Charge-transfer strings in the extended Hubbard model for copper oxide superconductors

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Near the $Cu^{2+} \rightarrow Cu^{+}$ valence instability, there are low-lying excitations in the extended Hubbard model for CuO_2 superconductors which consist of spatially extended, contiguous strings of Cu^{+}-O^{-} pairs. Such strings can be electrically neutral or carry charges $+e$ or $-e$. Results for the string band structure, their internal excitations, and possible attractive string-pairing interactions are presented. Important experimental implications are discussed.

It has been suggested that the Cu^{2+} and O^{2-} ionic charge states in the copper-oxide-based perovskite superconductors[1,2] may be close to a valence instability corresponding the formation of Cu^{+} and O^{-}.[3,4] The purpose of the present paper is to identify a novel type of low-lying excitation in such systems which occurs in the vicinity of this instability. In non-half-filled systems,[5,6] these excitations exist as charged quasiparticles which are likely to be responsible for metallic behavior and superconductivity.

The theory is based on a two-dimensional (2D) extended Hubbard model which describes a square lattice of hybridized copper (x^2-y^2) $3d$ orbitals and bond-parallel oxygen p orbitals,[5,6] as shown in Fig. 1(a). The Hamiltonian is[7-10]

$$H=\sum_i(\epsilon_i n_i+U_i n_{i\uparrow}n_{i\downarrow}) + \tfrac{1}{2}\sum_{i\neq j}[V_{ij}(n_i-n_i^{(0)})(n_j-n_j^{(0)})+\sum_s t_{ij}(c_{is}^{\dagger}c_{js}+\text{H.c.})]\,. \tag{1}$$

The first summation is over all Cu and O sites i with hole occupation numbers $n_{is}=c_{is}^{\dagger}c_{is}$ and $n_i=n_{i\uparrow}+n_{i\downarrow}$, where $c_{is}^{\dagger}$ creates a hole at site i with spins $s=\uparrow$ or $\downarrow$. The on-site energies and Coulomb repulsions are $\epsilon_i\equiv\epsilon_d$, $U_i\equiv U_d$ or $\epsilon_i\equiv\epsilon_p$, $U_i\equiv U_p$ if i denotes a Cu or an O site, respectively. The second summation in (1) is over all pairs of orbitals $i\neq j$. We include only the Cu–O nearest-neighbor (NN) hybridization,[5,6] with $|t_{ij}|=t$ for Cu–O NN pairs i,j. For the intersite repulsion, we use a simple screened point-charge model, parametrized by

$$V_{ij}=\tfrac{1}{2}(V/r_{ij})\exp(-\kappa r_{ij}+\kappa/2)\,,$$

where r_{ij} is the distance between sites i,j and $1/\kappa$ is the screening length, both measured in units of the Cu–Cu NN distance a. Thus, $V>0$ is the Cu–O NN intersite repulsion.[7,8] From the intersite Coulomb energy, we have subtracted the Madelung potential of a conveniently chosen ionic reference state $|\cdots n_{is}^{(0)}\cdots\rangle$, which is absorbed on the on-site energies ϵ_i.

We consider now the ionic ($t=0$) limit of (1). The model parameters are assumed to be such that, for the half-filled system (corresponding to the undoped La_2CuO_4 system, for example), $n_i=1$ (Cu^{2+}) for all d orbitals and $n_i=0$ (O^{2-}) for all p orbitals.[11] This Cu^{2+} vacuum state, shown in Fig. 1(a), serves as our reference state $|\cdots n_{is}^{(0)}\cdots\rangle$.[12] We also assume that the on-site repulsions $U_d\sim 6$–8 eV and $U_p\sim 3$–6 eV (Refs. 3, 4, 8, and 13) are sufficiently strong to suppress double occupancy ($n_i=2$) at all sites, so that doping-induced extra holes have to be accommodated as O^{-} ions, as shown in Fig. 2(a), whereas extra electrons would form Cu^{+} ions [Fig. 2(d)]. The stability of these states [Figs. 1(a), 2(a), and 2(c)] depends crucially on V_{ij} and on $e_I\equiv\epsilon_p-\epsilon_d$. The onset of the valence instability involves the formation of spatially extended strings of Cu^{+}-O^{-} pairs, as shown in Figs. 1(b) and 1(c) and 2(b) and 2(d). If created from the Cu^{2+} vacuum, such a string is electrically neutral

