

**Chemical potential shift in lightly doped to overdoped  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8+y}$  ( $\text{R}=\text{Pr}, \text{Er}$ )**

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(Received 21 January 2002; revised manuscript received 27 December 2002; published 1 May 2003)

We have studied the chemical potential shift in the high-temperature superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8+y}$  ( $\text{R}=\text{Pr}, \text{Er}$ ), where the hole concentration is varied from 0.025 to 0.17 per Cu, by precise measurements of core-level photoemission spectra. The result shows that the shift is depressed in the underdoped region as in the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO) but the depression is much weaker than in LSCO. The observed shift in the present system can be relatively well explained by numerical results on the doped two-dimensional Hubbard model and suggests that the change of the electronic structure induced by hole doping is less influenced by stripe fluctuations than in LSCO.

DOI: 10.1103/PhysRevB.67.172501

PACS number(s): 79.60.-i, 74.72.Hs, 71.30.+h

**I. INTRODUCTION**

Since the discovery of the high-temperature superconductors, one of the most important but unanswered questions has been how the electronic structure evolves from the antiferromagnetic insulator (AFI) to the superconductor (SC) as a function of doped hole concentration. In the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO), recent angle-resolved photoemission spectroscopy (ARPES) studies<sup>1,2</sup> have shown that in underdoped samples, the chemical potential  $\mu$  is pinned at  $\sim 0.4$  eV above the top of the lower Hubbard band (more precisely, top of the Zhang-Rice singlet band) and spectral weight is transferred from the lower Hubbard band to near  $\mu$  with hole doping. Also, it has been found from the photoemission measurements of core levels that the chemical potential does not move with hole doping in the underdoped region.<sup>3</sup> These observations indicate a breakdown of the rigid-band picture and are suggestive of a dramatic reorganization of the electronic structure upon hole doping. In fact, the suppression of the chemical potential shift has been attributed to the strong stripe fluctuations in LSCO as revealed by inelastic neutron scattering<sup>4</sup> because the charge stripes can be viewed as a kind of microscopic phase separation which will pin the chemical potential. More recently, it has been found that the chemical potential in the electron-doped superconductor  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  (NCCO) shows a monotonic shift without any sign of depression, indicating a more rigid-band-like behavior.<sup>5</sup> The absence of a depression of the shift in NCCO is consistent with the absence of stripe fluctuations in this system.<sup>6</sup>

As for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  (BSCCO), which has been most extensively investigated by ARPES,<sup>7</sup> core-level shifts were studied on  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ , where the hole concentration was varied with Y substitution, by van Veenendaal *et al.*<sup>8</sup> The deduced chemical potential showed an abrupt, large downward shift of  $\sim 0.7$  eV upon hole doping in the lightly doped region, which implies that the chemical potential moves from the in-gap region of the parent the insulator to the top of the lower Hubbard band upon hole doping. However, a subsequent study by Tjernberg *et al.*<sup>9</sup> showed a dif-

ferent doping dependence of the core-level shifts and the opening of a pseudogap was claimed based on their data. Valence-band and shallow core-level studies of optimally doped and overdoped BSCCO samples by Shen *et al.*<sup>10</sup> have shown a uniform shift for every spectral feature, showing evidence for a chemical potential shift. Therefore, more systematic studies over a wide concentration range are required to elucidate the intrinsic behavior of the chemical potential shift. So far, it has been difficult to prepare heavily underdoped BSCCO samples with good quality. Recently, high quality crystals of heavily underdoped BSCCO were systematically synthesized by rare-earth ( $\text{R}$ ) substitution for Ca and the doping dependence of thermodynamic and transport properties has been studied.<sup>11,12</sup>

In this paper, we report on a core-level photoemission study of the chemical potential shift  $\Delta\mu$  in those  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8+y}$  crystals as a function of doped hole concentration. The chemical potential shift was estimated from the core-level shifts as in the previous studies<sup>3,5,13</sup> utilizing the fact that the energies of core levels are measured in reference to  $\mu$  in photoemission experiments.

