

Electronic States and Novel Properties of Functional Transition-Metal Oxides: Tendency towards Charge-Density Modulation

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Recently it has become recognized that the modulation and fluctuations not only of spins but also of electronic charges play important roles in transition-metal oxides. Photoemission spectroscopy is a sensitive probe of charge responses and provides unique information about them. In this article, we present recent results of chemical potential shifts and angle-resolved photoemission spectra and discuss their implications for the novel physical properties such as high- T_c superconductivity in the cuprates and giant magnetoresistance in the manganites.

Keywords: High-temperature superconductivity, giant magnetoresistance, photoemission spectroscopy, stripe, charge ordering

1. INTRODUCTION

Transition-metal oxides have shown a variety of functional properties such as high-temperature (high- T_c) superconductivity, giant magnetoresistance (GMR) and metal-insulator transition. These properties are thought to arise from the combination of strong electron-electron repulsion among the transition-metal d electrons and strong hybridization between the transition-metal d and oxygen p electrons [1]. The fact that those physical properties are intimately related to magnetism and magnetic fluctuations seems reasonable because magnetism and magnetic fluctuations are natural consequences of strong electron correlation. Recently, it has become recognized that charge responses of the strongly correlated systems are also unique and may play important roles in the novel physical properties of the transition-metal oxides. Charge stripes in high- T_c cuprates [2] and charge (and orbital) ordering in GMR manganites [3] have aroused considerable interest in recent years.

Photoemission spectroscopy is a sensitive probe of charge response in such systems and should be sensitive to charge ordering and charge fluctuations because electronic charges are removed from the system in the photoemission process. Indeed, a recent angle-resolved photoemission (ARPES) study of the stripe phase in $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ ($x \approx 0.12$) [4] has

revealed stripe-type charge modulation through the observation of one-dimension-like Fermi surface segments. Also, the chemical potential shift, which can be measured by core-level and valence-band photoemission, is directly related to the charge susceptibility. Unusual pinning of the chemical potential shift in underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ suggests an electronic phase separation (on a microscopic scale), which is attributed to the dynamical stripe formation [5].

In this article, an overview is made on different types of charge responses in transition-metal oxides, on the basis of recent photoemission results.

2. CHEMICAL POTENTIAL SHIFT

Most of the transition-metal oxides that show remarkable physical properties belong to the class of materials called filling-control systems, and therefore physical quantities which varies as functions of carrier density n provide valuable information about the mechanism which gives rise to those properties. The density-derivative of the chemical potential (μ) of charge carriers $d\mu/dn$ is by definition equal to the inverse of the charge susceptibility ($1/\chi_c$) or charge compressibility ($1/\kappa$). That is, when the chemical potential shift becomes slow as a function of carrier density, the uniform charge response is enhanced. In an extreme case, spatial regions of different charge

densities coexist, i.e., the system is electronically phase-separated. In that case, an infinitesimally small change in the chemical potential leads to a finite change in the average charge density. Figure 1 shows the chemical potential shifts for various filling-control transition-metal oxides. As seen from the figure, enhanced charge response is seen in for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x < 0.12$ and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $x < 0.33$, where charge stripes or their fluctuations are believed to exist and the periodicity of the charge modulation is proportional to the hole concentration. The electronic "phase separation" should be distinguished from a chemical inhomogeneity, which often occurs in real oxide samples. The chemical potential shift is sensitive only to the charge response of the electronic system and not to the chemical inhomogeneity. It should also be noted that the electronic phase separation *cannot* occur on a macroscopic length scale because charge such a charge inhomogeneity would cost a huge amount of Coulomb energy. Only microscopic "phase separation" such as charge stripes in the high- T_c cuprates can be realized. The stripe phase can be viewed as a microscopic phase separation in the sense that the hole density in the hole rich region, i.e., in each stripe, is constant as in the case of underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ [6].