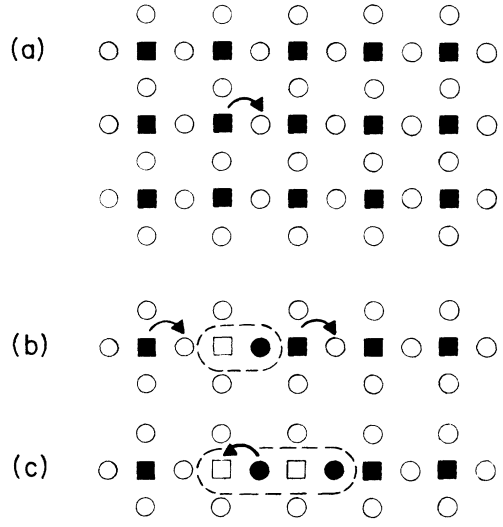

FIG. 1. Ionic (a) Cu^{2+} vacuum and (b),(c) neutral string states in the half-filled 2D CuO_2 square lattice. Square (circles) represent Cu sites (O sites). Open (closed) symbols represent unoccupied, $n_i=0$ (singly occupied, $n_i=1$) sites, corresponding to ionic charge states Cu^{+} or O^{2-} (Cu^{2+} or O^{-}). Only the string-carrying CuO chain is shown in (b) and (c). Arrows indicate some of the possible Cu–O NN transfer processes which increase or decrease the string length L along the chain direction. The Cu^{2+} vacuum in (a) can be regarded as an $L=0$ string, the strings in (b) and (c) have lengths $L=1$ and $L=2$, respectively.

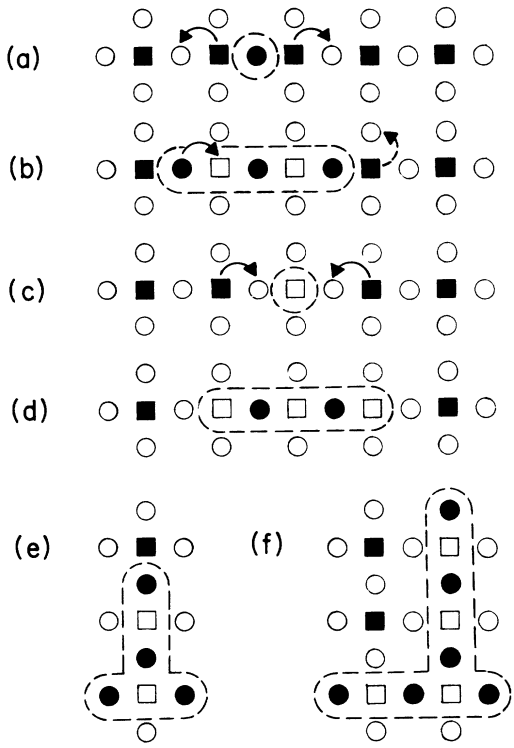

FIG. 2. (a)–(d) Electrically charged strings and (e),(f) two-string clusters in the CuO_2 square lattice. Symbols are defined as in Fig. 1. (a) and (b) show positively charged ($q=+$) strings of lengths $L=0$ and $L=2$, respectively; (c) and (d) represent negative charged ($q=-$) (anti-) strings with lengths $L=0$ and $L=2$, respectively. Full arrows indicate Cu–O NN transfer processes along the string direction which increase or decrease L. The dashed arrow in (b) indicates a transfer perpendicular to the initial string direction which would lead to a "bent" string state. (e) and (f) show T-shaped clusters, consisting of pairs of positively charge strings with lengths (e) $L=1$ and (f) $L=2$, joined at the intersection of perpendicular CuO chains.

