Chemical Potential Shift in Overdoped and Underdoped $La_{2-x}Sr_xCuO_4$

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The downward shift of the electron chemical potential μ with hole doping in $La_{2-x}Sr_xCuO_4$ has been deduced from the shifts of photoemission and inverse-photoemission spectra. While the shift is large (~1.5 eV/hole) in overdoped samples, it is suppressed (<0.2 eV/hole) in underdoped samples, implying a divergent charge susceptibility near the metal-insulator transition. In the overdoped regime, the μ and the electronic specific heat coefficient γ are consistently explained within Fermi-liquid theory, whereas the same analysis gives unphysical results in the underdoped regime, indicating the breakdown of the Fermi-liquid picture in the underdoped regime. [S0031-9007(97)04058-1]

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A long-standing, yet unresolved issue in the high-T_c cuprates is how the electronic structure evolves with hole doping from the antiferromagnetic insulator (Mott insulator) to the paramagnetic metal/superconductor. While it has been found that the renormalized conduction-electron mass m^* diverges towards a filling-control metal-insulator transition (MIT) in 3D Ti oxides [1] as predicted theoretically [2,3], the electronic specific heat coefficient γ ($\propto m^*$) diminishes towards the MIT in $La_{2-x}Sr_xCuO_4$ [4]. According to Fermi-liquid theory, charge susceptibility $\chi_c \equiv \partial n/\partial\mu$, where μ is the electron chemical potential and n is the band filling, is proportional to m^* and therefore the rate of the chemical potential shift $\partial\mu/\partial n$ should be suppressed if m^* diverges. However, how the chemical potential is shifted in the cuprates with hole doping has so far been quite controversial. In one picture, the chemical potential is fixed in the middle of the charge-transfer gap of the parent insulator and new states evolve around it with hole doping [5]. In another picture, the chemical potential is shifted to the bottom of the gap upon hole doping and is further shifted downwards with increased doping concentration [6,7]. Since measured photoemission spectra are referenced to μ, it is possible to infer the shift of μ from the shifts of photoemission spectral features [8]. In metallic samples of Y-substituted and oxygen-controlled $Bi_2Sr_2CaCu_2O_{8+\delta}$, a downward chemical potential shift of ~1 eV/hole has been observed by photoemission spectroscopy [8,9]. A downward chemical potential shift with hole doping in $La_{2-x}Sr_xCuO_4$ has also been concluded from the generally decreasing core-level binding energies [10].

In this Letter, we have made a detailed photoemission investigation of the chemical potential shift in $La_{2-x}Sr_xCuO_4$. $La_{2-x}Sr_xCuO_4$ is the simplest superconducting cuprate system in that it has single CuO_2 conducting layers and that the hole concentration δ in the CuO_2 layer is uniquely determined by the Sr (and/or excess oxygen) concentration in the LaO double layer: $\delta \equiv 1 - n \simeq x$.

Single crystals of $La_{2-x}Sr_xCuO_4$ were grown by the traveling-solvent floating-zone method. Uncertainties in the Sr concentration x were ±0.01. The $x = 0$ sample was slightly hole doped by excess oxygens: $y \sim 0.005$ in La_2CuO_{4+y}, judging from the Néel temperature of ~220 K [11] and hence $\delta \sim 0.01$. X-ray photoemission (XPS) measurements were performed using a Mg Kα ($h\nu = 1253.6$ eV) line. In inverse-photoemission (bremsstrahlung-isochromat spectroscopy: BIS) measurements, 1486.6 eV photons were detected. Incident electron current in the BIS measurements was limited to ~100 μA in order to minimize possible damages of sample surfaces. We note that even with the resolution of XPS (~1.0 eV) it was possible to measure binding energy shifts with an accuracy of ±40 meV, as we shall show below. The accuracy of the BIS measurements was ±0.15 eV. We found that any weak extrinsic features due to surface degradation or contamination hindered accurate determination of core-level peak positions, and therefore we had to keep the sample surfaces extremely clean. The spectra presented here were taken within ~45 min at liquid-nitrogen temperature (~80 K). Binding energies were calibrated using Au evaporated on each sample. There was no charging effect, which causes shifts of spectral features away from the Fermi level, even for the $x = 0$ sample as can be seen from the data presented below. It can be said from the measuring temperature and the accuracy of the measured energy shifts, that one can probe the charge response of $La_{2-x}Sr_xCuO_4$ on the energy scale of a few tens meV.