**II. EXPERIMENT**

Single crystals of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8+y}$  ( $\text{R}=\text{Pr}, \text{Er}$ ) were grown by the self-flux method and the x-ray diffraction pattern showed no trace of impurity phases. Details of sample preparation are given in Ref. 12. The hole concentration  $\delta$  per Cu atom was estimated from the empirical relationship between  $\delta$  and the room-temperature thermopower.<sup>14</sup> Errors in  $\delta$  thus estimated are less than  $\pm 10\%$  of  $\delta$ . The hole concentration and the critical temperature were  $\delta=0.17, 0.135$ , and  $0.1$  and  $T_c=86, 88$ , and  $48$  K for the  $x_{\text{Pr}}=0.1, 0.25$ , and  $0.43$  samples, respectively, and  $\delta=0.135$  and  $T_c=87$  K for the  $x_{\text{Er}}=0.1$  sample. The  $x_{\text{Er}}=0.5$  and  $1.0$  samples were antiferromagnetic insulators, and the hole concentration was  $\delta=0.05$  and  $0.025$ , respectively. The determination of the Néel temperatures  $T_N$  of the present samples were difficult because of the  $\text{Er}^{3+}$  local spins, but we may estimate  $T_N \sim 50$  K and  $230$  K for  $x_{\text{Er}}=0.5$  and  $1.0$

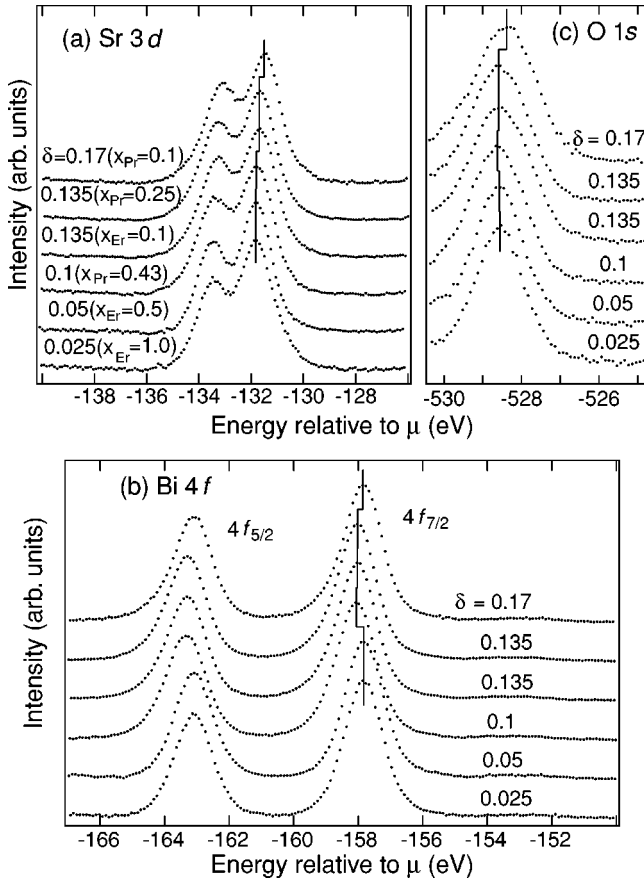


FIG. 1. Core-level XPS spectra of Er- and Pr-substituted BSCCO. (a) Sr 3d, (b) Bi 4f, and (c) O 1s. In each spectrum, the vertical bar denotes the peak position, and  $\delta$  denotes the hole concentration per Cu atom.

from comparison with  $T_N$  values of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+y}$ .<sup>15</sup>

X-ray photoemission spectroscopy (XPS) measurements were carried out using a Mg  $K\alpha$  source ( $h\nu=1253.6$  eV) and a VSW hemispherical analyzer. The energy resolution was about 0.8 eV, which was largely due to the width of the photon source. The samples were cleaved *in situ* to obtain clean surfaces and measured at  $\sim 80$  K. The base pressure in the analyzer chamber was  $\sim 1 \times 10^{-10}$  Torr. All the spectra presented here were taken within 4 h after cleaving, and no change was observed in the spectra during the measurement. In order to avoid sample degradation or contamination, the samples were cooled to about 80 K. In XPS measurements, high voltages of  $\sim 1$  kV have to be applied to the electron energy analyzer to decelerate photoelectrons, and it is usually difficult to measure the binding energies with an accuracy of  $< 100$  meV. In order to overcome this difficulty, we monitored the applied voltages directly and confirmed that the uncertainty could be reduced to less than 10 meV.<sup>5</sup> Furthermore, in order to eliminate other unexpected causes of errors, we measured the  $x_{\text{Pr}}=0.25$  and  $x_{\text{Er}}=0.1$  samples as a reference following the measurement of each sample. However, the line shapes were not always identical between the different samples, which sometimes results in uncertainties

