Interplay of Externally Doped and Thermally Activated Holes in $La_{2-x}Sr_xCuO_4$ and Their Impact on the Pseudogap Crossover

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We presented the recent Hall effect data for a number of carriers in $La_{2-x}Sr_xCuO_4$ as the sum of two components: the temperature independent term $n_0(x)$, which is due to external doping, and the thermally activated contribution. Their balance determines the crossover temperature $T^*(x)$ from the marginal Fermi liquid to pseudogap regime. The activation energy $\Delta(x)$ for thermally excited carriers equals the energy between the Fermi surface "arc" and the band bottom, as seen in angle-resolved photoemission spectroscopy experiments. Other implications for the (T, x)-phase diagram of cuprates are also discussed.

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The unifying feature for all cuprates is the presence of one or more CuO_2 planes. The consensus is that the in-plane electronic constituents, namely, the Cu d^9 levels and the oxygen p orbitals determine all cuprates' physics [1,2]. Even this simplified model turns out to be difficult for a complete theoretical analysis, and the properties of cuprates remain far from being understood. Below, from the experimental standpoint, we address mainly the properties of the single-plane cuprates $La_{2-x}Sr_xCuO_4$ (LSCO), the materials best studied so far.

The transition from the Mott insulating state into a metallic and superconducting state is driven in cuprates by external doping. We note that doping is *not* the thermodynamic path for metal-insulator transition.

Initially added holes go onto the oxygen sites, since the Cu(d^9) and the oxygen's levels in the parent antiferromagnet La_2CuO_4 are separated by a "charge transfer gap" of order ~1.2–1.5 eV [3]. It is less obvious with the increase of concentration x, because charges of dopant ions result in important changes in the system's energy balance. Indeed, already at rather small x [as seen from the angle-resolved photoemission spectroscopy (ARPES) data at $x \sim 0.03$ [4]] it is more proper to resort to a bands' description, at least, for the oxygen bands. This gives rise to the hybridization between oxygen and Cu levels [the Cu(d^9) level tends to partially conserve its local character owing to a strong tendency to the Jahn-Teller polaron formation inherent in the d^9 configuration]. Occupied neighboring Cu(d^9) sites experience strong interactions via mutual local lattice distortions. As to the exchange spin interactions, it is now clear that they play a secondary role by coupling spins on the adjacent Cu sites antiferromagnetically [5,6].

The fundamental question, however, is whether the Sr-doped holes unambiguously determine the number of charge carriers in LSCO. It has been the subject of intense research since the early days of the high-T_c era, mainly by means of measuring the Hall coefficient R_H as a function of the dopants' concentration x and the temperature (see, e.g., [7]). Thus, already in 1994 it has been established [8,9] that R_H in LSCO rapidly decreases in the temperature range up to 1000 K, as if the effective number of carriers significantly grows up with the increase in temperature. The recent Hall effect data $R_H(x, T)$ measured in the normal state of $Bi_2Sr_{2-x}La_xCuO_6$ in high fields seemed to indicate that the effective number of carriers exceeded the total number of doped holes even at low temperatures [10].

The notorious "pseudogap" (PG) feature further complicates the matter. The (T, x) plane for cuprates, e.g., $La_{2-x}Sr_xCuO_4$, is subdivided into two main parts by a crossover line $T^*(x)$ (see, e.g., [11]). To the right from $T^*(x)$ lies the so-called marginal Fermi-liquid (MFL) regime [12] that seems to merge with the traditional FL at even larger x. The area on the left-hand side is known in the literature as a "PG regime." Although no consensus exists yet regarding details, the PG regime seems to be spatially inhomogeneous. In particular, it was suggested (see discussion and references in [13]) that the $T^*(x)$ is the *line* for the start of a 1st order transition frustrated by the electroneutrality condition in the presence of rigidly embedded Sr ions. Although the PG regime may bear a dynamic character, the local carriers' concentration in the system below $T^*(x)$ would vary in space and time. Analysis of the NMR data in [13] confirmed the two-component character of the PG regime.

