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Local quasiparticle states near a Zn impurity with induced magnetic moment in a high-T_c superconductor

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The local quasiparticle density of states around a very strong nonmagnetic impurity with a Kondo-like magnetic moment induced at its nearest neighbors in a *d*-wave superconductor is studied. We show that the interference between the strong impurity potential scattering and the Kondo effect leads to novel quasiparticle spectra around the impurity, which are strikingly different from the case of a single unitary or magnetic impurity. The recent STM image of the local differential tunneling conductance around the Zn impurity in a high-T_c cuprate can be explained if the blocking effect of BiO surface layer between the tip and probed CuO_2 plane is taken into account.

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The scanning tunneling microscopy (STM) turns out to be a powerful probe of the local effects of individual impurity atoms or defects on the fundamental properties of high-T_c cuprates.[1–3] The measurements reveal the induction of a virtual bound quasiparticle state around the individual impurity, providing strong evidence of the *d*-wave pairing symmetry of high-T_c superconductors.[4] This experiment was motivated by the earlier predictions of Balatsky, Salkola, and co-workers.[5,6] However, the high resolution STM imaging of the effect of individual impurity atoms Zn substituted in a controlled manner for Cu in $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) (Ref. 1) also presented an unexpected spatial distribution of the local density of states (LDOS) strength at the resonance energy. It has a strongest intensity directly on or above the Zn site, local minimum on its nearest-neighbor sites and local maximum on second-nearest-neighbor sites. This distribution is opposite to all theories based on the strong atomic-like nonmagnetic impurity model,[5–8] which show a vanishing density of states directly at the impurity site and a strong resonance peak on its nearest neighbors. Recent NMR measurements of Zn (or Li) doped $YBa_2Cu_3O_{6+y}$ (Refs. 9–11) and the specific heat measurement of Zn-doped $YBa_2Cu_3O_{6.95}$ (Ref. 12) indicate that a Kondo like magnetic moment with $S=\frac{1}{2}$ is induced at the nearest neighbor sites of the Zn (or Li) impurity. Motivated by the latter experiments, the Kondo effect on the local quasiparticle states around an induced magnetic moment in a *d*-wave superconductor has been theoretically studied by several groups.[13–15] All these results show widely-split double-peak structure with respect to the zero bias at the impurity sites, and therefore do not agree with the STM imaging of the effects of a Zn impurity. We believe that these studies seem to be more suitable to describe the Kondo impurities such as Mn and Co substituted for Cu in high-T_c cuprates instead of Zn or even Ni whose spin is believed to have a ferromagnetic coupling with conduction electrons.[16–18] In order to compare with experiments, the scattering of quasiparticles due to both Zn and the induced magnetic moment around it needs to be carefully investigated. So far this problem has not been properly addressed, particularly in view of the scattering strength of a Zn impurity being close to the unitary limit as we will estimate below. Valence counting suggests that the Zn impurity maintains a nominal Cu^{2+} charge, the Zn^{2+} $[3d^{10}]$ with $S=0$ configuration indicates it would act as a nonmagnetic impurity. According to Ref. 19, the second and third ionization energies for Zn are respectively 18 eV and 39.8 eV, while the third ionization energy of Cu is 36.9 eV. In the cuprates, the relevant $3d$ Cu^{2+} electrons form a narrow $d_{x^2-y^2}$ band with bandwidth less than 2 eV. The center of the band, where the chemical potential lies, is located around -36.9 eV below the vacuum. The top of $3d^{10}$ level of a Zn^{2+} ion is at -39.8 eV which is below the bottom of the $d_{x^2-y^2}$ band. The conduction electrons near the chemical potential will experience a repulsive local potential $V_0 \approx(-18\ \text{eV})-(-36.9\ \text{eV})=18.9$ eV at the Zn site. For such a large local potential as compared to the bandwidth, Zn can almost be regarded as a unitary impurity, which has also been evidenced experimentally.[20] Our present considerations are thus very different from the case studied in Ref. 13 where the authors assume the Zn impurity has a weak attractive potential.

