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Rotational Symmetry Breaking in the Ground State of Sodium-Doped Cuprate Superconductors

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We use an extended t-J model to study a single hole bound to a Na\textsuperscript{+} acceptor in Ca\textsubscript{2-x}Na\textsubscript{x}CuO\textsubscript{2}Cl\textsubscript{2}. For parameters suitable to cuprates, the ground state has a twofold degeneracy, corresponding to even (odd) reflection symmetry around the x (y) axes. The conductance pattern of the broken symmetry state is anisotropic as the tip of a tunneling microscope scans above the Cu-O-Cu bonds along the x (y) axes. This anisotropy is pronounced at lower voltages but reduced at higher voltages. Our theory agrees qualitatively with recent data of scanning tunneling microscopy showing broken local rotational symmetry.

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The recent atomically resolved scanning tunneling microscopy (STM) studies by Davis and collaborators \cite{1,2} on strongly underdoped Ca\textsubscript{2-x}Na\textsubscript{x}CuO\textsubscript{2}Cl\textsubscript{2} revealed a surprisingly complex pattern with the square symmetry of the lattice broken on a local scale. The STM data were analyzed to obtain the local hole density of Cu-site using the method proposed by Randeria, Sensarma, Trivedi, and Zhang \cite{3} and also a related method proposed by Anderson and Ong \cite{4}. In these methods, the differential conductance signal is integrated from the chemical potential to a substantial voltage cutoff. Randeria \textit{et al.} \cite{3} pointed out that the ratio between its positive voltage (electron injection) and negative voltage (hole injection) signals measured the local hole density of the Cu-site independent of the strength of the troublesome tunneling matrix elements.

In Ca\textsubscript{2-x}Na\textsubscript{x}CuO\textsubscript{2}Cl\textsubscript{2}, the acceptor Na\textsuperscript{+}-ions substitute for Ca\textsuperscript{2+}-ions and sit in the center of a square of four Cu sites both above and below the outermost CuO\textsubscript{2} layer. The attractive potential for the doped holes generated by a Na\textsuperscript{+}-acceptor does not break the local square symmetry. The broken local square lattice symmetry observed in the STM data is most pronounced at the in-plane oxygen sites and for a lower voltage cutoff. This raises an interesting question about the origin of this broken local square symmetry.

In this Letter, we address this question and show that such broken symmetry states appear in the case of a hole confined to a cluster of sites centered at a Na\textsuperscript{+}-acceptor. Further, this broken local symmetry shows up in the STM mapping primarily as a modulation pattern above the O-sites in the outermost CuO\textsubscript{2}-layer.

We start by considering the STM tunneling process in detail in Ca\textsubscript{2-x}Na\textsubscript{x}CuO\textsubscript{2}Cl\textsubscript{2}. As pointed out by Rice and Tsunetsugu \cite{5}, the STM tip couples primarily to the 3p\textsubscript{z}-states of the outermost Cl layer, but the matrix element to tunnel directly into a hole located on the CuO\textsubscript{2} square directly underneath the Cl-ion vanishes by symmetry. The holes move in a band of singlets with d\textsubscript{x-y}\textsuperscript{2}-symmetry centered on Cu sites but strongly hybridized with the four nearest-neighbor (NN) O sites. The 3p\textsubscript{z}-Cl states, however, hybridize with the hole states centered on the four NN Cu sites \cite{6} through the direct overlap of the 3p\textsubscript{z}-Cl with 2p\textsubscript{x(y)}-O orbitals and also through the 4s-Cu orbital on the site directly below each Cl. The amplitude to inject an electron in a 3p\textsubscript{z}-Cl hole wave function is a superposition of hole states centered on the four NN Cu-sites (see Fig. 1).