In the interesting paper of [14] the Hall coefficient in $La_{2-x}Sr_xCuO_4$ has been remeasured for the broad range of Sr concentrations and up to 300 K. A decrease with temperature in the value of $R_H(T)$ is ascribed [14] to the thermal excitation of holes onto the "flat bands" near the van Hove (vH) singularities. ARPES data [15,16] show that flat bands in underdoped cuprates move upward and get closer to E_F with the x increase. Broadly speaking, the

emerging picture, again, would lead to a two-component description, this time, in terms of the "patches" in the momentum space: the ones near the excitations "arcs" on the nodal Fermi surface (FS) pieces [15,16] and the others at the vH points. Missing is the explanation why thermally excited holes would come about only from the vicinity of the $(0, \pi)$ points. In the band description all electrons with energies below the chemical potential participate in thermal repopulation. The vH singularity in the density of states (DOS) is too weak to single out contributions from the very bottom of the band.

Below we discuss [14] and other recent experiments that shed light on the problem of the number of carriers, their nature, and the stability of the Cu d^9-hole configuration, the latter being responsible for the existence of local spin $S = 1/2$ at a given Cu site. We analyzed experimental data on the Hall coefficient at elevated (up to 1000 K) temperatures [8,14,17] and found that in broad ranges of x and temperatures the data for carriers concentration from the Hall measurements n_{Hall} can be presented surprisingly well in a form

$$n_{\mathrm{Hall}}(x, T) = n_0(x) + n_1(x) \exp[-\Delta(x)/T]. \qquad (1)$$

[It is worth mentioning here that Eq. (1) describes the new results [18], too.] The x dependence of $n_0(x)$ is given in Fig. 1. As for $n_1(x)$, aside from the data scattering at small x, it is practically constant (~ 2.8) up to the vicinity of $x = 0.2$, where it drops abruptly. Note considerable deviations from the linear in x behavior in n_0. Although numerous factors (band anisotropy, interactions, and various scattering processes, etc.) can complicate the interpretation of the Hall effect data, it is known, however, that interactions drop out in the isotropic Fermi-liquid model [19] and even for a nonparabolic but isotropic shape of the FS [20], as well. In Fig. 1 deviations from the linear dependence begin rather early, being noticeable already at $x = 0.07$. The holelike FS "locus," as seen by ARPES, being centered at (π, π), remains practically isotropic up to $x = 0.11$ [15,16]. Therefore even the temperature independent amount of carriers grows faster than x with doping (similar to the data [10] for $Bi_2Sr_{2-x}La_xCuO_6$). Unlike the Hall effect data for $n_0(x)$ where common interpretation becomes unreliable at larger x, the activation character of the temperature-dependent term in Eq. (1) is the thermodynamic feature and, as such, should not be sensitive to the model. At small x, indeed, the exponential contribution describes carriers activated from levels lying deeply below the chemical potential.

In principle, activated carriers could come from different regions of the material because of its inherent nonhomogeneity in the real space. We assume, however, that activation takes place from some deeper parts of the LSCO energy spectrum. Indeed, according to the ARPES data [4,16,21], in addition to the "coherent" states at the nodal arcs on the FS locus at the chemical potential, in the vicinity of $(0, \pi)$ (and other vH points) there are present deeply lying energy bands featured by the high DOS. We suggest with [14] that electrons are thermally activated from the states near vH points and go into the nodal arcs at the chemical potential on the FS locus [4,16], where the activated electrons join the liquid of mobile carriers. Unlike [14], however, we first check this assumption quantitatively. We plotted in Fig. 2 data for the energy gap $\Delta(x)$ of Eq. (1) together with the ARPES data for the energy separating the underlying vH bands from the Fermi level.

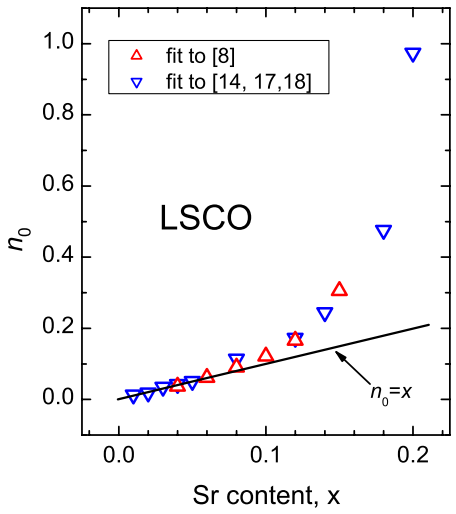

FIG. 1 (color online). The doping dependence of $n_0(x)$, obtained by the fitting of Eq. (1) to the experimental Hall coefficient temperature dependence [8,14,17,18] for LSCO.

