Exact diagonalization calculations of hole binding around Ni impurities in Ni-substituted cuprate superconductors

Kenji Tsutsui
Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Hyogo 679-5148, Japan

Atsushi Toyama
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

Takami Tohyama
Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-8502, Japan

Sadamichi Maekawa
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
and CREST, Japan Science and Technology Agency (JST), Tokyo 102-0075, Japan
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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 Cu $3d$, Ni $3d$, and O $2p$ orbitals. Using realistic parameters for the system, we find that a hole is predominantly bound to O $2p$ 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.

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I. INTRODUCTION

Atomic substitutions for copper in high-temperature cuprate superconductors induce significant impacts on macroscopic and local physical properties of the cuprates.[1] 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.[2] Such contrasting behaviors have been discussed in connection with the difference of spin state of Zn^{2+} with spin $S=0$ and Ni^{2+} with $S=1$.[1] For Ni substitution, however, it has been argued from several experiments[3–7] that a Ni impurity attracts a hole, giving Ni^{3+} with $S=\frac{1}{2}$. More recently, it has been suggested from x-ray-absorption-fine-structure (XAFS) measurements that the Ni impurity forms $Ni^{2+}\underline{L}$ state with $S=\frac{1}{2}$ ($\underline{L}$ 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 in magnetic-resonance energy,[12] enhancement of pseudogap 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 work, we show that the ZR doublet is certainly formed at Ni site embedded in the CuO_2 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.

The paper is organized as follows. Section II introduces the model for cuprates in which Ni ions are substituted for Cu ones. Section III shows the results of the Lanczos calculations for the ground states of the model and in Sec. IV, we propose that the direct evidence of hole binding around Ni appears in the RIXS spectra.

II. MODEL

For Cu and O ions, we consider Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals. An additional orbital $3d_{3z^2-r^2}$ is included on Ni ion substituted for Cu. Apical oxygen $2p_z$ 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

$$H_T = T_{pd}\sum_{\mathbf{i}\sigma} d^\dagger_{\mathbf{i}\sigma}\left(p_{\mathbf{i}-\frac{\mathbf{x}}{2}\sigma} - p_{\mathbf{i}+\frac{\mathbf{x}}{2}\sigma} - p_{\mathbf{i}-\frac{\mathbf{y}}{2}\sigma} + p_{\mathbf{i}+\frac{\mathbf{y}}{2}\sigma}\right)$$
$$- T'_{pd}\sum_{\mathbf{i}_0\sigma} d'^\dagger_{\mathbf{i}_0\sigma}\left(p_{\mathbf{i}_0-\frac{\mathbf{x}}{2}\sigma} - p_{\mathbf{i}_0+\frac{\mathbf{x}}{2}\sigma} + p_{\mathbf{i}_0-\frac{\mathbf{y}}{2}\sigma} - p_{\mathbf{i}_0+\frac{\mathbf{y}}{2}\sigma}\right)$$
$$+ \alpha T''_{pd}\sum_{\mathbf{i}_0\sigma} d'^\dagger_{\mathbf{i}_0\sigma}\left(p_{\mathbf{i}_0-\mathbf{z}\sigma} - p_{\mathbf{i}_0+\mathbf{z}\sigma}\right) + \text{H.c.}$$

$$+\varepsilon_d \sum_{\mathbf{i}\neq\mathbf{i}_0\sigma} n^d_{\mathbf{i}\sigma} + \varepsilon_{\mathrm{Ni}} \sum_{\mathbf{i}_0\sigma\gamma=d,d'} n^{\gamma}_{\mathbf{i}_0\sigma} + \varepsilon_p \sum_{\mathbf{i}\boldsymbol{\delta}\sigma} n^p_{\mathbf{i}+\frac{\boldsymbol{\delta}}{2}\sigma}, \tag{1}$$