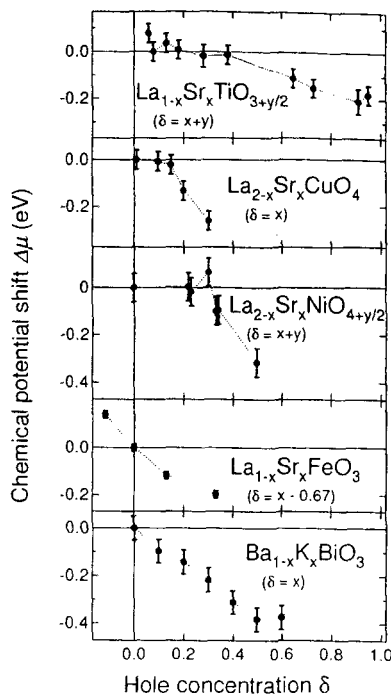


Fig. 1 Chemical potential shifts for various filling-control transition-metal oxides. The shift for $\text{La}_{1-x}\text{Sr}_x\text{TiO}_3$ is a normal-Fermi liquid behavior, where $d\mu/dn$ is inversely proportional to the density of quasi-particles at the Fermi level. For the other systems, see the text

If the charge-density modulation has a fixed periodicity, then the carrier density should normally change with doping on a microscopic scale, too, and no chemical potential pinning is anticipated. As shown in Fig. 1, this is indeed the case for $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$, where spin- and charge-density modulations with the periodicity of 6 and 3, respectively, along the (111) direction are observed around $x = 2/3$ [7]. In a charge-density-wave (CDW) system $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, too, there is no chemical potential pinning at any hole density x [8] probably because the wave vector for the CDW remains $(1/2, 1/2, 1/2)$ in units of $2\pi/a$.

3. HIGH- T_c CUPRATES

ARPES spectra of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ have shown the coexistence of insulator-like and superconductor-like electronic states for a narrow range of composition around the superconductor-insulator phase boundary $x \sim 0.05$ [9]. This observation may be due to an intrinsic electronic phase separation, which is made energetically possible because there is a boundary between the two phases, and/or due to chemical inhomogeneity. The same two-component behavior in the ARPES spectra disappears in the concentration range $0.05 \ll x < 1.2$, where the stripe formation occurs and the chemical potential does not shift. However, one-dimensional Fermi surface segments around $k = (\pi, 0)$ similar to those observed for $\text{La}_{2-x-y}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ (with static stripes) are found for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (with dynamical stripes) and coexist with the Fermi surface even in optimally doped and overdoped samples [10,11].

Chemical potential shift is more suggestive of the microscopic electronic "phase separation". Figure 2 shows the chemical potential shift deduced from core-level shifts covering the hole-doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ to the electron-doped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$. The figure shows that the chemical potential does not move in the hole concentration range $0 < x < 0.12$, where the incommensurability δ of the magnetic neutron peaks at $(\pi(1 \pm \delta), \pi(1 \pm \delta))$ increases linearly with x . Outside this region, the chemical potential shows a shift of ~ 1 eV/electron and the incommensurability is constant: $\delta \sim 0.12$ (hole-overdoped region) or ~ 0 (electron-doped region). This behavior fits the stripe picture that the distance between the stripes, which are belts of hole-rich regions with unchanged width, increases with doped hole concentration. The fact that the chemical potential pinning does not occur in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ is consistent with the robustness of the antiferromagnetic ordering in the electron-doped system.

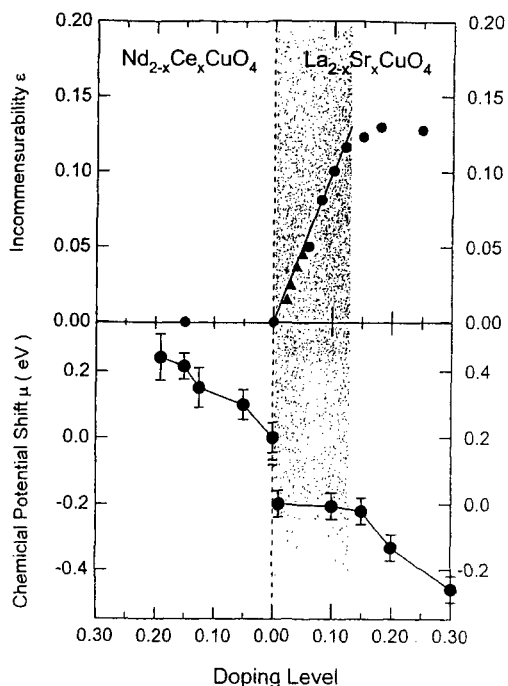


Fig. 2 Chemical potential shifts for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [5] and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [12]. Also plotted is the incommensurability δ of the neutron scattering peak around (π, π) [6,13,14]. In the shaded region, the chemical potential does not shift and the magnetic incommensurability varies linearly, suggestive of stripe formation.