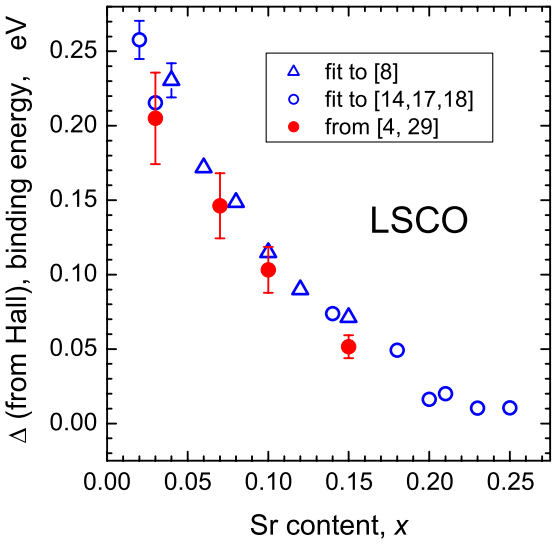

FIG. 2 (color online). The activation energy $\Delta(x)$ obtained by the fitting of Eq. (1) to the experimental Hall coefficient temperature dependence [8,14,17,18] for LSCO (open circles and triangles), vs the energy separating the underlying vH bands from the Fermi level (binding energy) which was deduced from Fig. 3(b) of [4] and Fig. 3 in [16] for various x (solid circles).

In our Fig. 2 we displayed four points for binding energy: three of them for 7%, 10%, and 15% doping were adopted from Fig. 3(b) of [16] and that one for 3% was deduced from Figs. 1(d) and 2(d) of the same reference. Moreover, same values of the binding energies for 3%, 7%, and 15% doping were estimated from the more recent intensity plots of [4] [Figs. 3(a)–3(c) correspondingly]. We assume the relative error to be about ±15%; the error bars for lower doping are considerably larger than for the optimal one. Note that the relative error for values of $\Delta(x)$ from Hall data are typically less than ±5%. For both quantities the extracted values are in excellent agreement, thus giving the strong argument in favor of our interpretation.

Note that the mere band singularity in DOS would not be enough to account for the thermal activation contribution in Eq. (1). We argue that in ARPES one measures only a part of the total energy of an electron because the latter is imbedded into the lattice. Thus, implicitly, we invoke a lattice trapping or localization of electrons near the vicinity of the vH points. (The importance of lattice or polaronic effects on the interpretation of ARPES data was pointed out also in [22]. The order of magnitude for the lattice component is estimated below as a few tens meV.)

Equation (1) describes well the Hall data [8,14,18] practically in the whole available temperature interval without revealing sharp features or changes in the behavior near the line of the hypothetical 1st order transition $T^*(x)$, mentioned above. We stress again that such features are not expected at the onset of the transition, because the transition does not fully realize itself: the frustrations caused by the Coulomb forces allow only fluctuations leading to a dynamical two-phase coexistence in the PG regime, instead of the macroscopic phase segregation. Consequently, $T^*(x)$ marks only a crossover between the left- and right-hand sides of the (T, x)-phase diagram for LSCO cuprates. We find it interesting that a good fit for $T^*(x)$ is obtained just from the comparison when the number of doped carriers x and activated ones become approximately equal:

$$T^*(x) \approx T_0(x) = -\Delta(x)/\ln x. \qquad (2)$$

In Fig. 3 we plotted $T^*(x)$ defined according to Eq. (2) and the crossover temperatures obtained differently from other experiments.

The decomposition into two contributions, Eq. (1), covers data [14] in the PG regime at smaller temperatures [14] and even reproduces well the low temperature Hall measurements in the high fields normal state of LSCO [25]. To which of the two PG subphases is one to correlate the Hall effect data? (The same question concerns the ARPES measurements.)

It seems reasonable to connect the Hall coefficient R_H with properties of the metallic component. Indeed, if stripes were pinned by defects, and the conductivity along the stripes were expected to bear the 1D character, that should suppress conduction in the transverse-to-stripes direction. These arguments have been tested [26] for the temperature dependence of the Hall coefficient in the Nd-doped LSCO material with different Sr content. The Hall coefficient $R_H(T, x)$ [26] has a characteristic drop at temperatures $T \sim 70$–100 K, at least for underdoped compositions. One finds similar features in the data [25] at the same temperature scale. The effect is strongest for $x = 0.12$, where the fraction of the stripe phase should be maximal.