$$H_d = U_d \sum_{\mathbf{i}\neq\mathbf{i}_0} n^d_{\mathbf{i}\uparrow} n^d_{\mathbf{i}\downarrow} + U_{\mathrm{Ni}} \sum_{\mathbf{i}_0\gamma} n^{\gamma}_{\mathbf{i}_0\uparrow} n^{\gamma}_{\mathbf{i}_0\downarrow} + U'_{\mathrm{Ni}} \sum_{\mathbf{i}_0\sigma\sigma'} n^d_{\mathbf{i}_0\sigma} n^{d'}_{\mathbf{i}_0\sigma'}$$
$$+ K_{\mathrm{Ni}} \sum_{\mathbf{i}_0\sigma\sigma'} d^{\dagger}_{\mathbf{i}_0\sigma} d'^{\dagger}_{\mathbf{i}_0\sigma'} d_{\mathbf{i}_0\sigma'} d'_{\mathbf{i}_0\sigma}$$
$$+ K_{\mathrm{Ni}} \sum_{\mathbf{i}_0} (d^{\dagger}_{\mathbf{i}_0\uparrow} d^{\dagger}_{\mathbf{i}_0\downarrow} d'_{\mathbf{i}_0\downarrow} d'_{\mathbf{i}_0\uparrow} + \mathrm{H.c.}), \tag{2}$$

where the summation of $\mathbf{i}$ runs over all of Cu and Ni sites, $\mathbf{i}_0$ denotes Ni sites, $\mathbf{x}(\mathbf{y})$ is the vector connecting neighboring Cu ions along the $x(y)$ direction, $\mathbf{i}_0 \pm \mathbf{z}$ represents apical oxygen sites above/below Ni sites, and $\boldsymbol{\delta}$ runs over $\mathbf{x}$, $\mathbf{y}$, and $2\mathbf{z}$. The operator $d_{\mathbf{i}\sigma}$ ($d'_{\mathbf{i}_0\sigma}$) is the annihilation operator for a $3d_{x^2-y^2}$ ($3d_{3z^2-r^2}$) hole with spin σ at site $\mathbf{i}(\mathbf{i}_0)$, $p_{\mathbf{i}\pm\frac{\boldsymbol{\delta}}{2}\sigma}$ is the annihilation operator for a $2p$ hole at site $\mathbf{i}\pm\frac{\boldsymbol{\delta}}{2}$ with spin σ. $n^{\gamma}_{\mathbf{i}_0\sigma} = \gamma^{\dagger}_{\mathbf{i}_0\sigma}\gamma_{\mathbf{i}_0\sigma}$ and $n^{p}_{\mathbf{i}+\frac{\boldsymbol{\delta}}{2}\sigma} = p^{\dagger}_{\mathbf{i}+\frac{\boldsymbol{\delta}}{2}\sigma} p_{\mathbf{i}+\frac{\boldsymbol{\delta}}{2}\sigma}$. T_{pd}, T'_{pd}, and T''_{pd} are the hopping integrals between $3d_{x^2-y^2}$ and $2p_\sigma$, between $3d_{3z^2-r^2}$ and $2p_\sigma$, and between $3d_{3z^2-r^2}$ and $2p_z$, respectively, with $T_{pd} = \sqrt{3}T'_{pd} = \frac{\sqrt{3}}{2}T''_{pd}$. The tetragonality of NiO_6 octahedron is represented by introducing α, where $\alpha=0$ and 1 correspond to the case of infinite distance of apex O-Ni bond and the case of equal distance between apex O-Ni and in-plane O-Ni bonds, respectively. The parameters $\varepsilon_d(\varepsilon_p)$ and U_d are the energy level of Cu $3d_{x^2-y^2}$ (O $2p$) and the Coulomb repulsion of Cu $3d_{x^2-y^2}$ orbital, respectively. $\varepsilon_{\mathrm{Ni}}$, U_{Ni}, U'_{Ni}, and K_{Ni} are the energy levels of Ni $3d$ orbitals, intraorbital and interorbital Coulomb repulsions, and the exchange interaction, respectively, with $U_{\mathrm{Ni}} = U'_{\mathrm{Ni}} + 2K_{\mathrm{Ni}}$. Hereafter we set $\varepsilon_d = 0$.