In this Communication we study the LDOS spectrum around a very strong nonmagnetic impurity with a Kondo-like magnetic moment induced at its nearest neighbors in a *d*-wave superconductor. Based on this model, it is shown that the presence of the strong potential scattering from the impurity leads to a stronger single resonant peak in the LDOS directly at the site of the magnetic moment, in contrast to the case for a single magnetic impurity.[14,15] Compared with the case of a single nonmagnetic unitary impurity, the LDOS is strongly enhanced by the Kondo effect from the induced magnetic moment. We also show that the pattern observed in the STM experiments can be qualitatively explained by taking into account the blocking effect[21] of the BiO surface layer which exists between the tunneling tip and the CuO_2 plane where the Zn impurities are located.

We model the *d*-wave superconductor defined on a two-dimensional lattice within a phenomenological BCS framework. The unitary impurity is taken to be at the origin $\mathbf{r}_0=(0,0)$. On nearest-neighbors to the impurity, the induced magnetic moment is described by the Anderson *s*-*d* exchange model. The repulsive interaction on the site, where the moment sits, is assumed to be infinite so that the double occupancy on this site is forbidden. We use the slave-boson mean-field approach[22,23] to study the Kondo effect of the induced magnetic moment. The system Hamiltonian can then be diagonalized by solving the Bogoliubov–de Gennes equations,[14]

$$\sum_{\mathbf{j}} \begin{pmatrix} H_{\mathbf{ij}} & \Delta_{\mathbf{ij}} \\ \Delta_{\mathbf{ij}}^{*} & -H_{\mathbf{ij}} \end{pmatrix} \begin{pmatrix} u_{\mathbf{j}}^{n} \\ v_{\mathbf{j}}^{n} \end{pmatrix} = E_n \begin{pmatrix} u_{\mathbf{i}}^{n} \\ v_{\mathbf{i}}^{n} \end{pmatrix}, \tag{1}$$

with the bosonic number b_0 and the d-wave bond pairing amplitude $\Delta_{\mathbf{ij}}$ subject to the self-consistent condition

$$\Delta_{\mathbf{ij}} = \frac{g_{\mathbf{ij}}}{2} \sum_{n} (u_{\mathbf{i}}^{n} v_{\mathbf{j}}^{n*} + u_{\mathbf{j}}^{n} v_{\mathbf{i}}^{n*}) \tanh(E_n/2k_BT), \tag{2}$$

and

$$b_0^2 = 1 - 2\sum_{n} \{|u_{\mathbf{r}_1}^{n}|^2 f(E_n) + |v_{\mathbf{r}_1}^{n}|^2[1-f(E_n)]\}. \tag{3}$$

Here

$$\begin{pmatrix} u_{\mathbf{i}}^{n} \\ v_{\mathbf{i}}^{n} \end{pmatrix}$$

is the quasiparticle wave function with eigenvalue E_n, which is measured with respect to the chemical potential μ. The single particle Hamiltonian $H_{\mathbf{ij}} = -\tilde{t}_{\mathbf{ij}} - \mu \delta_{\mathbf{i}\neq \mathbf{r}_1,\mathbf{j}} + V_0 \delta_{\mathbf{ir}_0} + (\epsilon_d + \lambda_0)\delta_{\mathbf{ir}_1}\delta_{\mathbf{ij}}$, where V_0 is the strength of impurity potential, ϵ_d is the bare energy level of the moment electron with respect to μ, and λ_0 is the Lagrange multiplier introduced to enforce the single occupancy constraint. The renormalized coupling strength $\tilde{t}_{\mathbf{ij}} = \mathcal{V} b_0$ for $(\mathbf{ij}) = (\mathbf{r}_1 + \boldsymbol{\delta}, \mathbf{r}_1)$ or $(\mathbf{r}_1, \mathbf{r}_1 + \boldsymbol{\delta})$ and t otherwise, where $\mathcal{V}$ is the bare coupling strength between the moment and conduction electrons, t is the hopping integral between conduction electrons, $\boldsymbol{\delta}$'s are the unit vectors of the square lattice. The strength of d-wave pairing interaction is represented $g_{\mathbf{ij}}$, the value of which is $g_{\mathbf{ij}} = 0$ for $(\mathbf{ij}) = (\mathbf{r}_1 + \boldsymbol{\delta}, \mathbf{r}_1)$ or $(\mathbf{r}_1, \mathbf{r}_1 + \boldsymbol{\delta})$ upon the assumption of different nature of the conduction and moment electrons[24] and constant g otherwise. The Fermi distribution function $f(E) = [1 + \exp(E/k_BT)]^{-1}$. Without loss of generality, we temporarily assume the magnetic moment to be at $\mathbf{r}_1 = (1,0)$.

