PHYSICAL REVIEW B **70**, 052501 (2004)

Chemical potentials of high-temperature superconductors

Mohamed Azzouz
Department of Physics and Astronomy, Laurentian University, 935 Ramsey Lake Road, Sudbury, Ontario, P3E 2C6, Canada

(Received 26 March 2004; published 3 August 2004)

I analyzed some of the available experimental data on the chemical potential within the rotating antiferromagnetic theory (RAFT) of high-temperature superconductors. I found that in order to interpret electron-photoemission data the doping dependence of the bare chemical potential μ has to be considered, but in order to interpret the work function data for the temperature dependence an effective chemical potential μ_{ef} that takes into account the effect of Coulomb repulsion has to be considered. A discussion of this finding within, and a comparison of RAFT to Anderson's spin-charge separation theory is made.

DOI: 10.1103/PhysRevB.70.052501 PACS number(s): 74.25.Fy, 74.25.Ha, 74.90.+n

Three issues related to the electronic structure in high-temperature superconductors (HTSC's) were examined in this work. These are the doping and temperature dependences of the chemical potential, and the temperature dependence of doping p. According to RAFT,[1,2] μ is controlled by the atoms residing between the CuO_2 layers, and is therefore temperature independent. This treatment yields excellent agreement for μ versus p with experiment.[3,4] However, Rietveld *et al.* measured the chemical potential in $YBa_2Cu_3O_{7-\delta}$ and found a significant temperature, T, dependence, and even a singularity in the derivative of μ at the superconducting (SC) transition temperature T_C.[5] The problem is therefore to reconcile this experimental T dependence with the T independence of the bare chemical potential μ in RAFT.

First of all I start by explaining how a T-independent chemical potential is obtained in RAFT. In order to address the issue of the T-dependence of the Hall coefficient R_H,[6–8] I assumed that the electrons density on CuO_2 layers is temperature dependent.[2] It is known that upon doping HTSC's parent compounds electrons are exchanged between the CuO_2 layers and the atoms doped (dopants) between the layers. But, I guess for convenience, it was always assumed that the transfer of electrons back and forth between the dopants and the layers is temperature independent. However, one could in principle write down a Hamiltonian that includes the degrees of freedom associated with both the layers and the dopants, and calculate the resulting temperature dependence of the density of charge carriers on the CuO_2 layers, along with the temperature dependence of the chemical potential of the system as a whole, since the number of carriers is globally conserved. But for simplicity, to leading order in thermodynamics, the CuO_2 layers are assumed to behave as an open system in contact with a particle reservoir (formed by the dopants) with a large number of electrons. The electron density on the layers is therefore T dependent and the chemical potential T independent. An interesting consequence of this treatment is the T linearity of the hole density in the underdoped regime, which is in good agreement with the linear T dependence of the Hall carrier density below the pseudogap (PG) temperature for $La_{2-x}Sr_xCuO_4$ for example.[9]

RAFT has been developed using the two-dimensional (2D) extended Hubbard model with Hamiltonian

$$H=-\sum_{i,j,\sigma} t_{ij}c^\dagger_{i,\sigma}c_{j,\sigma}-\mu\sum_{i,\sigma}c^\dagger_{i,\sigma}c_{i,\sigma}+U\sum_i n_{i,\uparrow}n_{i,\downarrow}-V\sum_{\langle i,j\rangle}n_{i,\uparrow}n_{j,\downarrow}, \tag{1}$$

where $-V<0$ is an effective inter-site attractive interaction and U the on-site Coulomb repulsion. t_{ij} designates inter-site electron hopping energies on a square lattice with N sites. RAFT describes HTSC's in terms of two competing order parameters, which are the SC gap amplitude $D_0=|\langle c_{i,\uparrow}c_{j,\downarrow}\rangle|$, with i and j labeling adjacent sites, and the rotating antiferromagnetic (AF) parameter $Q=|\langle c_{i,\uparrow}c^\dagger_{i,\downarrow}\rangle|$. Q is the amplitude of a rotating staggered magnetization, which has been proposed to model the PG behavior.[10] The mean-field Hamiltonian is

