Hole Binding around Ni Impurity in Cuprates

Kenji Tsutsui,1 Atsushi Toyama,2 Takami Tohyama,3 and Sadamichi Maekawa2,4

1Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Hyogo 679-5148, Japan.
2Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan.
3Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-8502, Japan.
4CREST, Japan Science and Technology Agency (JST), Tokyo 102-0075, Japan.

(Dated: August 25, 2009)

We examine the influence of Ni impurity in cuprates on the distribution of hole carriers by performing numerically exact diagonalization calculations for a model consisting of Cu3d, Ni3d, and O2p orbitals. Using realistic parameters for the system, we find that a hole is predominantly bound to O2p orbitals around the Ni impurity forming the Zhang-Rice doublet. This imposes strong restrictions on modeling Ni-substituted cuprates. We propose a resonant inelastic x-ray scattering experiment for Ni K-edge to confirm hole binding around the Ni impurity.

PACS numbers: 74.72.-h, 71.10.Fd, 71.55.-i

Atomic substitutions for copper in high-temperature cuprate superconductors induce significant impacts on macroscopic and local physical properties of the cuprates. Divalent transition metal ions such as zinc and nickel have been frequently substituted for Cu. It is well known that nonmagnetic Zn impurities suppress the superconducting transition temperature more strongly than magnetic Ni impurities. Concerning magnetic properties, neutron scattering experiments have shown that Zn impurities enhance the antiferromagnetic (AF) correlation length only slightly, whereas Ni impurities suppress incommensurate peaks strongly and stabilize the Neel ordering. Such contrasting behaviors have been discussed in connection with the difference of spin state of Zn2+ with spin S = 0 and Ni2+ with S = 1 [1]. For Ni substitution, however, it has been argued from several experiments [3, 4, 5, 6, 7] that a Ni impurity attracts a hole, giving Ni3+ with S = 1/2. More recently, it has been suggested from x-ray-absorption-fine-structure (XAFS) measurements that the Ni impurity forms Ni2+L state with S = 1/2 (L represents a ligand hole), i.e., Zhang-Rice (ZR) doublet state, binding a hole on neighboring oxygen orbitals [8]. The formation of the doublet may explain several experimental facts for Ni-substituted cuprates as discussed in Ref. [8]: small moment of Ni impurity [9, 10], weak suppression of coherence peaks [11], reduction of magnetic resonance energy [12], enhancement of pseudo-gap energy [13], and so on. In spite of accumulating experimental evidences of hole binding around Ni impurity, there is no theoretical support clarifying the formation of the ZR doublet as far as we know.

In this Letter, we show that the ZR doublet is certainly formed at Ni site embedded in the CuO2 plane, based on exact diagonalization calculations for small clusters with realistic parameter values. This theoretical result together with experimental ones mentioned above puts restrictions on theoretical models of Ni-substituted cuprates. We propose a site-selective experimental technique to confirm the presence of the ZR doublet, which is resonant inelastic x-ray scattering (RIXS) experiment for Ni K-edge. We predict low-energy structures inside the Mott gap, which can be direct evidence of hole binding around Ni impurity.

For Cu and O ions, we consider Cu3dxz−yz2 and O2pσ orbitals. An additional orbital 3d3z2−r2 is included on Ni ion substituted for Cu. Apical oxygen 2pσ orbitals below/above the Ni ion are also taken into account. By including hoppings between 3d and 2p orbitals and the Coulomb interactions among 3d orbitals, the Hamiltonian in the hole representation is given by $H_{dp} = H_T + H_d$ with

$$H_T = T_{pd} \sum_{\mathbf{i} \mathbf{r}} d_{\mathbf{i} \mathbf{r}}^\dagger \left( p_{i-x}^z - p_{i-x}^{-z} - p_{i-y}^{-z} + p_{i-y}^z \right)$$

$$- T_{pd} \sum_{\mathbf{i} \mathbf{r}} d_{\mathbf{i} \mathbf{r}}^\dagger \left( p_{i-x}^{-z} - p_{i-x}^z - p_{i-y}^z + p_{i-y}^{-z} \right)$$

$$+ \alpha T_{pd} \sum_{\mathbf{i} \mathbf{r}} d_{\mathbf{i} \mathbf{r}}^\dagger \left( p_{i-0} - p_{i+0} \right) + H.c.$$
hedron is represented by introducing α, where 0 < α < 1 for elongated octahedron along the z direction. The parameters ε_d (ε_p) and U_d are the energy level of Cu3d_{z^2−r^2} (O2p) and the Coulomb repulsion of Cu3d_{z^2−r^2} orbital, respectively. ε_Ni, U_Ni, U′_Ni, and K_Ni are the energy levels of Ni3d orbitals, intra- and inter-orbital Coulomb repulsions, and the exchange interaction, respectively, with U_Ni = U′_Ni + 2K_Ni. Hereafter we set ε_d = 0.