Following a procedure by Zhang and Rice,[14] let us introduce three kinds of O $2p$ Wannier orbitals, i.e., symmetric, antisymmetric, and nonbonding ones which are classified as hybridizing with only the Cu $3d_{x^2-y^2}$ orbital ($\phi^s_{\mathbf{i}\sigma}$), with both $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals ($\phi^a_{\mathbf{i}\sigma}$), and with neither ($\phi^n_{\mathbf{i}\sigma}$), defined by

$$\phi^s_{\mathbf{i}\sigma} = -iN^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{i}} \beta_{s\mathbf{k}} (S_x p_{x\mathbf{k}\sigma} - S_y p_{y\mathbf{k}\sigma}), \tag{3}$$

$$\phi^a_{\mathbf{i}\sigma} = iN^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{i}} \beta_{a\mathbf{k}} [\sqrt{2} S_x S_y (S_y p_{x\mathbf{k}\sigma} + S_x p_{y\mathbf{k}\sigma})$$
$$- i\alpha (S_x^2 + S_y^2) p_{z\mathbf{k}\sigma}], \tag{4}$$

$$\phi^n_{\mathbf{i}\sigma} = N^{-1/2} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{i}} \beta_{n\mathbf{k}} [\alpha (S_y p_{x\mathbf{k}\sigma} + S_x p_{y\mathbf{k}\sigma}) + \sqrt{2} i S_x S_y p_{z\mathbf{k}\sigma}], \tag{5}$$

where N is the system size, $S_{x(y)} = \sin\frac{k_{x(y)}}{2}$, $\beta_{s\mathbf{k}} = (S_x^2 + S_y^2)^{-1/2}$, $\beta_{n\mathbf{k}} = (2S_x^2 S_y^2 + \alpha^2 \beta_{s\mathbf{k}}^{-2})^{-1/2}$, $\beta_{a\mathbf{k}} = \beta_{s\mathbf{k}}\beta_{n\mathbf{k}}$, and the operators $p_{x\mathbf{k}\sigma}$, $p_{y\mathbf{k}\sigma}$, and $p_{z\mathbf{k}\sigma}$ are the Fourier transformations of $p_{\mathbf{i}+\frac{\mathbf{x}}{2}\sigma}$, $p_{\mathbf{i}+\frac{\mathbf{y}}{2}\sigma}$, and $\frac{1}{\sqrt{2}}(p_{\mathbf{i}+\mathbf{z}\sigma} - p_{\mathbf{i}-\mathbf{z}\sigma})$, respectively. Using these Wannier orbitals, the hopping terms of the Hamiltonian (1) reads

$$H_T = 2T_{pd} \sum_{\mathbf{ij}\sigma} \tau_{\mathbf{ij}} d^{\dagger}_{\mathbf{i}\sigma} \phi^s_{\mathbf{j}\sigma} - 2T'_{pd} \sum_{\mathbf{i}_0\mathbf{j}\sigma} \tau'^{s}_{\mathbf{i}_0\mathbf{j}} d'^{\dagger}_{\mathbf{i}_0\sigma} \phi^s_{\mathbf{j}\sigma}$$
$$+ 2\sqrt{2} T'_{pd} \sum_{\mathbf{i}_0\mathbf{j}\sigma} \tau'^{a}_{\mathbf{i}_0\mathbf{j}} d'^{\dagger}_{\mathbf{i}_0\sigma} \phi^a_{\mathbf{j}\sigma} + \mathrm{H.c.}$$
$$+ \varepsilon_p \sum_{\mathbf{i}\sigma\eta=s,a} \phi^{\eta\dagger}_{\mathbf{i}\sigma} \phi^{\eta}_{\mathbf{i}\sigma} + \varepsilon_{\mathrm{Ni}} \sum_{\mathbf{i}_0\sigma\gamma=d,d'} n^{\gamma}_{\mathbf{i}_0\sigma}, \tag{6}$$