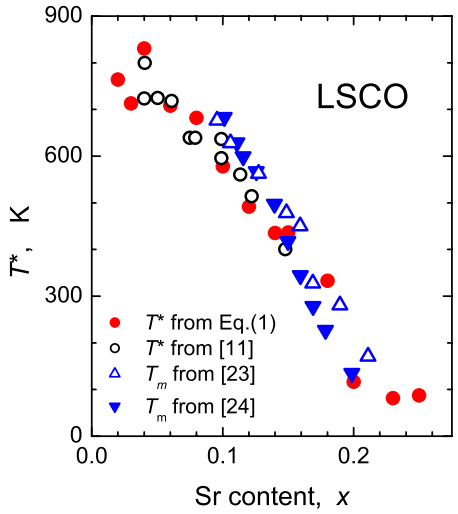

FIG. 3 (color online). The PG crossover temperature $T^*(x)$ obtained with the help of Eq. (1) with the activation energy $\Delta(x)$ shown in Fig. 2 (solid circles); from the crossover temperature of the resistivity curves (open circles); as the temperature (T_m) corresponding to the maximum of the magnetic susceptibility measured in [23] (solid triangles) and [24] (open triangles).

As to ARPES, as a fast measurement, it provides the instant snapshots of deep energy levels for metallic islands that probably does not change essentially when taken above or below $T^*(x)$ [27]. Making use of the excellent agreement in Fig. 2 of the Hall activation energy with the ARPES results [4,16], we have extended our gap analysis in terms of Eq. (1) to the data [14] at higher x. Notably, the result shows a plateau at x just above ~0.2 in Fig. 2. According to [4,15,16], the FS locus experiences the topological change from the holelike "FS" centered at (π, π) to the electronlike one centered at (0, 0) very close to $x = 0.2$. The "gap" seen in Fig. 2, obtained from the interpolation of Eq. (1) into this concentration range, produces in our opinion, an estimate for inherent energy scales of lattice effects (~ 10 meV).

In the ARPES experiments one starts seeing the FS locus in LSCO already at $x = 0.03$. However the FS obtained in this way covers a large area of the Brillouin zone that then varies in "agreement" with the "Luttinger count" $1 - x$ [15]. Since it is established [4] that the propagating (coherent) excitations come about only in narrow arcs near the nodal directions, there are no contradiction between [15] and the trend seen in Fig. 1.

It is worth mentioning a peculiar resistivity feature in cuprates that is fully consistent with our general line of arguing. For extremely small Sr doping the thermal excitation of carriers gives rise to the temperature independent contribution to conductivity. It comes about due to the fact mentioned above that each thermally activated charge carrier creates a local defect in the CuO_2 plane. These defects play the role of scattering centers and contribute to resistivity at high temperatures. The density of these defects equals the density of charge carriers produced by thermal activation. Hence the same activation energy governs the lifetime of charge carriers. It results in temperature independent resistivity. This property manifests itself experimentally as saturation of the temperature dependence for resistivity at extremely low doping [17,18].

Contributions to the activated component of the Hall coefficient in Eq. (1) come from the vicinity of the vH points where a spectrum shows a pronounced 1D behavior. That gives another argument for emptied sites to reveal the localized behavior. We suggest that activated carriers in Eq. (1) may add a temperature independent contribution into resistivity at high temperatures as well.

A simple consideration that does not compromise the ideas of the MFL [12] but may still be essential for understanding the linear in T resistivity *well below* T^* (e.g., for such a doping level as $x = 0.15$ [28,29]) is that deeply inelastic scattering processes, by removing one of the conservation law's constraints in the ordinary FL approach, would immediately produce such a linear in T dependence.

At last, we note the behavior $n_0(x)$ in Fig. 1 near $x \sim 0.2$ [we mentioned above the drop of $n_1(x)$ at the same x]. This concentration has already been identified in [30,31] as an emerging quantum critical point for cuprates. Appearance of the plateau in Fig. 3 at exactly the same x is in correspondence with this expectation.

To summarize, we have decomposed the effective number of carries in $La_{2-x}Sr_xCuO_4$ for the whole range of x and temperatures into the sum of two components: the T-independent contribution $n_0(x)$ and the thermally activated term. We found the quantitative agreement between the activation energy and the ARPES results for the position of the so-called flat band. The well-defined activation gap $\Delta(x)$ is in favor of localized levels formed by electronic states in the vicinity of the vH patches.

The actual concentration of mobile carriers is not equal to the number of the externally introduced holes. Thus spins are not fixed at the given Cu sites and may move along, further confirming that the PG regime is a regime of dynamically coexisting and competing subphases [13].

Finally, the balance between the two components in the number of carriers determines T^*, the line for the PG crossover, in good agreement with the results of other experiments.

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