Following a procedure by Zhang and Rice [14], let us introduce three kinds of O2p Wannier orbitals, i.e., symmetric, antisymmetric, and nonbonding. Among them, we can neglect the nonbonding orbital since it is decoupled from other orbitals. For a system with N unit cells, the symmetric and antisymmetric Wannier orbitals are given by φ^s_{iσ} = −iN−ρ \sum_k e^{i\bar{k}\cdot\bar{r}} β_{k}(S_x p_x σ−S_y p_y σ), and φ^a_{iσ} = iN−ρ \sum_k e^{i\bar{k}\cdot\bar{r}} β_{k}i[S_x S_y (S_y p_x σ+S_x p_y σ)−iα(S^2_x + S^2_y) p_{z2}], where S_γ(y) = sin \bar{k}_γ(y) \sqrt{2}, and the case of a single Ni impurity in the system, it is convenient to introduce a new antisymmetric operator given by φ^a_{iσ} = β−1 \sum_{i′j} τ_{ij} φ^s_{i′σ} with β = \sum_{i,j} |τ_{ij}|^2, since φ^s_{iσ} only couples to the impurity. Then, the number of the orbitals in the system becomes 2N + 2.

We use the Lanczos-type exact diagonalization technique on a N = \sqrt{8} x \sqrt{8} unit-cell cluster with a single Ni impurity under periodic boundary conditions [13]. The parameter values have been estimated to be T_P ≃ 0.95 ~ 1.3 eV, U_d ≃ 8 ~ 10.5 eV, ε_p ≃ 2 ~ 3.5 eV [10]. In the present study, we take T_P = 1 eV, U_d = U_Ni = 8 eV, K_Ni = 0.8 eV, and ε_p = 3 eV. ε_Ni is an unknown parameter and α is taken to be 1/√2 for simplicity.

Insulating cuprates are known to be charge-transfer (CT) type, where the CT energy Δ between Cu and O is smaller than U_d [17]. Nickel oxides also belong to the CT type, but the charge transfer energy Δ_Ni is larger than Δ [18]. Δ is given by Δ = E(d^{10}L)−E(d^8) = ε_p, where E is the energy of a Cu-O unit for a given configuration without hopping terms. Similarly Δ_Ni = E(d^8L)−E(d^7) = Δ−ε_Ni−U_Ni+3K_Ni. We assume that Δ_Ni for the Ni impurity is similar to the bulk systems, since the CT energy is predominantly determined by the energy level of 3d orbitals when ligand and environment are the same [18]. Therefore, we take Δ_Ni > Δ in the present study of Ni impurity, leading to ε_Ni < −5.6 eV.

Figure 1(a) shows hole number ⟨n⟩ on each orbital of the cluster as a function of the difference of the CT energies Δ ≡ Δ_Ni − Δ. Filled upward and downward triangles represent Ni 3d_{z^2−r^2} (denoted as d) and 3d_{a1g−r_2g} (d′), respectively. φ^s and φ^a on Ni site are shown by open triangles. Filled (open) circles denote Cu d (Cu d′) orbitals at the nearest neighbor (n.n.) sites from Ni. (b) The difference of ⟨n⟩ between one-hole-doped and undoped ground states. Open squares and diamonds denote φ^s orbitals at the second and third n.n. sites, respectively. Other symbols are the same as (a). The vertical broken line represents the position where the ground-state symmetry changes.