$$H\approx\sum_{\mathbf{k}_<}\mathcal{C}^\dagger_{\mathbf{k}}\mathcal{H}\mathcal{C}_{\mathbf{k}}+N(UQ^2+4VD_0^2-Un^2-\mu_{ef}), \tag{2}$$

where $\mu_{ef}=\mu-Un$, $n=\langle c^\dagger_{i,\sigma}c_{i,\sigma}\rangle\equiv\rho/2$ is the electron density per site and spin, and

$$\mathcal{C}^\dagger_{\mathbf{k}}=(c^{A}_{-\mathbf{k}\uparrow}{}^\dagger,c^{B}_{-\mathbf{k}\uparrow}{}^\dagger,c^{A}_{\mathbf{k}\downarrow},c^{B}_{\mathbf{k}\downarrow},c^{A}_{\mathbf{k}\uparrow},c^{B}_{\mathbf{k}\uparrow},c^{A}_{-\mathbf{k}\downarrow}{}^\dagger,c^{B}_{-\mathbf{k}\downarrow}{}^\dagger). \tag{3}$$

The Hamiltonian density is

$$\mathcal{H}=\begin{pmatrix}\mathcal{H}' & \mathcal{U}_Q\\ -\mathcal{U}_Q & -\mathcal{H}'\end{pmatrix},$$

with $\mathcal{H}'$ and $\mathcal{U}_Q$, two 4×4-matrices, given by

$$\mathcal{H}'=\begin{pmatrix}-\mu'(\mathbf{k}) & \epsilon(\mathbf{k}) & 0 & D(\mathbf{k})\\ \epsilon(\mathbf{k}) & -\mu'(\mathbf{k}) & D(\mathbf{k}) & 0\\ 0 & D(\mathbf{k}) & \mu'(\mathbf{k}) & -\epsilon(\mathbf{k})\\ D(\mathbf{k}) & 0 & -\epsilon(\mathbf{k}) & \mu'(\mathbf{k})\end{pmatrix},$$

$$\mathcal{U}_Q=\begin{pmatrix}0 & 0 & QU & 0\\ 0 & 0 & 0 & -QU\\ -QU & 0 & 0 & 0\\ 0 & QU & 0 & 0\end{pmatrix}.$$

The summation $\Sigma_{\mathbf{k}_<}$ takes into account the sum over $\mathbf{k}$ and its opposite, and also over the two AF sublattices A and B. $\epsilon(\mathbf{k})=-2t(\cos k_x+\cos k_y)-4t'''[\cos(k_x)\cos(2k_y)+\cos(k_y)\cos(2k_x)]$ and $D(\mathbf{k})=2VD_0(\cos k_x-\cos k_y)$. t, t', t'',

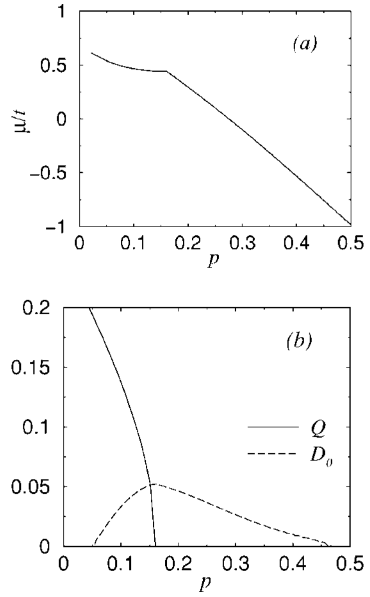

FIG. 1. μ in (a), and Q and D_0 in (b) are plotted vs doping p at $T=0$. The parameters $U=2.8t$, $V=0.85t$, $t'=-0.16t$, $t''=-0.01t$, and $t'''=-0.05t$ are used throughout this paper.

and t''' are the hopping energies to first, second, third, and fourth nearest-neighbor sites, respectively. The quantity

$$\mu' = \mu_{ef} + 4t'\cos k_x \cos k_y + 2t''(\cos 2k_x + \cos 2k_y) \quad (4)$$

is the mean-field-quasiparticles (QP) chemical potential. In a Fermi liquid (FL), the QP and bare chemical potentials are the same, and the sole effect of electron interaction on μ is the re-distribution of states about the Fermi energy. Here, the chemical potential shifts by a term that is T dependent and other terms that are **k** dependent. Q and D_0 are determined by self-consistent integral equations found in Ref. 1. These are solved by fixing the bare chemical potential μ and allowing the density ρ to vary with T, a procedure different than in ordinary metals.