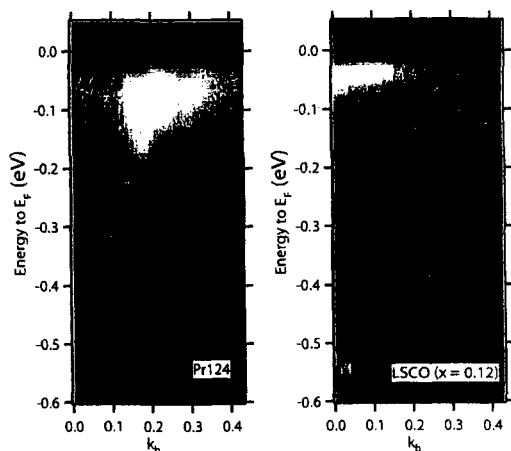


Fig. 3 ARPES spectra along $(\pi, 0)$ - (π, π) of $\text{PrBa}_2\text{Cu}_4\text{O}_8$ [16] and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.12$ [17].

According to the Hall effect measurements of the static stripe phase in $\text{La}_{2-x}\text{Nd}_y\text{Sr}_x\text{CuO}_4$ ($x \approx 0.12$), it is suggested that a purely one-dimensional metallic state is realized [15]. The nature of the one-dimensional metal in the stripe phase should be characterized in more detail. If this is an isolated one-dimensional

metal, then ARPES spectra, e.g., along $(\pi, 0)$ - (π, π) , should resemble those of a metallic quasi-one-dimensional compound. In Fig. 3, we compare ARPES spectra from one-dimensional metallic Cu-O chains in $\text{PrBa}_2\text{Cu}_4\text{O}_8$ and those from $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $x = 0.12$. One can see from the figure that, although the dispersive feature crosses the Fermi level at $k_b \sim \pi/4$ in both cases, corresponding to the quarter-filled one-dimensional metallic states, the dispersional width is very different between the two cases: it is ~ 0.3 eV and < 0.1 eV for $\text{PrBa}_2\text{Cu}_4\text{O}_8$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, respectively. Presumably, the band is narrow in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ because holes in the stripe embedded in the CuO_2 plane interact with neighboring Cu spins, whereas holes in the isolated Cu-O chains in $\text{PrBa}_2\text{Cu}_4\text{O}_8$ can propagate without such interaction and has the band width of the order of the transfer integral t .

4. GMR MANGANITES

The origin of the GMR behavior in the perovskite-type manganites has been debated for many years since it was pointed out that double exchange mechanism is not sufficient to explain the large resistivity change [18]. Among many proposals, phase separation into metallic and insulating regions has been suggested to be the origin of the GMR behavior [19]. We have studied the chemical potential shift in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and found no evidence for chemical potential pinning as shown in Fig. 3 [20]. This means that there is no obvious electronic phase separation or its fluctuations and that the coexistence of metallic and insulating phases on a large length scale (of ~ 100 nm) observed by electron microscopy [19] may be due to chemical inhomogeneity. The absence of electronic phase separation into regions with different hole concentrations is consistent with the above general argument that it would cost huge Coulomb energy.

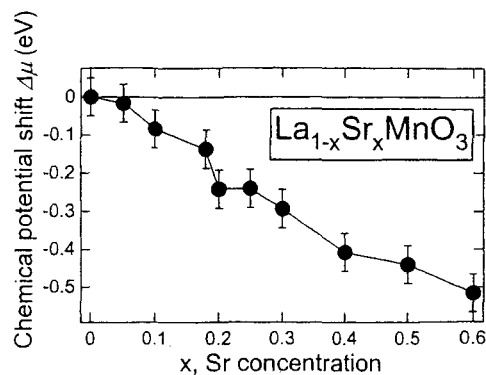


Fig. 4 Chemical potential shift in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [20].

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