where $\tau_{\mathbf{ij}} = \frac{1}{N}\Sigma_{\mathbf{k}} \beta_{s\mathbf{k}}^{-1} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})}$, $\tau'^{s}_{\mathbf{ij}} = \frac{1}{N}\Sigma_{\mathbf{k}} \beta_{s\mathbf{k}} (S_x^2 - S_y^2) e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})}$, and $\tau'^{a}_{\mathbf{ij}} = \frac{1}{N}\Sigma_{\mathbf{k}} \beta_{s\mathbf{k}}^2 \beta_{a\mathbf{k}}^{-1} e^{i\mathbf{k}\cdot(\mathbf{i}-\mathbf{j})}$. Their value is the largest if $\mathbf{i}-\mathbf{j}$ is small, for example, $\tau_{\mathbf{i}=\mathbf{j}} = 0.958$, $\tau'^{s}_{\mathbf{i}=\mathbf{j}} = 0$, $\tau'^{s}_{\mathbf{i}=\mathbf{j}+\mathbf{x}} = -0.258$, and $\tau'^{a}_{\mathbf{i}=\mathbf{j}} = 0.915$. Note that we can neglect the nonbonding orbital since it is decoupled from other orbitals. Moreover, in the case of a single Ni impurity in the system, i.e., a N-site system in which one of the N sites is replaced by a Ni impurity, it is convenient to introduce a new antisymmetric operator given by $\tilde{\phi}^a_{\sigma} = \tilde{\beta}^{-1} \Sigma_{\mathbf{j}} \tau'^{a}_{\mathbf{i}_0\mathbf{j}} \phi^a_{\mathbf{j}\sigma}$ with $\tilde{\beta}^2 = \Sigma_{\mathbf{j}} |\tau'^{a}_{\mathbf{i}_0\mathbf{j}}|^2$ since $\phi^a_{\mathbf{j}\sigma}$ only couples to the impurity. Then, the number of the orbitals in the system becomes $2N+2$, where the $3d_{x^2-y^2}$ and ϕ^s orbitals on each site and two additional orbitals of $3d_{3z^2-r^2}$ and ϕ^a on the Ni impurity site are taken into account.

We use the Lanczos-type exact diagonalization technique on $N = 2\times 2$ and $\sqrt{8}\times\sqrt{8}$-unit-cell clusters with a single Ni impurity under periodic boundary conditions, as well as a two-site ($N=2$) cluster under open boundary conditions. We will show the results for the $N = \sqrt{8}\times\sqrt{8}$ cluster in the following.[15]

The parameter values have been estimated to be $T_{pd} \simeq 0.95-1.3$ eV, $U_d \simeq 8-10.5$ eV, and $\varepsilon_p \simeq 2-3.5$ eV.[16] In the present study, we take $T_{pd}=1$ eV, $U_d = U_{\mathrm{Ni}} = 8$ eV, $K_{\mathrm{Ni}} = 0.8$ eV, and $\varepsilon_p = 3$ eV. $\varepsilon_{\mathrm{Ni}}$ is an unknown parameter and α is taken to be $1/\sqrt{2}$ 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 $\Delta = E(d^{10}\underline{L}) - E(d^9) = \varepsilon_p$, where E is the energy of a Cu-O unit for a given configuration without hopping terms. Similarly $\Delta_{\mathrm{Ni}} = E(d^9\underline{L}) - E(d^8) = \Delta - \varepsilon_{\mathrm{Ni}} - U_{\mathrm{Ni}} + 3K_{\mathrm{Ni}}$. 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 $\Delta_{\mathrm{Ni}} > \Delta$ in the present study of Ni impurity, leading to $\varepsilon_{\mathrm{Ni}} < -5.6$ eV.

III. HOLE BINDING AROUND Ni

Figure 1(a) shows hole number $\langle n\rangle$ on each orbital of the cluster as a function of the difference of the CT energies $\tilde{\Delta} \equiv \Delta_{\mathrm{Ni}} - \Delta$ in the undoped case (nine holes in the eight-unit-cell system). The ground state has the A_1 irreducible representation of C_{4v} point group within the parameter region of $\tilde{\Delta}$ shown in Fig. 1. As shown in Fig. 1(a), the hole densities on Ni $3d$ (ϕ^s) orbitals are increasing (decreasing) with increasing the value of $\tilde{\Delta}$. This is because the on-site energy $\varepsilon_{\mathrm{Ni}}$ of the Ni $3d$ orbitals is decreasing with increasing $\tilde{\Delta}$. Figure 1(a) also shows that the value of the Ni d (ϕ^s) orbital is