\begin{equation}
\begin{aligned}
P^{\dagger}_{\text{Cl},\sigma}(\Psi_{0}^{\dagger}) & \propto \sum_{\tau} (i, \text{Cl}|i + \tau, \text{Cu})c^{\dagger}_{1+\tau,\sigma}(\Psi_{0}^{\dagger}) \\
& \propto \sum_{\tau} (-1)^{M_{\tau}}f^{\dagger}_{1+\tau,\sigma}(\Psi_{0}^{\dagger})
\end{aligned}
\end{equation}

where \( p_{\text{Cl},\sigma}^{\dagger}(c^{\dagger}_{1+\tau,\sigma}) \) are creation operators for electrons in the 3p\textsubscript{z}-Cl orbital at site \( i \) (planar coordinate) and the d\textsubscript{p} hybridized orbital centered on the Cu-site at \( i + \tau \) in the outermost CuO\textsubscript{2} layer, respectively, with \( (i, \text{Cl}|i + \tau, \text{Cu}) \) as their overlap, \( \tau = \pm x, \pm y \) is a planar vector connecting NN Cu sites, and \( |\Psi_{0}^{\dagger}\rangle \) denotes the single-hole ground state with energy \( E_{0}^{1}\). Assuming the square lattice is four-fold rotational invariant, the overlaps are independent of \( \tau \) except for their sign, leading to Eq. (1). For d\textsubscript{x-y}\textsuperscript{2} symmetry of the Cu-orbital, we have \((-1)^{M} = -1\).
Tersoff and Hamann [7], we write the differential conductance in the center square. The sign represents the phase of the Cu- and Cl-orbital wave function.

\[ \frac{dI(r)}{dV} \propto \sum_{\alpha,m} |m|a_{\alpha,i}^\dagger \Psi_{0}^{1h} |^2 \delta(\omega - E_m + E_{0}^{1h}) \]  

where \( a_{\alpha,i}^\dagger \) is the electron creation operator at position \( r \), \( |m\rangle \) are eigenstates of the half-filled system with energy \( E_m \), and \( \omega = eV \). When the tip is scanned from above the Cl site at \( i \) to a NN site, \( i + \tau \), we have

\[ a_{\alpha,i+\tau}^\dagger \Psi_{0}^{1h} = \langle r|i, Cl \rangle a_{\alpha,i}^\dagger \Psi_{0}^{1h} + \langle r|i + \tau', Cl \rangle a_{\alpha,i+\tau'}^\dagger \Psi_{0}^{1h}. \]  

The integrated current at \( r \) up to a positive voltage \( V \) is then,

\[ I(r, \omega) \propto \sum_{\alpha,m} \left| \langle m \rangle \sum_{\tau} (-1)^M \langle r|i, Cl \rangle c_{i+\tau,\alpha}^\dagger \right|^2 \Theta(\omega - E_m + E_{0}^{1h}) \]  

where \( \Theta \) is a step function. The variation of the tunneling current as one scans between two NN Cl sites is sensitive to the relative phase to inject electrons on NN Cu sites in \( |\Psi_{0}^{1h}\rangle \). The important role of quantum interference effect in interpreting STM images has also been discussed for multiple tunneling channels on sulfur surfaces [8]. To this end, we examine the lowest energy single hole states for clusters up to 16 Cu-sites including an attractive acceptor potential in the center square.

The two-dimensional \( t-t' \)-\( J \) model for the cluster is defined by the Hamiltonian,

\[ \mathcal{H} = -\sum_{\langle i,j \rangle} \epsilon_{i} c_{i,\sigma}^\dagger c_{j,\sigma} - t \sum_{\langle i,j \rangle} \langle c_{i,\sigma}^\dagger c_{j,\sigma} + H.c. \rangle \]  

\[ -t' \sum_{\langle\langle i,j \rangle\rangle} \langle c_{i,\sigma}^\dagger c_{j,\sigma} + H.c. \rangle + J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j. \]  