Next we examine how a hole introduced into the system is distributed among the orbitals. In the range of Δ shown in Fig. 1 we find that with increasing Δ the ground state with one additional hole (10 holes in total) changes quantum number at Δ ~ 1.2 eV from the total spin S = 1 and A_2 irreducible representation of C_4v (degenerated with B_1) to S = 0 and B_1. The difference of hole number, δ⟨n⟩, on each orbital between the one-hole doped and undoped ground states is plotted in Fig. 1(b). We find that for Δ ≥ 1.2 a hole introduced in the system occupies predominantly on Ni φ^s orbital, i.e., an oxygen Wannier orbital that mainly couples to Ni3d_{z^2−r^2}. In total, more than 60% of the hole enters into Ni-related orbitals. This is consistent with experimental suggestions [3, 4, 5, 6, 7, 8] that a Ni impurity may bind a hole and form the ZR doublet. Note that negative δ⟨n⟩ for
Ni $d'$ is the consequence of strong energy gain by accommodating holes into the orbitals with $x^2-y^2$ symmetry. For $\Delta \gtrsim 1.2$, the doped hole is distributed mainly on oxygen orbitals away from the Ni impurity. Since an effective CT energy for Ni oxides has been reported to be $\sim 5$ eV \cite{18}, it is reasonable to consider that $\Delta > 1.2$ eV. Therefore, the present result strongly supports the binding of a hole around a Ni impurity in real Ni-substituted cuprates.

In order to confirm the stability of the ZR doublet, we compared binding energy of the ZR doublet on a NiO$_6$ cluster with that of the ZR singlet on a CuO$_4$ cluster. We found that the ZR doublet is more stable than the ZR singlet when $\Delta_{\text{Ni}}$ is larger than $\Delta$ by 0.3 eV. This is qualitatively consistent with the data shown in Fig. 1(b), implying that the stability of the ZR doublet is governed by local character around Ni. In the limit of $(U_d, U_{\text{Ni}}, \Delta, \Delta_{\text{Ni}}) \gg T_{pd}$ that is approximately satisfied in the present parameter set, the binding-energy difference of the doublet and the singlet, $\delta E_{\text{B}}$, may be given by

$$\delta E_{\text{B}} = 2T_{pd}^2 \left( \frac{4}{U_d - \Delta} + \frac{2}{U_{\text{Ni}} + K_{\text{Ni}} - \Delta_{\text{Ni}}} - \frac{3}{\Delta_{\text{Ni}}} \right),$$

We notice that dominant negative contribution to $\delta E_{\text{B}}$ comes from the third term in (4). This implies the importance of the condition that $U_{\text{Ni}}$ ($\sim 8$ eV) is not much larger than $\Delta_{\text{Ni}}$ ($\sim 5$ eV).

When a hole is bound to a Ni impurity, localized Cu spins are expected to be unaffected and thus AF correlation may remain. Defining $S_i^z = (n^d_{i,1} - n^d_{i,1} + \phi^d_{i,1} \bar{\phi}^d_{i,1} - \phi^d_{i,1} \bar{\phi}^d_{i,1})/2$, we show in Fig. 2 the equal-time spin-spin correlation function $\langle S_i^z S_j^z \rangle$ between two Cu sites in undoped and one-hole doped cases with $\Delta = 1.4$ and 0.9 eV. Here, $\Delta$ is chosen near the boundary of two regions shown in Fig. 1(b). In the undoped case, the correlation on the same (different) sub-lattice is positive (negative), implying the presence of AF order. For $\Delta = 1.4$ eV, $\langle S_i^z S_j^z \rangle$ in the one-hole doped case is very similar to the undoped case. This is a natural consequence of hole binding around Ni impurity. On the other hand, the correlation is dramatically changed from the undoped case when $\Delta = 0.9$ eV. This is due to the destruction of AF order caused by carrier motion.

To directly observe hole binding around Ni impurity, we need to use site-selective probes. One of them would be XAFS that has been performed recently \cite{8}. As another probe, we propose a RIXS experiment for Ni K-edge, which can detect charge excitations related to the bound hole. In the Ni K-edge RIXS, the emission of a photon with a dipole transition between Ni 4p and Ni 1s states occurs resonantly by tuning incoming photon energy to Ni K absorption edge. In the intermediate state, we introduce Coulomb interaction between 3d and 1s-core holes \cite{20}, given by $H_{1s-3d} = U_c \sum_{\sigma} (n_{i,\uparrow} c_{i,\downarrow} n_{i,\downarrow} c_{i,\uparrow})$, where $n_{i,\sigma}$ is the number operator of 1s-core hole. By assuming that the 4p photo-electron enters into the bottom of the 4p bands \cite{20}, the RIXS spectrum for Ni K-edge as well as Cu K-edge is expressed as