Our numerical calculation is performed on a square lattice with size $N_L = N_x \times N_y = 35 \times 35$ and averaged over 36 wave vectors in the supercell Brillouin zone. The strong scattering potential from the impurity is taken to be $V_0 = 100$, which yields a phase shift 0.487π (very close to 0.5π for the unitary limit), the bare energy level $\epsilon_d = -2$, the chemical potential $\mu = -0.2$, and the pairing interaction $g = 1.2$. Here we measure the energy in units of t and the length of the lattice constant a. A trivial solution to Eq. (1) with $\lambda_0 = -\epsilon_d$ and $b_0 = 0$ is always found, which describes the moment decoupled from the conduction electrons. However, the physically desired value of these two parameters are determined by minimizing the free energy with the procedure as detailed in Ref. 14. With the chosen parameter values, we find a critical value of the coupling strength $\mathcal{V}_c \approx 0.9$, below which the moment is decoupled from the conduction band. Compared with the single Kondo impurity case, the larger $\mathcal{V}_c$ obtained here is due to the fact that the conduction electron density is strongly depressed on the impurity site nearest-neighboring to the moment so that the screening effect is weakened. When $\mathcal{V} > \mathcal{V}_c$, this free local spin state gives way to the Kondo screened state. For $\mathcal{V} = 1.0$, it is found that $\lambda_0 = 2.15$ and $b_0 = 0.56$. The self-consistent solution also gives a d-wave order parameter which is strongly suppressed around the strong impurity at the scale of the coherence $\xi_0 \equiv \hbar v_F/\pi\Delta_g$, where v_F is the Fermi velocity and $\Delta_g \approx 0.4$ is the bulk d-wave energy gap.

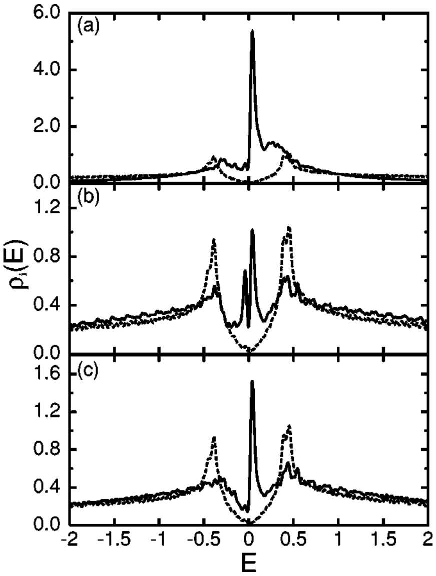

FIG. 1. The local density of states on the nearest-neighboring sites of the close-to-unitary impurity $A = (1,0)$ (a), $B = (0,1)$ (b), and $C = (-1,0)$ (c). Also shown with the dashed line the LDOS on the corner site of the supercell, which resembles the bulk DOS for a clean d-wave superconductor. Here the A site is the position of the induced moment with the impurity located at the (0,0) site.

Once the self-consistent solution is obtained, the LDOS is then calculated according to

$$\rho_{\mathbf{i}} = 2\sum_{n} [|u_{\mathbf{i}}^{n}|^2 \delta(E_n - E) + |v_{i}^{n}|^2 \delta(E_n + E)], \tag{4}$$