A constraint of no double electron occupation is implied. \( \langle i, j \rangle \) and \( \langle\langle i, j \rangle\rangle \) refer to NN and next-nearest-neighbor (NNN) sites \( i \) and \( j \). The on site potential of the four NN Cu sites of the Na\(^{+} \)-acceptor is \( \epsilon_{i} = \epsilon_{\text{Cu}} \), while \( \epsilon_{i} = 0 \) for the rest of the sites. The single-hole ground state of Eq. (5) with \( t' = 0 \) was obtained previously using exact diagonalization for small clusters by von Szczepanski et al. [9], Rabe and Bhatt [10], and Gooding [11]. The ground state with spin \( S = 1/2 \) was found to be orbitally doubly degenerate in certain parameter regimes [10–12]. When a NNN hopping \( t' \) is included, our results below show that the doubly degenerate \( S = 1/2 \) states are lowest in energy within a reasonable parameter range. The symmetry of the lowest energy state however is sensitive to boundary condition and parameters. In our calculations, we choose \( t = 1 \) and \( J = 0.3 \), suitable for the cuprates, and study the ground state as a function of \( t' \) and \( \epsilon_{i} \) in clusters of 12- and 16-sites (see Fig. 2).

Exact diagonalization of small \( t-t' \)-\( J \) clusters has been reported earlier [13–16]. For a 16 \(-\) \((4 \times 4)\) site cluster with periodic boundary condition (PBC), the ground state of a single hole has a four-fold symmetry with hole momentum \((\pm \pi/2, \pm \pi/2)\) if \( t' < 0 \), and a twofold symmetry with hole momentum \((\pi, 0)\) or \((0, \pi)\) if \( t' > 0 \). The impurity potential affects not only the local charge and spin distributions but also the symmetry of the ground state wave function [10,11]. In this study, we focus on the reflection symmetries with respect to \( x \) and \( y \) axes passing through the sodium dopant (\( P_x \) and \( P_y \)), respectively. Since \( [P_{\alpha}(y), H] = 0 \), we may classify states according to the quantum numbers of \( P_x \) and \( P_y \). We denote the state with \( (P_x, P_y) = (+1, -1) \) as phase (I), and the doubly degenerate states \((+1, 1)\) and \((-1, +1)\) as phase (II), and \((-1, -1)\) as phase (III). In Figs. 3(a) and 3(b), we show the

FIG. 1 (color online). Schematic crystal structure of \( \text{Ca}_2\text{Cu}_{2}\text{O}_2\text{Cl}_2 \) around a \( \text{Ca}^{2+} \) ion or a doped \( \text{Na}^{+} \)ion. The sign represents the phase of the Cu- and Cl-orbital wave function.

FIG. 2 (color online). The configuration of 12-site (a) and 16-site cluster (b). The dashed line corresponds to the reflection axis for \( P_{\alpha}(y) \). The cross marks the tip position on the middle point of two NN Cu sites along the \( x \) and \( y \) axes. In (b), eight independent bonds are labeled with numbers.
ground state phase diagram a regime with the doubly degenerate energy level evolution as differential conductance $I_x$ where $I = 0.0027$ and 0.0255. Metamagies are very close in energy. Small perturbation of that the four low-lying states with different reflection symmetries are very close in energy. Small perturbation of the Hamiltonian in Eq. (5) to obtain $\psi^{\Gamma_0}(\xi)$, the four-fold symmetric states at the $Cu$ sites remains rotationally symmetric in this state. However, because of the interference between different $Cu$ sites to the four-fold degenerate states. Consider the tip positions above the two geometrically symmetric points halfway between the $Cu$ site $i$ and its $NN$ sites $i + x$ or $i + y$ with a $Na^+$-acceptor located at $i + x/2 + y/2$. Since $\langle i | Cl, Cl \rangle = \langle i | \tau, Cl \rangle$ for the midpoint $r$, the integrated differential conductance $I^{(y)}(\omega) = I(\xi, \tau, \omega)$ at position $i + \xi(\tau/2)$ with the cutoff energy $\omega$ is

$$I^{(y)}(\omega) = \sum_{\sigma} I^{(y)}_{\sigma}(\omega),$$

$$I^{(y)}_{\sigma}(\omega) \propto \sum_m (m|(-1)^M (c_{i+x,\tau,\sigma}^+ c_{i+y,\tau,\sigma}) |\psi^{\Gamma_0} \rangle \Theta(\omega - E_m + E_{\sigma}^{\Gamma_0}),$$