Figure 1(a) shows μ versus doping $p=1-\rho$ at zero T for the set of Hamiltonian parameters given in the caption. The behavior displayed by μ compares well with electron photoemission spectroscopy (EPS) experiments[3,4] for μ is pinned in the underdoped regime, but shifts rapidly in the overdoped regime. Figure 1(b) shows Q and D_0 as a function of p. Q vanishes at $p=p_{QCP}\approx 0.16$, signaling the occurrence of a quantum transition. p_{QCP} is thus a quantum critical point (QCP). Superconductivity is stable for $0.05<p<0.45$ and is optimal at $p\approx p_{QCP}$. RAFT identifies the PG behavior with the phase with $Q>0$. Also according to RAFT, in the normal phase with $Q>0$ below p_{QCP} the FL behavior is replaced by a new liquid state characterized by more than one QP.[11] The QP operators are linear combinations of up and down spin operators, and particularly in the large-U/t limit, one can show that the number of independent QP's is approximately two, and that these have a character reminiscent of charge-spin separation in a way similar to that found in the one-dimensional Kondo-lattice model.[12] Note however that these QP operators carry both charge and spin degrees of freedom. The spin-charge separation theory of Anderson starts from an existing 2D Fermi surface and considers bosonized excitations of electron's spin and charge. As far as I know, work on relating the boson operators to the true electron operators $c_{\mathbf{k},\uparrow}$ and $c_{\mathbf{k},\downarrow}$ has yet to be completed. In the normal state with $D_0=0$, I speculate that the corrections in Q beyond the mean-field point would yield both spin and charge bosonlike fluctuations. Finally, according to Anderson, the spin-up and spin-down forward scattering is responsible for the breakdown of the FL theory in two dimensions because of the persistence of a finite phase shift at the Fermi surface.[13] It perhaps is not a coincidence that $Q=|\langle c_{i,\downarrow}c^{\dagger}_{i,\uparrow}\rangle|\neq 0$ breaks the FL state within RAFT even at the mean-field level. RAFT could therefore constitute a possible starting point for the theory of the normal state of HTSC's.

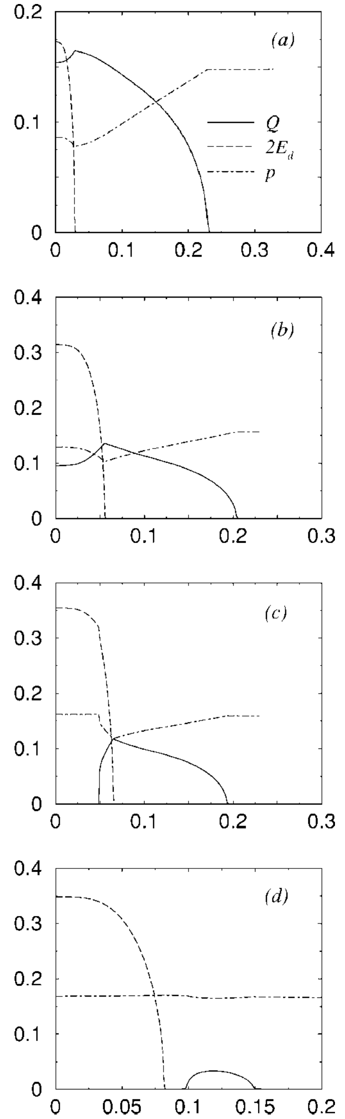

FIG. 2. Q, $D_0=E_d/4V$, and $p(T)$ are displayed versus T.

