least at high temperatures the main contribution into the e-e-scattering would be due to inelastic processes.

5. SUPERCONDUCTIVITY CHANNEL

Let us discuss in some details the Cooper channel. Note that, according to (3), two electrons ($\mathbf{k}$, $-\mathbf{k}$) join a cluster through hybridization matrix element, $V$. Generally, not only two (as in bipolaron approach) but any number of particles may be virtually trapped into the cluster, including odd numbers.

Scattering in the Cooper channel can be singled out with respect to others due to the Cooper phenomena itself which is the basis of the BCS-theory. Another possibility, in Eq. (10) the resonance amplitude prevails in the two particle channel. The latter sounds rather similar to current ideas regarding “pre-paired” states or to the bipolaronic physics. (Virtual two-particle bound states have first been introduced in [13]). Note, however, that unlike the concept of stable bipolarons, these states may be only temporarily occupied, according to (10).

If, as we assume, the “attraction” in the Cooper channel is due to the tendency to cluster, it is worth mentioning that the mere assumption of anisotropic hybridization, i.e. $V_{\mathbf{k}}$ from eq. (8), is already enough to produce symmetry of, at least $|\Delta(\mathbf{k})|$, similar to that one of the pseudogap.

In the classic BCS-theory the Cooper channel is singled out by the logarithmic singularity, $g_{\text{eff}} \ln (\tilde{\omega}/T_c) \sim 1$, where $\tilde{\omega}$ is a cut-off and $g_{\text{eff}}$ is the effective interaction strength. In frameworks of the above scheme, in the metallic regime $\varepsilon_f$ is first well above the chemical potential (and so is $E_0$ in (10)). With $\varepsilon_f$ going down, $\tilde{g}_{\mathbf{k}}-\mathbf{k}$ in (10) ($\propto g_{\text{eff}}$) increases and so does $T_c$. In the BCS-like expression each of $\varepsilon_f$, $E_0$, and even $\Gamma$ from (10) may play the role of a cut-off, $\tilde{\omega}$. It is more difficult to interpret the superconductivity in terms of a BCS-like picture on the “underdoped” side. The decrease of $T_c$ may be ascribed to the disruption of communication between itinerant electrons and increased clusters of the “new phase” (the polaronic factors in eq. (9)). Experiment shows the most pronounced isotope effect namely in the “underdoped” regime, which qualitatively agrees with this speculative idea.

6. STRIPES

The phase separation has been considered so far as a virtual process in a stoichiometric material driven by motion of the localized level, $\varepsilon_f$, downward into the conduction band. An amount of the “foggy” phase, however, may result in sort of self-organized intermittent structure, which currently became a very active topic [14,15]. Although lattice effects may easily produce even a static super-structure, including stripes, there are no means to address the issue on a quantitative basis, especially, if disorder is to be taken into account. The most direct evidence favoring a mechanism of stripes formation, is the physical phase separation which occurs in the oxygen-enriched La$_2$CuO$_{4+\delta}$. From $\delta \simeq 0.06$ one may estimate effective distance between single occupied Cu-sites as two-four lattice distances. Superstructure for the oxygen-rich phase has been seen, indeed, in neutron experiments both along the $c$- and in-plane-directions [16,17].

7. CONCLUSIONS

We suggest a unifying view for different regimes in cuprates on the metallic side of the Mott transition in terms of the relative position of a localized level, $|\varepsilon_f|$, assumed to reside mostly on the Cu-sites, with respect to the chemical potential in an itinerant band.

This view has already led to the conclusion [6] that a charge phase separation is to precede the Mott transition due to the obvious fact that lattice energy of a few such local sites would diminish by forming clusters.

The size of clusters being limited by the electroneutrality provision, is probably rather small. As the result, the clusters may form a “foggy” state, where quantum mechanical fluctuations play an important role. Among options to minimize the Coulomb effects by forming static or quasi-static periodic structure, stripes are one of possibilities. The charge phase separation manifests itself in oxygen-rich La$_2$CuO$_4$.

Intersection of the flat “band” formed by local levels, with an itinerant band results in peculiarities of the density of states, reminiscent of the “pseudogap” phenomena, if an appropriate anisotropic hybridization is present.

Although there are many polaronic features implicitly involved into the phenomena, polarons or bipolarons themselves, as stable charge carriers, are not necessary for the main physics.

Mechanism of superconductivity in which pairing goes through the virtual trapping of the Cooper electrons by clusters, was discussed in a phenomenological manner.

For different regimes the suggested view may be reconciled with a number of microscopic models.

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