Figure 1 shows the XPS spectra of the O 1s, La 3d, and Cu 2p core levels and the BIS spectra of the La 4f level. Energy shifts of the core levels were determined by comparing the positions of spectral features whose line shapes do not change with composition: The La 4f BIS

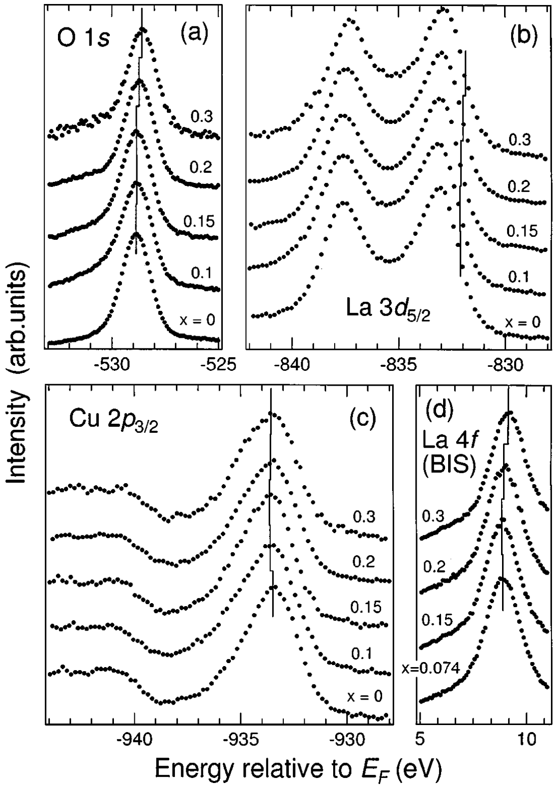

FIG. 1. Core-level XPS (O 1s, La 3d, Cu 2p) and La 4f BIS spectra of $La_{2-x}Sr_xCuO_4$. Energies are referenced to the chemical potential (i.e., the Fermi level).

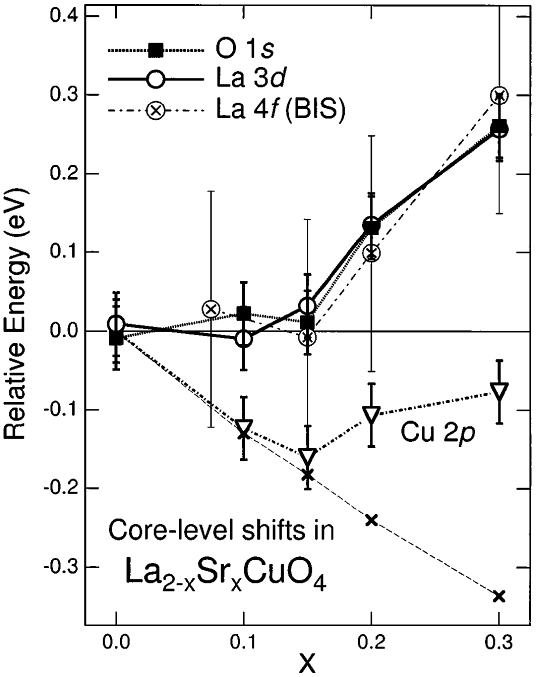

FIG. 2. Energy shifts relative to the undoped sample ($\delta = 0$) plotted against hole concentration δ.

and O 1s line shapes remain largely unchanged, but the high binding energy side of the La 3d peak shows some changes possibly due to slight surface degradation or contamination, even with the above experimental precautions. (The low kinetic energies of photoelectrons from La 3d would have increased surface sensitivity.) Therefore, the low binding energy side of the La 3d peak is used to obtain the shift of La 3d. The obtained shifts relative to $x = 0$ are plotted as a function of $\delta \simeq x$ in Fig. 2. The O 1s, La 3d, and La 4f levels show almost the same shifts with δ, namely, large ($\sim$1.5 eV/hole) shifts towards lower binding energies for the overdoped ($x \gtrsim 0.15$) samples and small ($<$0.2 eV/hole) shifts for the underdoped ($x \lesssim 0.15$) samples. The line shape of the Cu 2p core level, on the other hand, shows a strong x dependence [12]; its peak position is shifted towards higher binding energies in the underdoped regime and then towards lower binding energies in the overdoped regime. This complicated Cu 2p shift could be decomposed into two simple components, as shown in Fig. 2: the shift which is nearly linear in δ and the shift common to all the core levels [13].