$$I(\Delta \omega) = \sum_f |\langle f| D_K^{\dagger} G(\omega_i) D_K |0\rangle|^2 \delta (\Delta \omega - E_f + E_0),$$

where $D_K = \sum_{i,s} e^{i \delta \mathbf{k} \cdot \mathbf{r}_i} s^i_{1σ} + \text{H.c.}$ with the creation operator $s^i_{1σ} (p^i_{4σ})$ of 1s-core hole (4p electron). $\sum_i$ denotes summation over Ni (Cu) sites for Ni (Cu) K-edge. $K_{i(f)}$ is the wave vector of the incoming (outgoing) photon with energy $\omega_i(f)$, and $\Delta \omega = \omega_i - \omega_f$. $G^{-1}(\omega_i) = \omega_i + i \Gamma - H_{4p} - H_{1s-3d} - H_{1s,4p}$, where $H_{1s,4p}$ is composed of the energy separation $\varepsilon_{\text{Ni(Cu)}}$ between the Ni (Cu) 1s level and the bottom of the 4p band, and $\Gamma$ is the inverse of relaxation time in the intermediate state. $|0\rangle$ is the ground state with energy $E_0$, $|f\rangle$ is the final state of RIXS with energy $E_f$. We use $\Gamma = 1$ eV and $U_c = 4$ eV \cite{21}. $I(\Delta \omega)$ is calculated by using a modified version of the conjugate-gradient method together with the Lanczos technique.

Figure 3 shows Cu K-edge (upper panel) and Ni K-edge (lower panel) RIXS spectra in undoped and one-hole-doped cases for $\Delta = 1.4$ eV. The spectra at zero momentum transfer ($\mathbf{K}_i - \mathbf{K}_i = 0$) are shown for Cu K-edge. In the undoped case, the edge of the CT gap is located at $\sim 2.1$ eV and $\sim 3.2$ eV for Cu and Ni, respectively. The difference comes from different CT energies. This is qualitatively consistent with experimental observations for La$_2$CuO$_4$ ($\sim 2.2$ eV) and La$_2$NiO$_4$ ($\sim 4$ eV) \cite{21}. Furthermore, recent RIXS experiments for Ni-substituted La$_2$CuO$_4$ also show similar behaviors \cite{22}. In Cu K-edge RIXS, the spectrum around 4.5-6 eV is associated with the excitations from bonding to antibonding states in CuO$_4$ plaquette \cite{23, 24}. A similar structure appears in the energy region from 6 to 7 eV for Ni K-edge RIXS.

The Ni K-edge spectrum is strongly affected by hole-doping as shown in the lower panel of Fig. 3. In particular, new spectral structures appear at $\Delta \omega \sim 1.35$ eV and $\sim 2.13$ eV within the CT gap. Examining eigenstates generating the new structures, we find that the hole number of Cu $\sigma^*$ is larger than that in the ground state, while the hole number at the Ni site is smaller. This means that
the ZR singlet on Cu are dominating in the corresponding excited states. Since the hole number at the Ni site is large in the ground state due to the formation of the ZR doublet, the new spectral structures are associated with excitations from the ZR doublet to ZR singlet. Therefore, if we observe spectral weights inside the CT gap for excitations from the ZR doublet to ZR singlet. There-fore, if we observe spectral weights inside the CT gap for Ni-substituted cuprates, it can be identified as direct evidence of hole binding around Ni impurity. Note that the spectrum for Cu K-edge is almost unchanged upon hole-doping although a small hump is seen around 1 eV.

We have neglected direct O-O hoppings in 1. The hoppings may cause the decrease of Δ, leading to less stability of the ZR doublet as seen from 1. However, we found that the boundary at Δ ~ 0.3 eV for single clusters without the hopping parameter Tpp increases only by 0.1 eV for a realistic value of Tpp (= 0.5 eV).