where $I_{\sigma}$ is the spin-dependent integrated differential conductance. This conductance can be calculated by diagonalizing the Hamiltonian in Eq. (5) to obtain $|\psi^{\Gamma_0}\rangle$ and also all the eigenstates $|m\rangle$ with energies $E_m$ at half-filling. Note that $I^{(y)}(\omega) = I^{(y)}(\omega)$ by symmetry if $|\psi^{\Gamma_0}\rangle$ is nondegenerate. In the parameter regime where $|\psi^{\Gamma_0}\rangle$ is doubly degenerate (see Fig. 2), $I^{(y)}$ and $I^{(y)}$ can be different. In Fig. 4(a), we plot $I^{(y)}(\omega)$ and $I^{(y)}(\omega)$ versus the cutoff energy $\omega$ obtained from the 12-site cluster calculations, for a hole ground state with symmetry $(+1, -1)$ and spin $S_z = 1/2$. The asymmetry of $I$ between the two tip scans is apparent and is more pronounced at a lower $\omega$ and becoming weaker at higher $\omega$. To see the asymmetry more clearly, we also plot the ratio of the conductances at the two tip points,

$$\eta(\omega) = I^{(y)}(\omega)/I^{(y)}(\omega).$$

It is interesting to note the strong cutoff energy dependence of the asymmetry in the conductance. For example, $\eta = 0.3$ for $\omega = J$, rises to $\eta = 0.85$ at $\omega = 4J$. As $\omega \to \infty$, $\eta = 1.04$, showing only very weak asymmetry. Our results are consistent with the recent STM observation [1], where strong asymmetry has been found at a lower $\omega = 150$ meV ($\sim J$), much weaker or unobservable asymmetry at $\omega = 600$ meV ($\sim 4J$). In Fig. 4(b) and 4(c), we show the spin-dependent conductances $I_{\sigma}(\tau/2, \omega)$ as functions of $\omega$ in different spin channels. Our theory predicts that the asymmetry is spin-dependent. In the high $\omega$ limit, the ratio $I_{\uparrow}^{(y)}/I_{\downarrow}^{(y)} \sim 1.23$ in the spin-up channel and $I_{\uparrow}^{(y)}/I_{\uparrow}^{(y)} \sim 0.88$ in the spin-down channel. Compensation between two different spin singlet and triplet channels leads to weaker asymmetry in the total ratio, $I^{(y)}(\tau/2, \omega) \sim 1.0$. However, rapid spin flip processes around the $Na^+$-acceptor may make spin-resolved STM experiments difficult. However, in very underdoped samples, the spin may be frozen around the

![FIG. 3 (color online). Ground state phase diagram in the parameter space of $t'$ and $\epsilon_s$ in (a) 12-site cluster (black dashed line) and 16-site cluster (solid line) with open boundary condition. (b) 16-site cluster with PBC. Regime D: the doubly degenerate state; regime S: the singly degenerate state. The thick black line in (b) corresponds to the four-fold symmetric states at $\epsilon_s = 0$. (c) Energy levels as functions of $\epsilon_s$ at $t' = 0.12$ as indicated by the dashed line in (b). $E_3$ denotes the energy in phase I. The dashed line is for doubly degenerate states while the dotted line is for phase III.](237004-3)

![FIG. 4 (color online). The total integrated differential conductance on two cross (X) sites in Fig. 2(a) along the x- (solid line) and along the y-axis (dashed line) as functions of the cutoff energy $\omega$ together with the anisotropy ratio $\eta$ (thick solid line). The results for spin-up channel (b), and spin-down channel (c). In the calculations (b) and (c), the single-hole state has a spin $S_z = 1/2$.](237004-4)
Na\(^+\)-acceptor so that spin-resolved STM experiments may be possible.