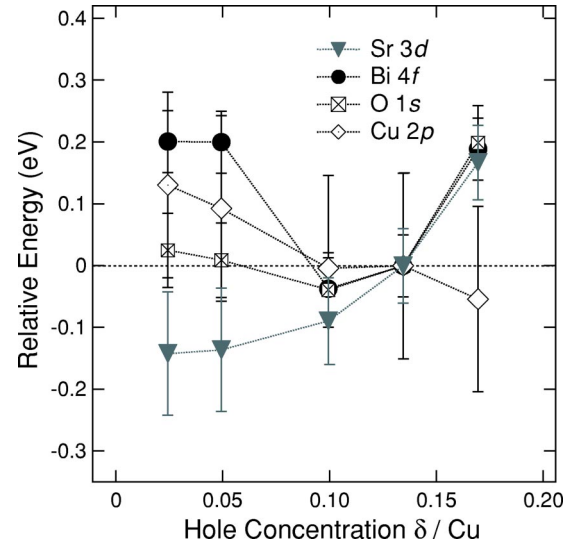


FIG. 2. Energy of each core level (relative to  $\delta=0.135$ ) for Er- and Pr-substituted BSCCO as a function of hole concentration  $\delta$ .

up to  $\pm 100$  meV in determining the shifts (as indicated by error bars in Figs. 2–4).

### III. RESULTS AND DISCUSSION

In order to deduce the chemical potential shift from a set of the core-level shift data, we utilize the relationship that the shift  $\Delta E$  of a core-level energy measured relative to  $\mu$  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,  $K\Delta Q$  is the chemical shift,  $\Delta V_M$  is a shift due to a change in the Madelung potential, and  $\Delta E_R$  is the change in the core-hole screening.<sup>16</sup> It has been demonstrated that  $\Delta V_M$  is negligibly small within a filling-controlled system of transition-metal oxides.<sup>3,5,13</sup> Core-hole screening by conduction electrons can also be excluded from the main origin of the core-level shifts in transition-metal oxides.<sup>3,5</sup> Therefore, it is reasonable to expect that  $\Delta V_M$  and  $\Delta E_R$  are negligibly small in the present system, too, and therefore to assume  $\Delta E = -\Delta\mu + K\Delta Q$ , as we shall see below. Also, it should be noted that the shift  $\Delta E$  can be uniquely determined from experimental data only when the line shape does not change with hole doping. In the present case, Cu and Bi may change their valences, while Sr is expected to remain divalent  $\text{Sr}^{2+}$  ( $\Delta Q=0$ ) in metal oxides. In fact, the Sr core level does not show a significant line-shape change and would most faithfully reflect the chemical potential shift ( $\Delta E = -\Delta\mu$ ) as described below.

Figure 1 shows the Sr 3d, O 1s, and Bi 4f core-level XPS spectra of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{R}_x\text{Cu}_2\text{O}_{8+y}$  ( $R=\text{Pr, Er}$ ). The line shapes of the Sr 3d and Bi 4f core levels are almost identical between the different compositions.<sup>17</sup> In Fig. 2, the positions of these core levels are plotted as functions of hole concentration  $\delta$  per Cu atom. The figure shows that the Sr 3d peak moves upwards monotonously with increasing  $\delta$ . As for the Bi 4f peak, it moves downwards as  $\delta$  increases in the region  $\delta < 0.1$ , unlike Sr 3d. One can understand this tendency if the mean valence of Bi decreases in the  $\delta < 0.1$