The formation of the ZR doublet at Ni site imposes restrictions on modeling impurity effects in cuprate superconductors, in particular, on the construction of single-band models like t-J-type model 25, 26, 24, 22, 23, 30. We should treat a Ni impurity as a S = \frac{1}{2} spin in hole-doped cases. The spin is expected to couple to the neighboring Cu spins antiferromagnetically with an interaction parameter determined by competition between superexchange processes and the process of the motion of the φs hole. Other holes that hop to the impurity position may feel repulsive interaction. This model is close to those used in Ref. 25. More precise effective t-J-type model is now under construction.

In summary, we have carried out the numerically exact diagonalization on the eight-unit-cell cluster with a Ni impurity site representing Ni-substituted cuprate superconductors. Using realistic parameters of the cuprates, we have found that a hole can be bound in the NiO4 plaquettes forming the ZR doublet. This is due to the fact that the ZR doublet is more stable in energy than the ZR singlet on Cu. This finding supports theoretically recent experimental suggestion of the presence of the ZR doublet. Also this imposes strong restrictions on modeling Ni-substituted cuprates. We have proposed that the hole binding can be seen in RIXS for Ni K-edge. We hope that the proposed RIXS experiment will be done in the near future.

We are grateful to H. Hiraka, K. Ishii, J. Mizuki, K. Yamada, and W. Koshiba for helpful discussions. This work was supported by Nanoscience Program of Next Generation Supercomputing Project and Grant-in-Aid for Scientific Research from MEXT, and the inter-university cooperative research program of IMR, Tohoku Univ. Computations were carried out in IMR, Tohoku Univ.; ISSP, Univ. of Tokyo; and YITP, Kyoto Univ.

[1] H. Alloul et al., Rev. Mod. Phys. 81, 45 (2009).
[2] R. J. Birgeneau et al., J. Phys. Soc. Jpn. 75, 111003 (2006).
[3] V. Bhat et al., Physica C 191, 271 (1992).
[4] T. Nakano et al., Phys. Rev. B 58, 5831 (1998).
[5] H. Hiraka et al., Phys. Soc. Jpn. 74, 2197 (2005).
[6] M. Matsuda et al., Phys. Rev. B 73, 140503 (2006).
[7] H. Hiraka et al., Phys. Soc. Jpn. 76, 074703 (2007).
[8] H. Hiraka et al., Phys. Rev. Lett. 102, 037002 (2009).
[9] G. Xiao et al., Phys. Rev. B 42, 8752 (1990).
[10] P. Mendels et al., Europhys. Lett. 46, 678 (1999).
[11] E. W. Hudson et al., Nature (London) 411, 920 (2001).
[12] Y. Sidis et al., Phys. Rev. Lett. 84, 5900 (2000).
[13] A. V. Pimenov et al., Phys. Rev. Lett. 94, 227003 (2005).
[14] F. C. Zhang and T. M. Rice, Phys. Rev. B 37 (1988) R3759; ibid. 41, 7243 (1990).
[15] We also examined N = 2 and N = 2 × 2 clusters and found that size dependence is small. The N = 8 cluster is shown in Fig. 2(a).
[16] See, for example, references in Physics of Transition Metal Oxides, S. Maekawa et al., Springer Series in Solid-State Sciences, Vol. 144 (2004).
[17] J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. 55, 418 (1985).
[18] A. E. Bocquet et al., Phys. Rev. B 53, 1161 (1996).
[19] ΔNI of δE_{J0} = 0 in 1 is ~ 6.5 eV, which is much larger than that estimated exactly from the single cluster.
[20] K. Tsutsui, T. Tomyama, and S. Maekawa, Phys. Rev. Lett. 83, 3705 (1999); ibid. 91, 117001 (2003).
[21] E. Collart et al., Phys. Rev. Lett. 96, 157004 (2006).
[22] K. Ishii et al., unpublished.
[23] J. P. Hill et al., Phys. Rev. Lett. 80, 4967 (1998).
[24] T. Íde and A. Kotani, J. Phys. Soc. Jpn. 68, 3100 (1999).
[25] D. Poilblanc et al., Phys. Rev. B 50, 13020 (1994).
[26] Y. Ohta et al., Physica C 263, 94 (1996).
[27] J. Riera et al., Phys. Rev. B 54, 7441 (1996).
[28] I. Kuroda et al., Physica B 237-238, 103 (1997).
[29] H. Tsuchiura et al., Phys. Rev. Lett. 84, 3165 (2000).
[30] T. Xiang et al., Phys. Rev. B 66, 174504 (2002).