The shift ΔE of a core level (or a localized empty level such as La 4f) with varying chemical composition measured relative to μ is given by $\Delta E = \Delta\mu + K\Delta Q + \Delta V_M + \Delta E_R$, where $\Delta\mu$ is the change in the chemical potential, ΔQ is the change in the number of valence electrons on the atom considered, ΔV_M is the change in the Madelung potential, and ΔE_R is the change in the extra-atomic relaxation energy [14]. Here, ΔQ produces changes in the electrostatic potential at the core-hole site as well as in the intraatomic relaxation energy of the core-hole final state. ΔE_R is due to changes in the screening of the core hole potential by metallic conduction electrons and polarizable surrounding ions. The "linear" component of the Cu 2p core-level shift can be attributed to the increase in the Cu valence with hole doping ($\propto -\Delta Q$) from Cu^{2+} towards Cu^{3+}, i.e., so-called "chemical shift" [15]. Then, the shift common to all the four levels should reflect the chemical potential shift $\Delta\mu$. In order to evaluate ΔV_M for different core levels, we calculated changes in the Madelung potentials by taking into account the doping dependence of the crystal structure [16] and assuming the average charges of $(3 - x/2)+$, $(2 + x)+$, and $2-$ at the La/Sr, Cu, and O sites, respectively. The results showed that ΔV_M are approximately linear in x and towards different directions for different atomic sites. Hence, the nonlinear and identical shifts of the La 3d, La 4f, and O 1s levels indicate that ΔV_M is strongly screened by the redistribution of electric charges and therefore can be neglected. ΔE_R would also be negligible because this would shift both filled and empty levels toward the chemical potential and hence in the opposite directions. We note that the line shapes of the core levels do not show asymmetric broadening characteristic of metallic screening [17] for all compositions, indicating negligible metallic core-hole screening. The parallel shifts of the La 3d and O 1s core levels are consistent with this view since metallic screening would contribute more to an oxygen core hole in the metallic CuO_2 plane. Presumably, the carrier concentration ($\sim 10^{21}$ holes/cm^{-3}) is too low to produce ordinary metallic screening. Instead, the very large dielectric constant of lightly doped La_2CuO_4 [18] may have lead to a strong dielectric screening of the core hole. Thus we conclude that the common shift observed in the core levels and the La $4f$ level faithfully reflects the chemical potential shift $\Delta\mu$. The $\Delta\mu$ deduced from the average of the O $1s$ and La $3d$ core-level shifts is plotted in Fig. 3(a) as a function of δ. From a purely experimental point of view, one cannot completely rule out the possibility that, although unlikely, the small $\Delta\mu$ for $x \lesssim 0.15$ is a result of cancellation between an intrinsic lowering of μ and increasing charging effect with decreasing x. From a thermodynamic point of view, if a downward shift of μ with decreasing hole concentration existed, the system would undergo an electronic phase separation and results in $\partial\mu/\partial n = 0$.

Let us first analyze the chemical potential shift in the overdoped regime, where the system is believed to be a Fermi liquid. For an isotropic Fermi liquid [20],

$$\frac{\partial\mu}{\partial n} = \frac{1 + F_s^0}{N^*(\mu)} \equiv \left(\frac{m_b}{m^*}\right)\frac{1 + F_s^0}{N_b(\mu)}, \tag{1}$$