which is proportional to the local differential tunneling conductance as measured by the STM experiments. Our numerical result indicates that the LDOS is vanishing at the impurity site, consistent with previous calculations.[6,7] Figure 1 shows the LDOS as a function of energy on nearest-neighbor sites to the impurity site, $A = (1,0)$ [i.e., the magnetic moment site], $B = (0,1)$, $C = (-1,0)$, $D = (0,-1)$ and on the corner site of the supercell. Due to the spatial inverse symmetry, the LDOS on sites B and D are identical. Notice that the LDOS on the corner site of the supercell recovers the bulk density of states of a clean d-wave superconductor, which indicates that the supercell size and the number of wave vectors in the Brillouin zone is large enough to uncover the physics intrinsic to an isolated impurity with an induced moment. The LDOS on the nearest-neighbor sites shows the existence of near-zero energy resonant states through the near-zero energy peaks. Compared with a strong nonmagnetic impurity or a single Kondo impurity, the close-to-unitary impurity with an induced moment shows much richer characteristics of the quasiparticle resonant states in its vicinity: (i) In striking contrast to a single Kondo impurity case,[14,15] the LDOS on the magnetic moment site-A only displays a strong single near-zero-energy peak, which comes in a unique manner from the presence of the strong impurity scattering. (ii) Different from a strong nonmagnetic impurity,[6,8] the LDOS on site-B and site-D exhibits the splitting of the near-zero-energy peak. This difference is mainly due to the presence of the moment near the unitary impurity, which plays the role of a weak scattering center and reduces the effective hopping integral locally. As a comparison, we have also considered a (10)-oriented dimer consisting of two nearest-neighboring close-to-unitary impurities and found that the splitting is much increased. Therefore, in the Kondo resonance regime, the close-to-unitary impurity plus a nearby moment composite can be effectively regarded as a very strong nonmagnetic impurity with a tail. Since the influence of the induced moment is very weak on site-C, the LDOS on this site only shows a single near-zero energy peak. (iii) As a result of the Kondo resonance, the intensity of the near-zero-energy peak on site-A is about four times as large as that on other three nearest-neighbor sites of the impurity. Thus far we have considered the local quasiparticle resonant states around the strong impurity with a moment induced statically. When a Zn impurity is substituted for Cu in a high-T_c cuprate, the $S=\frac{1}{2}$ moment associated with Cu^{2+} is removed from the system. As a result the local antiferromagnetic pairing is broken and a moment with spin-$\frac{1}{2}$ is induced at any of the four neighbor sites of the impurity with equal probability. Our treatment here is consistent with the NMR experimental indication that *the Zn impurity only reveals already-existing moments, localized on Cu sites of the doped antiferromagnet*[10] *and the induced spins on the nearest neighboring copper sites are not correlated*.[25] It is different from the approach based on a putative single moment around the Zn impurity like a spin cluster. After averaging over the four moment-position configurations around the impurity, the combined contribution from sites-A through D leads to the averaged LDOS $\rho_{\mathbf{i}}^{\mathrm{avg}}=(\rho_A+\rho_B+\rho_C+\rho_D)/4$ at any of these four sites. As shown in Fig. 2, $\rho_{\mathbf{i}}^{\mathrm{avg}}$ is characterized by a very strong sharp peak close to zero energy.[26] Compared to the case of a single close-to-unitary impurity, the corresponding peak intensity is enhanced by about 40%. Also interestingly, the LDOS spectrum shows a narrow side-peak with a rather weak intensity. The highly asymmetric double-peak structure distinguishes it with a sharp and narrow dip in between and their separation is only about 5% of $2\Delta_g$. In comparison, the double peaks obtained for a single Kondo impurity has a separation as large as 50% of $2\Delta_g$.[14]

To understand the LDOS spectrum and the spatial distribution of its strength at the resonance bias observed in the STM experiment, we need to know the nature of the surface layer in BSCCO on which the tip is directly probing. There is ample experimental evidence that the cleaved surface along

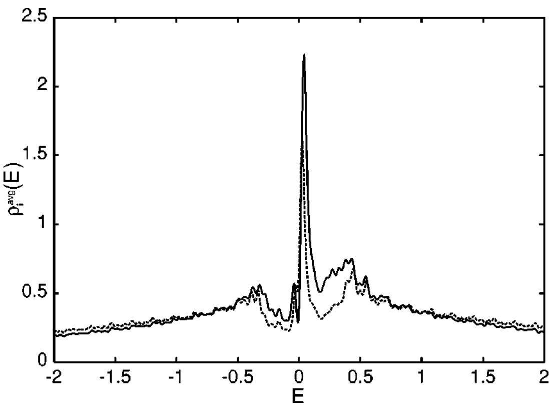

FIG. 2. The local density of states on the nearest-neighboring site of the nonmagnetic close-to-unitary impurity after the average over the four moment-position configurations. As a comparison, shown with the dashed line, the LDOS on the corresponding site for a single close-to-unitary impurity without induced magnetic moment.