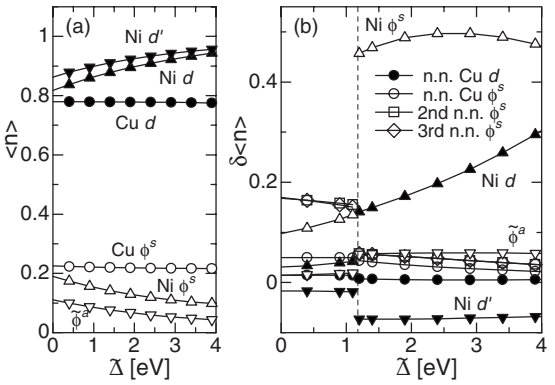

FIG. 1. (a) Averaged hole number $\langle n\rangle$ on each orbital in undoped ground state of an eight-unit-cell cluster as a function of the CT energy difference $\tilde{\Delta}\equiv\Delta_{\mathrm{Ni}}-\Delta$. Filled upward and downward triangles represent Ni $3d_{x^2-y^2}$ (denoted as d) and $3d_{3z^2-r^2}(d')$, respectively. ϕ^s and $\tilde{\phi}^a$ on Ni site are shown by open triangles. Filled (open) circles denote Cu d (Cu ϕ^s) orbitals at the nn sites from Ni. (b) The difference of $\langle n\rangle$ between one-hole-doped and undoped ground states. Open squares and diamonds denote ϕ^s orbitals at the second and third nn sites, respectively. Other symbols are the same as (a). The vertical broken line represents the position where the ground-state symmetry changes.

larger (smaller) than that of the d' ($\tilde{\phi}^a$) with each parameter value of $\tilde{\Delta}$. This is because the strength of hybridization between Ni d' and $2p$ orbitals is smaller than that between Ni d and $2p$ ones, with using parameter $\alpha<1$. The total number of holes at the Ni site (the sum of Ni d, Ni d', Ni ϕ^s, and $\tilde{\phi}^a$) is almost 2 (1.99 at $\tilde{\Delta}=0.4$ eV and 2.04 at $\tilde{\Delta}=3.9$ eV), which means that nominally Ni^{2+} is formed. The local spin state is of high spin ($S=1$). Remaining holes are distributed on Cu d and Cu ϕ^s orbitals, forming Cu^{2+} on each Cu site. Note that $\langle n\rangle$ on the Cu orbitals at the second and third nearest-neighbor (nn) sites from Ni is nearly the same as those of the nn sites.

Next we examine how a hole introduced into the system is distributed among the orbitals. In the range of $\tilde{\Delta}$ shown in Fig. 1, we find that with increasing $\tilde{\Delta}$ the ground state with one additional hole (ten holes in total) changes quantum number at $\tilde{\Delta}\sim 1.2$ eV from the total spin $S=1$ and A_2 irreducible representation (degenerated with B_1) to $S=0$ and B_1. The difference of hole number, $\delta\langle n\rangle$, on each orbital between the one-hole-doped and undoped ground states is plotted in Fig. 1(b). We find that for $\tilde{\Delta}\gtrsim 1.2$ a hole introduced in the system occupies predominantly on Ni ϕ^s orbital, i.e., an oxygen Wannier orbital that mainly couples to Ni $3d_{x^2-y^2}$. In total, more than 60% of the hole enters into Ni-related orbitals. This is consistent with experimental suggestions[3–8] that a Ni impurity may bind a hole and form the ZR doublet. Note that negative $\delta\langle n\rangle$ for Ni d' is the consequence of strong energy gain by accommodating holes into the orbitals with x^2-y^2 symmetry. Below $\tilde{\Delta}\sim 1.2$, 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,[18] it is reasonable to consider that $\tilde{\Delta}>1.2$ eV.