where $N^*(\mu)$ is the density of states (DOS) of renormalized quasiparticles (QP's), m_b and $N_b(\mu)$ are the bare (unrenormalized) band mass and the band DOS at μ, respectively, and F_s^0 (>0) is a Landau parameter which represents the isotropic spin-symmetric part of the QP-QP repulsion. Since $\gamma = (\pi^2/3)k_B^2 N^*(\mu)$, one can predict $\Delta\mu$ from measured γ, if F_s^0 is known. $\Delta\mu$ predicted for $F_s^0 = 0$ is shown by a solid curve in Fig. 3(b). Because $\partial\mu/\partial n$ thus predicted is 8 ± 2 times smaller than observed $\partial\mu/\partial n$ in the overdoped regime, we obtain $F_s^0 \sim 7 \pm 2$. From γ [4] and $N_b(\mu)$ [19], $m^*/m_b \equiv N^*(\mu)/N_b(\mu) \sim 2.5 \pm 0.5$. These values are compared with those of liquid ^{3}He at ambient pressure, $F_s^0 = 9.15$ and $m^*/m_b = 2.76$ [21]. In the underdoped regime, while the present results indicate that the charge susceptibility is enhanced ($\chi_c \longrightarrow$ "∞") as $\delta \longrightarrow 0$ ($n \longrightarrow 1$), the specific heat coefficient diminishes ($\gamma \longrightarrow$ "∞") [4]. If the Fermi-liquid relation (1) is applied to these behaviors, we have $F_s^0 \longrightarrow -1$, which obviously contradicts the basic assumption that F_s^0 represents repulsive interaction. This suggests the breakdown of the Fermi-liquid description in the underdoped regime. (Inclusion of anisotropy in the Fermi-liquid analysis would not change the conclusion qualitatively.)

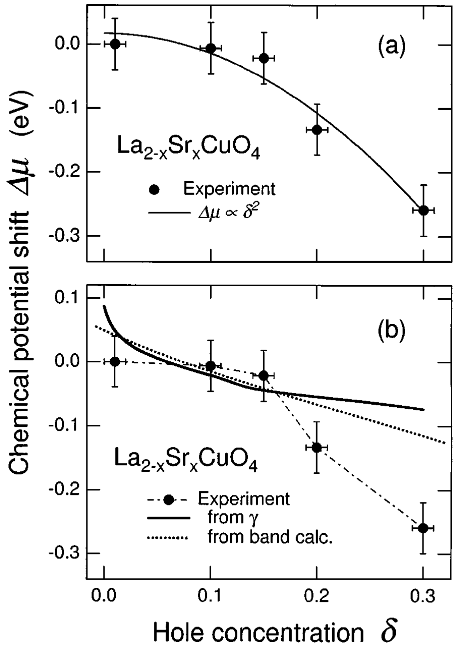

FIG. 3. (a) Chemical potential shift $\Delta\mu$ plotted against the hole concentration δ. The dashed line is $\Delta\mu \sim -\delta^2$ as predicted by the Monte Carlo simulation [3]. (b) $\Delta\mu$ compared with the shift predicted from the specific heat coefficient γ [4] assuming $F_s^0 = 0$ and that derived by $N_b(\mu)$ of the band-structure calculation [19].

Suppression of the chemical potential shift for $\delta \longrightarrow 0$ has been suggested by numerical studies of the 2D Hubbard model [3,22]. In the Monte Carlo study, the calculated chemical potential shift follows $\Delta\mu \propto -\delta^2$ for $0 < \delta \lesssim 0.3$ (hence $\chi_c \propto \delta^{-1}$) [3]. Actually, the experimental data are compatible with $\Delta\mu \propto -\delta^2$ within experimental error, as shown in Fig. 3(a). Note that the observed behavior, $\chi_c \longrightarrow$ "0" for $\delta \longrightarrow 0$, has not been predicted by mean-field theories such as the Gutzwiller approximation and the dynamical mean-field approximation, which predict $\chi_c \longrightarrow 0$ for $\delta \longrightarrow 0$ [23]. This implies that quantum fluctuations are important near the MIT critical point.