region and the Bi 4*f* level shows a so-called “chemical shift” on top of the chemical potential shift. The O 1*s* peak shift is intermediate between Bi 4*f* and Sr 3*d*: One can see from Fig. 1(c) that the linewidth is almost identical between  $\delta=0.025$  and  $\delta=0.05$ , but becomes broader and somewhat asymmetric as  $\delta$  increases to  $\geq 0.1$ . This behavior is consistent with the previous study, where the O 1*s* core-level spectra were decomposed into several components.<sup>9,18</sup> This means that the shift between  $\delta=0.05$  and 0.1 is a result of different components showing different shifts. Presumably, the broadening is caused by the different shifts of the O 1*s* core levels from the different oxygen sites in this small- $\delta$  region. Therefore, all the core levels (except for Cu 2*p*) in the range  $\delta>0.13$  show parallel shifts, which suggests that the shifts are solely due to the chemical potential shift, supporting the previous conclusion.<sup>10</sup> In the region  $\delta<0.05$ , again, the Sr, Bi, and O core levels are shifted in the same way, indicating that the chemical potential shift is the main origin of the core-level shifts in the heavily underdoped regions.

As for the Cu 2*p* core-level spectra (not shown), the peak becomes broader as  $\delta$  increases in the Er samples. In the Pr samples, the Pr 3*d* core level overlaps with the Cu 2*p* core levels and, therefore, it was difficult to identify the doping dependence of the line shape. Instead, we used the peak position to crudely estimate the shift of the Cu 2*p* level. In Fig. 2, we have plotted the shift of the Cu 2*p* peak positions for the Pr and Er samples. Thus, we find that the Cu 2*p* core level moves downwards with  $\delta$ . This behavior can be understood if the chemical shift, which is caused by the creation of a “Cu<sup>3+</sup>” component on the higher-binding-energy side of the Cu<sup>2+</sup> main component, overwhelms the effect of the chemical potential shift, as in the case of LSCO.<sup>3</sup> The present result is consistent with Ref. 9 while it is in disagreement with Ref. 8 in the heavily underdoped region, where a large jump in the core-level shift has been observed: A possible cause of the discrepancy is that some samples with large Y content studied in Ref. 8 were doped with *n*-type carriers.

Figure 3 shows the chemical potential shift  $\Delta\mu$  relative to  $\delta=0$  thus deduced for the Er- and Pr-substituted BSCCO samples. The shift is slow in the underdoped regime and becomes faster as the hole concentration increases. The depression of the chemical potential shift in the underdoped region, i.e.,  $|\partial\mu/\partial\delta|\rightarrow 0$  as  $\delta\rightarrow 0$ , has been predicted by numerical studies of the two-dimensional Hubbard model<sup>19,20</sup> and *t*-*J* model.<sup>21</sup> In the Monte Carlo simulations,<sup>19</sup> the calculated  $\Delta\mu$  follows  $\Delta\mu\propto -\delta^2$ . The measured  $\Delta\mu$  in BSCCO can be relatively well fitted to  $-\delta^2$  as shown in Fig. 3. Note that this behavior has not been predicted by mean-field theories such as the Gutzwiller approximation and the dynamical mean-field approximation, which predict that  $|\partial\mu/\partial\delta|\rightarrow\infty$  as  $\delta\rightarrow 0$ .<sup>22</sup> In the previous work,<sup>9</sup> the different shifts between the Cu, Bi, and O core levels and the Ca, Y, and Sr core levels in Y-substituted BSCCO have been attributed to the opening of a pseudogap in the underdoped region. They have proposed that the different core levels are shifted differently depending on whether the electronic states associated with that atom are