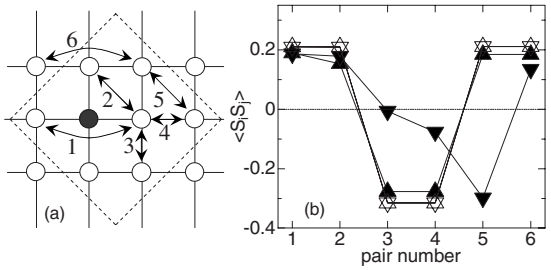

FIG. 2. (a) Diagram for an eight-unit-cell cluster (the inside of dotted lines) where the filled and open circles denote Ni and Cu sites. (b) Spin-spin correlation function for the pairs numbered in (a). The upward (downward) triangles show data for $\tilde{\Delta}=1.4(0.9)$ eV, and the open and filled symbols denote the undoped and one-hole-doped cases, respectively.

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 Cu O_4 cluster. We found that the ZR doublet is more stable than the ZR singlet when Δ_{Ni} is larger than Δ 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. This result also excludes the possibility that the formation of the bound state around the Ni impurity is an artifact of periodic boundary conditions imposed on the N-site clusters due to interference effects between periodic Ni impurities. In the limit of $(U_d, U_{\mathrm{Ni}}, \Delta, \Delta_{\mathrm{Ni}}) \gg T_{pd}$ that is approximately satisfied in the present parameter set, the binding-energy difference of the doublet and the singlet, δE_{B}, may be given by[19]

$$\delta E_{\mathrm{B}} = 2T_{pd}^2\left(\frac{4}{U_d-\Delta}+\frac{2}{\Delta}-\frac{3}{U_{\mathrm{Ni}}+K_{\mathrm{Ni}}-\Delta_{\mathrm{Ni}}}-\frac{1}{\Delta_{\mathrm{Ni}}}\right). \quad (7)$$

We notice that dominant negative contribution to δE_{B} comes from the third term in Eq. (7). This implies the importance of the condition that U_{Ni} ($\sim$8 eV) is not much larger than Δ_{Ni} ($\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 $\mathbf{S_i}=\frac{1}{2}\Sigma_{\tau,\tau'}(d^\dagger_{\mathbf{i},\tau}\boldsymbol{\sigma}_{\tau\tau'}d_{\mathbf{i},\tau'}+\phi^{s\dagger}_{\mathbf{i},\tau}\boldsymbol{\sigma}_{\tau\tau'}\phi^s_{\mathbf{i},\tau'})$ with $\boldsymbol{\sigma}$ the Pauli matrix, we show in Fig. 2 the equal-time spin-spin correlation function $\langle \mathbf{S_i}\cdot\mathbf{S_j}\rangle$ between two Cu sites in undoped and one-hole-doped cases with $\tilde{\Delta}=1.4$ and 0.9 eV. Here, $\tilde{\Delta}$ is chosen near the boundary of two regions shown in Fig. 1(b). In the undoped case, the correlation on the same (different) sublattice is positive (negative), implying the presence of AF order. For $\tilde{\Delta}=1.4$ eV, $\langle \mathbf{S_i}\cdot\mathbf{S_j}\rangle$ 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 $\tilde{\Delta}=0.9$ eV. This is due to the destruction of AF order caused by carrier motion.

We have neglected direct O-O hoppings in Eq. (1). The hoppings may cause the decrease in Δ, leading to less stability of the ZR doublet as seen from Eq. (7). However, we

found that the boundary at $\tilde{\Delta} \sim 0.3$ eV for single clusters without the hopping parameter T_{pp} increases only by 0.1 eV for a realistic value of T_{pp}(=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 such as t-J-type model.[20–25] We should treat a Ni impurity as a $S=\frac{1}{2}$ spin in hole-doped cases because the Ni impurity of $S=1$ forms the ZR doublet of $S=\frac{1}{2}$ with one of doped holes. 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 ϕ^s hole. Other holes that hop to the impurity position may feel repulsive interaction. This model is close the those used in Ref. 20, where they considered a $S=\frac{1}{2}$ magnetic impurity that corresponds to the ZR doublet, and found bound states composed of the $S=\frac{1}{2}$ impurity and a mobile hole. Such bound states may correspond to those of the ZR doublet and a hole. More precise effective t-J-type model is now under construction.