To better understand our results, we analyze the ground state and the conductance in a 4-site cluster. Altman and Auerbach [19] found that the single-hole ground state of a 4-site Hubbard model with moderate on-site repulsion \(U\) is twofold degenerate with spin-1/2. We study the single-hole ground state of the \(t-t'\)-model and focus on the spin-1/2 sector. Note that the acceptor potential plays no role in the 4-site cluster. The ground state is doubly degenerate with the energy \(E_g = -\frac{t}{2} - \sqrt{3t^2 + (t' + t)^2}\), with reflection symmetries (+1, -1) and (-1, +1). Assuming the former to be ground state leads to (apart from an overall prefactor) \(I_1^s(\omega) = \frac{1}{3} \cos^2 2 \Theta(\omega - J), I_1^c(\omega) = \frac{2}{3} \cos 2 \Theta(\omega - J), I_1^t(\omega) = 0,\) and \(I_1^x(\omega) = \cos 2 \Theta(\omega - 2J), \) with \(\tan \gamma = \sqrt{3t/(J + t' + E_g)}\). Because of the nature of the many body wave function, the conductance in Eq. (6) may involve either destructive or constructive interference among different components, even an exact cancellation in the case of \(I_1^t\). Summing over spins, gives \(I'(\omega) = I_1^s + I_1^c = 2 \cos^2 2 \Theta(\omega - J),\) while \(I'(\omega) = \cos^2 2 \Theta(\omega) + \sin^2 2 \Theta(\omega - 2J).\) It is obvious that \(\eta(\omega)\) becomes infinite for \(\omega \in (0, J)\), while \(\eta(\omega) = 1/2\) for \(\omega \in (J, 2J)\) and \(\eta(\omega) = 2 \cos 2 \gamma\) for \(\omega > 2J.\) For \(t'/t = -0.1\) and \(\omega > 2J, \eta \sim 0.97.\) Therefore, the asymmetry becomes rather weak with increasing bias voltage. The ratio of the integrated conductances in the \((-1, 1)\) ground state can be obtained by interchanging \(x\) and \(y\) and is given by \(\eta^{-1}.\) We have also calculated the integrated conductance for the hole injection tunneling and found it also to be rotational asymmetric as is the ratio between the electron injected and hole injected conductances.

In the broken rotational symmetry state, the local charge density at each of four NN Cu sites around a Na\(^+\)-acceptor is uniform, but the NN Cu-Cu bonding amplitudes are not equal. For instance, in the \((+1, -1)\) ground state of the 16-site cluster, the expectation values of hopping amplitude \(\langle c_i^+ c_j\rangle\) as well as spin-spin correlation function \(\langle S_i S_j \rangle\) for various bonds are listed in Table I. The hopping amplitude along bond 1 is slightly stronger than that of bond 2, while the spin-spin correlation function exhibits a much stronger asymmetry. If the acceptor leads to localization of holes a larger hopping amplitude and weaker spin-spin correlation function appear in its vicinity, but further away, the hole density becomes very small and the spin-spin correlation function approaches \(-0.34.\) Localization can be strengthened by the electron-phonon interaction, and also the spin-coupling may favor polaron formation [20]. It will be interesting to examine possible polaron effects in the presence of the local broken symmetry.

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TABLE I. The hopping integral and spin-spin correlation function for various bonds in a 16-site cluster with PBC for \(t' = -0.1\) and \(\epsilon_c = 1.0\). The bonds are labeled in Fig. 2(b).

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<tr>
<th>bond index</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>\langle c_i^+ c_j \rangle</td>
<td>0.342</td>
<td>0.328</td>
<td>0.122</td>
<td>0.129</td>
<td>0.020</td>
<td>0.014</td>
<td>0.012</td>
<td>0.016</td>
</tr>
<tr>
<td>\langle S_i S_j \rangle</td>
<td>0.167</td>
<td>0.074</td>
<td>0.161</td>
<td>0.167</td>
<td>0.329</td>
<td>0.336</td>
<td>0.347</td>
<td>0.334</td>
</tr>
</tbody>
</table>

[12] The double degenerate ground state was not found in Ref. [9], due to the specific cluster they considered.