the c-axis is always the BiO layer. The superconducting CuO_2 layer on which Zn impurities are located and the STM tip would like to explore, lies about 5.1 Å below the surface BiO layer. The crystal structure shows that each Bi atom sits vertically on the top of each Cu atom or Zn atom, and there is also an O atom associated with SrO layer between them. When the STM tip is trying to probe the Cu/Zn sites, the core electrons of the Bi^{3+} ion (with radius 1.03 Å) and also O^{2-} (with radius 1.4 Å) sitting on top of it will inevitably block[21] the tunneling current from directly passing through the Cu/Zn sites, where both Cu^{2+} and Zn^{2+} have the ionic radius 0.74 Å. Because the STM image has such a high spatial resolution to the atomic scale, the tunneling current from the tip to the CuO_2 plane is only distributed within a small area, the linear dimension of which is about one lattice constant. Therefore, the measured LDOS above the *probed* Zn or Cu site is mainly contributed from its four nearest-neighboring sites, which can be approximately expressed as $\rho_{\mathbf{i}}^{\mathrm{exp}}=A\Sigma_{\boldsymbol{\delta}}\rho_{\mathbf{i}+\boldsymbol{\delta}}^{\mathrm{avg}}$. Here $A<1$ is a constant depending on the distance between the tip and the four nearest-neighboring Cu

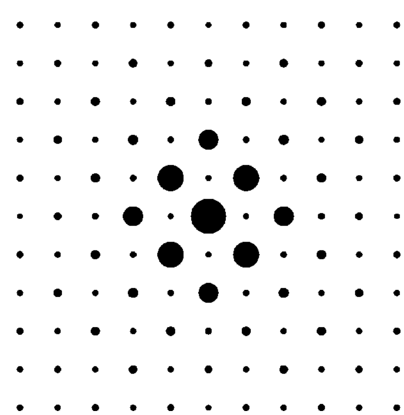

FIG. 3. A two-dimensional bubble view of the spatial distribution of the local density of states at the resonance energy $E=0.02$ around the nonmagnetic unitary impurity with a magnetic moment. The bubble size on each Cu site scales with the LDOS intensity.

atoms. As a result, the STM spectrum on the Zn site observed by experiment is in good agreement with $\rho_{\mathbf{i}}^{\mathrm{exp}}$ at $\mathbf{i}=(0,0)$ which has the identical characteristic as that shown in Fig. 2. Experimentally, a small-side peak adjacent to the left of the strong resonant peak was indeed observed in the STM measurement.[1] This is consistent with our result in Fig. 2 and it could very well be a signature of the induced Kondo-like magnetic moment around the impurity. On the other hand, we find that $\rho_{\mathbf{i}}^{\mathrm{avg}}$ shows no resonant peak on the second-nearest neighbor sites while a resonant peak with a weaker intensity on the third-nearest neighbor sites. All the resonant peaks, if showing up at some of the sites around the impurity, are actually located at the same energy position and their intensities become much reduced as the sites get away from the impurity. After the blocking effect is taken into account, the exhibited oscillation pattern in the spatial distribution of $\rho_{\mathbf{i}}^{\mathrm{exp}}$ at the resonance energy (see Fig. 3) agrees qualitatively with the measured differential-tunneling conductance image.[1]

To conclude, we have considered the effect of a very strong nonmagnetic impurity with induced magnetic moment in a *d*-wave superconductor. To be applicable to the Zn impurity substituted for Cu in copper-oxide cuprates, the model has taken care of both the strong potential scattering from this nonmagnetic impurity itself and the Kondo effect of the induced moment. We find that the induced magnetic moment strongly enhances the local quasiparticle density of states near the impurity. In addition, the blocking effect of the BiO surface layer between the STM tip and the probed CuO plane is essential to explain the observed resonance peak on the Zn site and the spatial pattern of the differential tunneling conductance around a Zn impurity in BSCCO.

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