There exists a clear effect of Q and D_0 on the density ρ or doping p. In Fig. 2, Q, D_0 and $p(T)$ are displayed as a function of T for several initial zero-T doping densities $p(T=0)$. It is found that for doping levels near the half-filling point $p(T=0)=0$, Q behaves as in a second-order phase transition with only one order parameter, meaning that it monotonously increases as T decreases to zero. For $p(0) > 0.05$, D_0 becomes nonzero and as a consequence Q decreases with T for $T < T_C$. For $p(0)$ in the neighborhood of p_{QCP} the competition from superconductivity is so strong that Q is nonzero only for an interval of the temperature well above $T=0$. The state with $Q=0$ displays a re-entrance behavior at lower temperatures as seen in Fig. 2(c). The normal-state properties are therefore affected for $p \sim p_{QCP}$ even though Q vanishes at zero T. The existence of the PG has the strongest effect on the T dependence of $p(T)$. As soon as the PG vanishes completely in the overdoped regime, $p(T)$ shows a much smaller variation with T. Very close to optimal doping Fig. 2(d) shows that the state with $Q \neq 0$ is stable above T_C. This behavior is interesting in the light of the experimental evidence for a non FL state characterizing this region. I will report further on this behavior in the near future.

Regarding the Hall effect, in order to compare $p(T)$ with the experimental data for the Hall number n_H, I made an additional assumption according to which the charge carriers in HTSC's consist of only one single type, which is either holelike in the underdoped regime or electronlike in the overdoped regime. Some experimental data are in favor of this assumption.[8,14] Within RAFT, the electron occupation probability revealed the existence of pockets reminiscent of the hole pockets in doped Mott-Hubbard insulators.[1] In the underdoped regime, I will compare the T dependence trends in $p(T)$ and n_H. The present results for $p(T)$ and the available data for n_H share two very interesting features for which the PG is responsible. As seen in Figs. 2(a)–2(c), $p(T)$ shows a minimum at T_C and a linear T dependence for $T_C < T < T^*$. The data of Chaudhari *et al.* for n_H measured in the case of epitaxial films of $YBa_2Cu_3O_{7-\delta}$ show a minimum at exactly T_C and a linear T dependence for $T_C < T < T^*$ too.[6] Also, the linear behavior of $p(T)$ is in excellent agreement with the data of Batlogg *et al.* below the PG temperature.[9] In addition, Hwang and coworkers data show the presence of a maximum (minimum) in R_H (n_H) at T_C.[15]

Using spin-charge separation, Anderson explained the $1/T$ behavior of R_H by proposing that the motions perpendicular and parallel to the Fermi surface have different relaxation times, and that only spinons determine the Hall mean-free time for the motion parallel to the Fermi surface.[13] In Anderson's theory, the confinement of electrons within the CuO_2 planes is essential, and the conduction along the c-axis is achieved incoherently when spinons and holons recombine to yield electrons that tunnel to the adjacent planes. In the present treatment, a given electron that moves from a charge reservoir to a CuO_2 layer does so as a bare electron, but once on the layer it renormalizes down to RAFT's QP's. In RAFT, I can view the c-axis electron motion as being mediated by the charge reservoir, which gives rise to an incoherent motion because of the decay into QP's of the electrons within the CuO_2 layers. The 2D Fermi surface stays unaffected by this c-axis motion in agreement with Anderson's suggestion that the c-axis hopping energy $t_\perp$ does not affect the 2D Fermi surface.

In the remainder of this work, I addressed the issue of the experimentally observable chemical potential in HTSC's. The idea of a T independent chemical potential μ seems to contradict the experimental results of Rietveld *et al.* who measured an anomalous temperature dependence in μ at T_C.[5] According to RAFT, there may be two sources of T dependence in the chemical potential when it is measured. The first source is due to the fact that when one varies experimentally T, doping varies, leading to a varying chemical potential μ as well, because $\mu(p)$ is doping dependent. This is an implicit T dependence of μ. Note however that in the underdoped regime μ varies negligibly with p. It is therefore unlikely that this implicit dependence is significant. In the calculations performed here, fixing μ avoids this implicit T dependence. The second source of T dependence is explicit and may result from the QP chemical potential μ'. The T dependence of the latter is contained in the term $\mu_{ef} = \mu - U\rho(T)/2$.