One may suspect that the suppression of the chemical potential shift for small δ is caused by the pinning of the chemical potential by the impurity potential of substituted Sr or other defects. Such a pinning effect cannot be excluded for the semiconducting $x = 0$ ($\delta \sim 0.01$) sample. However, the same effect would not occur in metallic samples ($\delta > 0.05$) when the impurity potential is weak enough. In fact, the acceptor binding energy has been estimated to be as small as ~40 meV for semiconducting La_2CuO_{4+y} with $y \sim 0.001$ and is rapidly reduced to below ~10 meV for $y \sim 0.01$ [18]. These small acceptor binding energies indicate that, if pinning occurs, the chemical potential in the $x = 0$ sample is located very close to the bottom of the band gap of La_2CuO_4, and that for the metallic samples the pinning effect is too weak to affect the chemical potential shift. Zaanen and co-workers [24] have suggested that doped holes are segregated in the boundaries of antiferromagnetic domains in a stripe form and may pin μ. In fact, the system becomes metallic already at $\delta \sim 0.05$ and the stripe correlation can normally exist as dynamical fluctuations [25]. The presence of the spin-charge stripes itself in $La_{2-x}Sr_xNiO_4$ and Nd-doped La cuprates [26] means that the Sr impurity potential is practically negligible when the stripe correlation is observed.

The experimental observation $\gamma \longrightarrow$ "0" for $\delta \longrightarrow 0$ in the underdoped samples, on the other hand, has not been predicted by any theoretical studies on 2D metals. The apparently conflicting behaviors of γ and χ_c may be resolved if we assume that a tiny excitation (pseudo)gap is opened at μ within the renormalized QP band for any small δ. Recent angle-resolved photoemission studies have indicated the opening of a "normal-state" gap above T_c in underdoped $Bi_2Sr_2CaCu_2O_{8+y}$ [27] as described by a mean-field treatment of the *t-J* model [28]. Alternatively, strong antiferromagnetic spin fluctuations in the underdoped regime may give rise to a pseudogap at μ [29]. Pairing fluctuations (or preformed Cooper pairs) are another possible explanation for the suppression of γ in spite of the enhanced χ_c. It should be noted that the experimental results for the underdoped samples are not compatible with the simple small hole pocket either because the same expression (1) and $\gamma = (\pi^2/3)k_B^2 N^*(\mu)$ should hold if we regard $N^*(\mu)$ as the QP DOS around the "small Fermi surfaces."

Finally, the present result for the overdoped samples is similar to the result ($\partial\mu/\partial n \sim 1$ eV/electron) for metallic $Bi_2Sr_2Ca_{1-y}Y_yCu_2O_8$ [8] and $Bi_2Sr_2CaCu_2O_{8+\delta}$ [9]. The rapid shift of ~8 eV/electron observed for semiconducting $Bi_2Sr_2Ca_{1-y}Y_yCu_2O_8$ samples [8] would be reminiscent of an insulator with a finite band gap: $\partial\mu/\partial n \longrightarrow \infty$. The finite $\partial\mu/\partial n$ would be due to a low but finite density of localized states within the band gap, which are created by the Ca-Y disorder adjacent to the CuO_2 planes.

In summary, we have experimentally determined the doping dependence of the chemical potential shift $\Delta\mu$ in $La_{2-x}Sr_xCuO_4$ and observed a suppression of the shift in the underdoped regime. The result indicates that the charge susceptibility is enhanced towards $\delta \sim 0$, most likely reflecting critical fluctuations near the MIT. Comparing the result with the linear specific heat coefficient γ, the behaviors of μ and γ are consistently explained within Fermi-liquid theory in the overdoped regime if a large Landau parameter $F_s^0 \sim 7$ is assumed. On the other hand, the same comparison indicates a breakdown of the Fermi-liquid description in the underdoped regime, suggesting the opening of a tiny (pseudo)gap at the chemical potential. It is interesting to see how the chemical potential behaves near MIT in 3D and quasi-1D systems, too, since such information combined with electronic specific heats would give deep insight into the Fermi-liquid vs non-Fermi-liquid behaviors of unconventional metals. The temperature dependence of the chemical potential shift would also reflect the highly nontrivial nature of correlated electrons near MIT.

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[1] Y. Tokura *et al.*, Phys. Rev. Lett. **70**, 2126 (1993).

[2] X. Y. Zhang, M. J. Rozenberg, and G. Kotliar, Phys. Rev. Lett. **70**, 1666 (1993).

[3] N. Furukawa and M. Imada, J. Phys. Soc. Jpn. **62**, 2557 (1993).