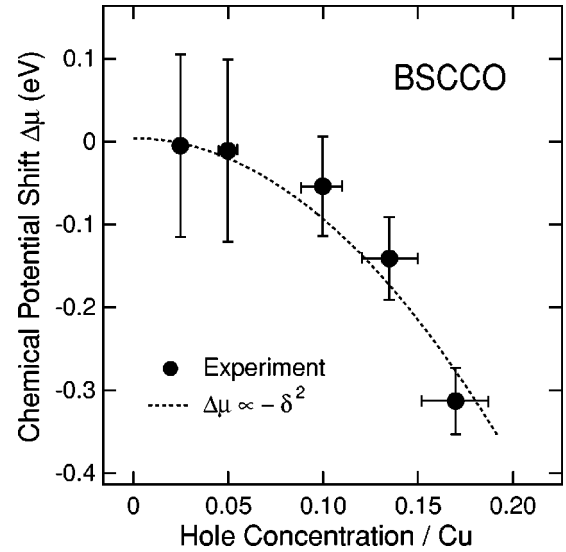


FIG. 3. Chemical potential shift  $\Delta\mu$  in Er- and Pr-substituted BSCCO as a function of doped hole concentration  $\delta$ . A fit of  $\Delta\mu \propto -\delta^2$  is shown by a dashed curve.

involved in the pseudogap opening or not. However, Bi states are certainly not involved in the pseudogap opening since the pseudogap phenomena certainly occur in the CuO<sub>2</sub> plane.

In Fig. 4, we compare  $\Delta\mu$  for BSCCO with that for LSCO. Both  $\Delta\mu$  curves show similar doping dependences in the sense that the shift is slow in the underdoped region and fast in the overdoped region. However,  $\Delta\mu$  is strongly depressed in underdoped LSCO as if the chemical potential is pinned by some levels, while such a pinninglike behavior is not evident or much weaker in BSCCO (although a systematic deviation from the  $-\delta^2$  behavior due to a weak  $\mu$  pinning cannot be excluded from Fig. 3). Further, the shift in BSCCO is faster than that in LSCO in the entire hole concentration region. These differences indicate that the change in the electronic structure from the AFI to the SC with hole doping is different at least quantitatively between the two systems. In LSCO, it has been found by an ARPES study that  $\mu$  is located in states which are created within the band gap

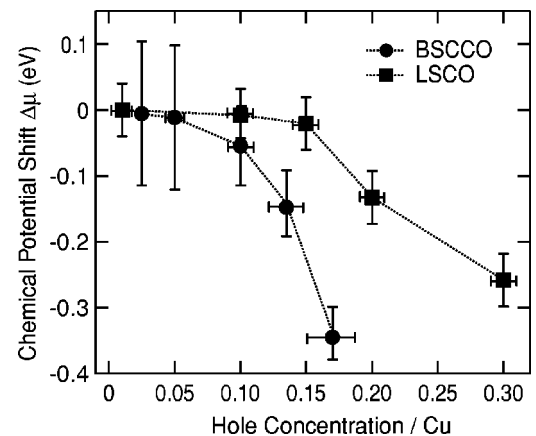


FIG. 4. Comparison of the chemical potential shift in Er- and Pr-substituted BSCCO with that in LSCO.

of the parent insulator  $\text{La}_2\text{CuO}_4$ . ARPES data of underdoped BSCCO, on the other hand, appear to show a gradual upwards shift of the lower Hubbard band [around  $\mathbf{k}=(\pi,0)$ ] with hole doping,<sup>23</sup> indicating no pinning behavior. It is highly desired to perform a systematic ARPES study lightly doped to underdoped BSCCO. Because the pinning behavior of the chemical potential in LSCO has been attributed to charge fluctuations of the stripe type,<sup>3</sup> the weakness or absence of the pinning behavior in BSCCO indicates that stripe fluctuations, if they exist, are weaker in this system.

#### IV. CONCLUSION

We have measured the chemical potential shift in BSCCO. The measured shift becomes slow in the underdoped region but is better fitted to  $-\delta^2$  predicted by the

numerical study of the two-dimensional Hubbard model than in the case of LSCO. The difference from LSCO is attributed to the weakness of stripe-type charge fluctuations in BSCCO.

#### ACKNOWLEDGMENTS

The authors would like to thank J. Matsuno for useful advice and A. Ino and T. Mizokawa for discussions. This work was supported by a Grant-in-Aid for Scientific Research in Priority Area “Novel Quantum Phenomena in Transition Metal Oxides” and a Special Coordination Fund for the Promotion of Science and Technology from the Ministry of Education, Culture, Sports, Science and Technology and New Energy and Industrial Technology Development Organization (NEDO).

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