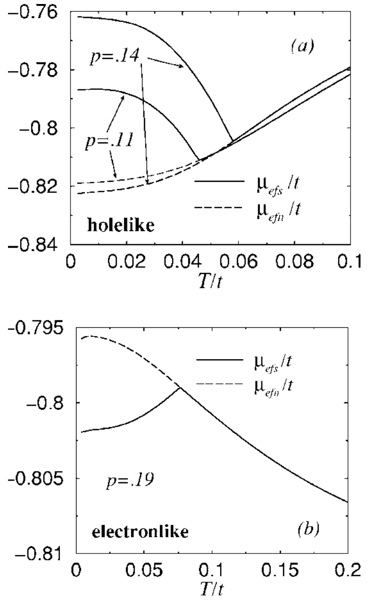

FIG. 3. The effective chemical potential μ_{ef} is plotted as a function of temperature for (a) $p=0.11$ and 0.14 in the underdoped regime and (b) $p=0.19$ in the overdoped regime.

Next, in an attempt to reconcile my results (for μ) with the anomaly shown by the chemical potential at T_C, I studied the temperature dependence of μ_{ef}. The anomaly in the chemical potential as given by Rietveld *et al.* is

$$\left. \frac{d(\mu_s - \mu_n)/dT}{c_s - c_n} \right|_{T=T_C} = \frac{d \ln T_C}{d\rho}, \tag{5}$$

where $\mu_n(c_n)$ and $\mu_s(c_s)$ are, respectively, the chemical potentials (specific heats) in the normal and SC states.[5] For μ_{ef}, RAFT yields

$$\left. \frac{d}{dT}(\mu_{efs} - \mu_{efn}) \right|_{T=T_C} = \left. \frac{U}{2}\frac{d}{dT}(p_n - p_s) \right|_{T_C}, \tag{6}$$

where $\mu_{efn}(p_n)$ and $\mu_{efs}(p_s)$ are the effective chemical potentials (doping densities) in the normal and SC states, respectively. Equation (6) shows that the anomaly in the QP chemical potential is related to the on-site Coulomb repulsion U.

Figure 3 illustrates the anomaly in μ_{ef} for doping densities $p(T=0)=0.11$ and $p(T=0)=0.14$ in the underdoped regime, and $p(T=0)=0.19$ in the overdoped one. For $p(T=0)=0.11$ and $p(T=0)=0.14$, the slope of $(\mu_{efs}-\mu_{efn})/t$ at T_C is, respectively, -1.7 and -2.4 giving a negative $d\ln T_C/d\rho$. This agrees with the fact that the charge carriers are holelike in the underdoped regime.[5] For $p=0.19$, the slope is approximately 0.16, leading to electronlike charge carriers in agreement once again with experiment. According to this analysis, the nature of the charge carriers changes at optimal doping where T_C is maximum. The slope in the overdoped regime is comparable in magnitude to the value reported in Ref. 5 for $YBa_2Cu_3O_{7-\delta}$, but is one order of magnitude greater in the underdoped regime. The shape of the curves in Fig. 3 compares very well to experiment;[5] below T_C in the underdoped regime, $(\mu_{efs}-\mu_{efn})/t$ rises linearly as T decreases then saturates as T approaches zero.