[4] N. Momono *et al.*, Physica (Amsterdam) **233C**, 395 (1994); J.W. Loram *et al.*, Physica (Amsterdam) **162C**, 498 (1989); T. Nishikawa *et al.*, Physica (Amsterdam) **209C**, 553 (1993).

[5] J.W. Allen *et al.*, Phys. Rev. Lett. **64**, 595 (1990).

[6] H. Eskes *et al.*, Phys. Rev. B **50**, 11 980 (1994).

[7] M. A. van Veenendaal, G. A. Sawatzky, and W. A. Groen, Phys. Rev. B **49**, 1407 (1994).

[8] M. A. van Veenendaal *et al.*, Phys. Rev. B **47**, 446 (1993).

[9] Z.-X. Shen *et al.*, Phys. Rev. B **44**, 12 098 (1991).

[10] G. Rietveld, M. Glastra, and D. van der Marel, Physica (Amsterdam) **241C**, 257 (1995).

[11] B. Dabrovski *et al.*, Physica (Amsterdam) **162C–164C**, 99 (1989).

[12] A close inspection of the line shapes of Cu $2p$ for large x's suggests the presence of two peaks, probably corresponding to overlapping Cu^{2+} and Cu^{3+} components. If this is the case, the apparently "linear" shift of the Cu $2p$ core level is a result of the varying relative intensities of the two components. The Ti $2p$ core-level photoemission spectra of $Y_{1-x}Ca_xTiO_3$ clearly show two components, Ti^{3+} and Ti^{4+}, whose relative intensities change with x following the average valence of Ti [K. Morikawa *et al.*, Phys. Rev. B **54**, 8446 (1996)].

[13] The same decomposition has successfully been made for $La_{1-x}Sr_xCuO_{2.5}$ [T. Mizokawa *et al.*, Phys. Rev. B **55**, R13373 (1997)]; $La_{1.17-x}Pb_xVS_{3.17}$ [A. Ino *et al.* (to be published)]; $La_{1-x}Sr_xTiO_3$ [T. Yoshida *et al.* (to be published)].

[14] S. Hüfner, in *Photoelectron Spectroscopy* (Springer-Verlag, Berlin, 1995), Chap. 2, p. 35.

[15] The experimental data seem to show that there is no $K\Delta Q$ contribution to the O $1s$ core-level shift, although it is believed that a large part of doped holes enter the O $2p$ orbitals. This is probably because of the large spatial extent of the O $2p$ orbitals compared to Cu $3d$.

[16] V. Voronin *et al.*, Physica (Amsterdam) **218C**, 407 (1993); M. Braden *et al.*, Physica (Amsterdam) **223C**, 396 (1994).

[17] G.K. Wertheim and P.H. Citrin, in *Photoemission in Solids,* edited by M. Cardona and L. Ley (Springer-Verlag, Berlin, 1978), Vol. I, Chap. 5, p. 197.

[18] C. Y. Chen *et al.*, Phys. Rev. Lett. **63**, 2307 (1989).

[19] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).

[20] N. Furukawa and M. Imada, J. Phys. Soc. Jpn. **61**, 3331 (1992).

[21] D. S. Greywall, Phys. Rev. B **27**, 2747 (1983).

[22] E. Dagotto *et al.*, Phys. Rev. Lett. **67**, 1918 (1991).

[23] A. George and W. Krauth, Phys. Rev. Lett. **69**, 1240 (1992).

[24] J. Zaanen and A.M. Oleś, Ann. Phys. (Leipzig) **5**, 224 (1996).

[25] M. I. Salkola, V. J. Emery, and S. A. Kivelson, Phys. Rev. Lett. **77**, 155 (1996).

[26] J. M. Tranquada *et al.*, Nature (London) **375**, 561 (1995).

[27] D. S. Marshall *et al.*, Phys. Rev. Lett. **76**, 4841 (1996); H. Ding *et al.*, Nature (London) **382**, 51 (1996).

[28] T. Tanamoto, H. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. **61**, 1886 (1992).

[29] J. J. Deisz, D. W. Hess, and J. W. Serene, Phys. Rev. Lett. **76**, 1312 (1996).