IV. DIRECT OBSERVATION OF HOLE BINDING

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.[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 the energy of incoming photon to Ni K absorption edge. In the intermediate state, we introduce Coulomb interaction between $3d$ and $1s$ core holes,[26] given by $H_{1s\text{-}3d} = U_c \Sigma_{\mathbf{i}_0,\gamma,\sigma,\sigma'} n^{\gamma}_{\mathbf{i}_0\sigma} n^{s}_{\mathbf{i}_0\sigma'}$, where $n^{s}_{\mathbf{i}_0\sigma}$ is the number operator of $1s$ core hole. By assuming that the $4p$ photoelectron enters into the bottom of the $4p$ bands,[26] the RIXS spectrum for Ni K edge as well as Cu K edge is expressed as

$$I(\Delta\omega) = \sum_f |\langle f| D^{\dagger}_{\mathbf{K}_f} G(\omega_i) D_{\mathbf{K}_i} |0\rangle|^2 \delta(\Delta\omega - E_f + E_0), \quad (8)$$

where $D_{\mathbf{K}} = \Sigma'_{\mathbf{i},\sigma} e^{i\mathbf{K}\cdot\mathbf{i}} p^{\dagger}_{4p,\mathbf{i}\sigma} s^{\dagger}_{\mathbf{i}\sigma} + \text{H.c.}$ with the creation operator $s^{\dagger}_{\mathbf{i}\sigma}(p^{\dagger}_{4p,\mathbf{i}\sigma})$ of $1s$ core hole ($4p$ electron). $\Sigma'_{\mathbf{i}}$ denotes summation over Ni (Cu) sites for Ni (Cu) K edge. $\mathbf{K}_{i(f)}$ is the wave vector of the incoming (outgoing) photon with energy $\omega_{i(f)}$ and $\Delta\omega = \omega_i - \omega_f$. $G^{-1}(\omega_i) = \omega_i + i\Gamma - H_{dp} - H_{1s\text{-}3d} - H_{1s,4p}$, where $H_{1s,4p}$ is composed of the energy separation $\varepsilon^{\mathrm{Ni(Cu)}}_{1s\text{-}4p}$ between the Ni (Cu) $1s$ level and the bottom of the $4p$ band, and Γ is the inverse of relaxation time in the intermediate state. $|0\rangle$ is the ground state with energy E_0 and $|f\rangle$ is the final state of RIXS with energy E_f. We use $\Gamma = 1$ eV and $U_c = 4$ eV.[30] $I(\Delta\omega)$ 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 $\tilde{\Delta} = 1.4$ eV. The spectra at zero-momentum transfer ($\mathbf{K}_f - \mathbf{K}_i = 0$) are shown for Cu K edge. In the undoped case, the edge of the CT gap is located at ~ 2.1 and ~ 3.2 eV for Cu and Ni, respectively. The difference comes from different CT energies. This is qualitatively consistent with experimental observations for La_2CuO_4 (~ 2.2 eV) and La_2NiO_4 (~ 4 eV).[27] Furthermore, recent RIXS experiments for Ni-substituted La_2CuO_4 also show similar behaviors.[28] 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.[29,30] A similar structure appears in the energy region from 6 to 7 eV for Ni K-edge RIXS.

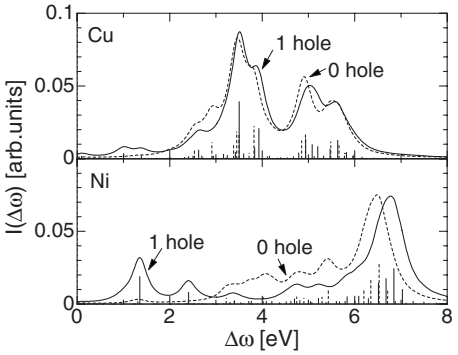

FIG. 3. RIXS spectra for Cu (upper panel) and Ni (lower panel) K edges in an eight-unit-cell cluster with a Ni impurity. The solid and broken lines denote the undoped and one-hole-doped cases, respectively. $\tilde{\Delta} = 1.4$ eV. The δ functions (the vertical lines) are convoluted with a Lorentzian broadening of 0.2 eV.

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 $\Delta\omega \sim 1.35$ and ~ 2.13 eV within the CT gap. Examining eigenstates generating the new structures, we find that the hole number of Cu ϕ^s 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 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.

V. 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 NiO_4 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.

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