Considering the T dependence of μ_{ef} is very appealing. However, note that it is μ_{ef} that is compared with experiment as far as T dependence is concerned, but the bare chemical potential μ for the doping dependence. This inconsistency could have resulted from the assumption that the interlayer doped atoms form a thermodynamic reservoir of electrons. To solve this problem, perhaps one has to relax this assumption and consider the exchange of electrons between the interlayer atoms and the CuO_2 layers to be T dependent while allowing for the chemical potential to change with temperature as well. However, the present leading-order treatment should produce the correct trends; I expect that any T dependence in μ would only give smaller higher-order contributions. Therefore, one can assume that the present approach is correct, and the remedy may be the following. Experimentally, the doping dependence of μ is obtained using EPS, a technique used to probe locally shifts in core electron levels from which chemical potential shifts are deduced. This means that in this case EPS is not sensitive to the effective chemical potential μ_{ef}, which depends on valence electrons interactions (here when two electrons occupy together the same site). I propose that the work function measurements probed μ_{ef} whereas EPS probed μ. In EPS, it is the bare electrons that are emitted from the sample. The chemical potential measured in this way should reflect that of electrons that have undressed from any renormalization due to various interactions. In the Rietveld *et al.* experiment, electrons stay inside the sample. In this case, I think that it is the chemical potential of the mean-field QP's μ' (so of μ_{ef}) that enters into play. It is possible to check the present proposal of two different chemical potentials by experimentally measuring the effect of temperature on the chemical potential in core electron EPS at fixed doping densities.

In conclusion, I addressed within RAFT the temperature and doping dependences of the chemical potential of high-T_C cuprates. I predict that two chemical potentials characterize these materials. One is the bare chemical potential μ, which can be probed in EPS experiments. The other one is an effective chemical potential μ_{ef} that is seen by electrons renormalized by Coulomb (and other) interactions. These two chemical potentials reconcile RAFT's proposal of a temperature independent chemical potential (μ) with the observation in work function measurements of a T dependent (μ_{ef}) one. One way of testing the present prediction is to measure the temperature dependence of EPS data. Finally, I discussed the fact that RAFT and the idea of the chemical potential being governed by the atoms doped between the CuO_2 layers are consistent with the Anderson theory of spin-charge separation, in that the interlayer electron hopping $t_\perp$ does not affect the 2D Fermi surface.

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Laurentian University Research Fund (LURF).

---

[1] M. Azzouz, Phys. Rev. B **67**, 134510 (2003).

[2] M. Azzouz, Phys. Rev. B **68**, 174523 (2003).

[3] A. Ino, T. Mizokawa, A. Fujimori, K. Tamasaku, H. Eisaki, S. Uchida, T. Kimura, T. Sasagawa, and K. Kishio, Phys. Rev. Lett. **79**, 2101 (1997).

[4] N. Harima, A. Fujimori, T. Sugaya, and I. Terasaki, Phys. Rev. B **67**, 172501 (2003).

[5] G. Rietveld, N. Y. Chen, and D. van der Marel, Phys. Rev. Lett. **69**, 2578 (1992); see also D. van der Marel and G. Rietveld, *ibid.* **69**, 2575 (1992).

[6] P. Chaudhari, R. T. Collins, P. Freitas, R. J. Gambino, J. R. Kirtley, R. H. Koch, R. B. Laibowitz, F. K. LeGoues, T. R. McGuire, T. Penney, Z. Schlesinger, A. P. Segmüller, S. Foner, and E. J. McNiff, Jr., Phys. Rev. B **36**, 8903 (1987).

[7] M. Suzuki, Phys. Rev. B **39**, 2312 (1989).

[8] H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).

[9] B. Batlogg, H. Y. Hwang, H. Takagi, R. J. Cava, H. L. Kao, and J. Kwo, Physica C **235–240**, 130 (1994).

[10] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

[11] The word QP does not have the same meaning as in the Fermi liquid theory. The QP operators will appear in a work by H. Saadaoui, M. Azzouz, and K. C. Hewitt on Raman spectroscopy.

[12] M. Azzouz, Phys. Rev. B **62**, 710 (2000).

[13] P. W. Anderson, in *The Theory of Superconductivity in High-T_C Cuprates* (Princeton University Press, Princeton, NJ, 1997).

[14] J. L. Tallon and J. W. Loram, Physica C **349**, 53 (2001).

[15] H. Y. Hwang, B. Batlogg, H. Takagi, H. L. Kao, J. Kwo, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **72**, 2636 (1994).