[Figs. 1(b) and 1(c)]. If originating from a free-carrier (O^- or Cu^+) site, the string carries a charge of either $+e$ [Figs. 2(a) and 2(b)] or $-e$ [Figs. 2(c) and 2(d)]. By summing up the ionic ($t=0$) terms in (1), we get the total energy $E_q(L)$ needed to create strings of charge $q=0,+,-$ as a function of the string length L, that is, the number of Cu^+-O^- segments (as defined in Figs. 1 and 2). For $L\gg 1$, we find

$$E_q(L)\cong Va_q+L(e_I-bV)\,, \tag{2}$$

where $b>1$ is independent of q. With $E_q(L)$ measured relative to the energy of the corresponding $L=0$ state [Figs. 1(a), 2(a), and 2(c)], a_q and b depend only on the shape of V_{ij}, i.e., on κ in our model. We have $a_0=1$, $a_\pm=0$, $b=2$ in the strongly screened limit ($\kappa\to\infty$) and $a_0=\frac{1}{2}$, $a_\pm=\frac{1}{2}-\ln 2\cong -0.19$, $b=2\ln 2\cong 1.39$ for $\kappa\to 0$. Thus, if the string tension $e_s\equiv e_I-bV$ is negative, the $L=0$ states in Figs. 1(a), 2(a), and 2(c) are unstable towards formation of strings with $L\to\infty$. If $e_s>0$, on the other hand, $E_0(L)$ increases monotonically with L and the Cu^{2+} vacuum is stable. For charged strings, we find $E_+(L)=E_-(L)<E_0(L)$ if $L\geq 1$. In particular, for $L=1$, $E_q(1)=e_s+f_qV$, where $f_0=(b-1)>0$, but $f_\pm=f_0-1$ or $f_0-\frac{1}{2}<0$ for $\kappa=\infty$ and $\kappa=0$, respectively. Thus, if $e_s>0$, it costs an energy of at least $e_s+(b-1)V$ to create a neutral string from the vacuum. However, $E_\pm(L)$ can be substantially lower than $E_0(L)$ (and possibly even negative) for small L if $0<e_s\ll V$.

Next, we consider the effect of the hybridization t when $e_s>0$. We assume that t is in the range of 1–2 eV (Refs. 6 and 8) and, hence, smaller than $V\sim e^2/(\epsilon_\infty a/2)\sim 2.5$–4 eV, using a typical background dielectric constant $\epsilon_\infty\sim 2$–3 and a Cu–O NN distance $a/2\cong 1.9$ Å. We shall therefore treat the problem, for the time being, in the limit $e_s,t\ll V$ with $U_p,U_d=\infty$. For a nearly-half-filled system, we can then identify a manifold of low-lying ionic states whose zeroth-order ($t=0$) energy differs from that of the higher-energy states by amounts of order V or more. For example, for a single extra hole in the Cu^{2+} vacuum, these low-lying states are just the charged string states [cf. Figs. 2(a) and 2(b)] discussed above. To lowest order in t/V, we can then treat the low-energy dynamics of the system by projecting H onto this low-lying subspace and neglect small admixtures from the "virtual" higher-energy states. Thus, we neglect virtual creation of additional neutral strings because of their higher energy $E_0(L)\gtrsim V$. We also neglect transitions into "bent" string states, indicated in Fig. 2(b), which permit a string, propagating along an x chain, say, to transfer on a y chain, but require an additional intermediate energy of order V (at least, if $\kappa<1$). This energy barrier tends to restrict the string propagation to a one-dimensional (1D) Cu–O chain. The problem of a single extra hole is thus mapped onto an infinite-U extended Hubbard chain which allows us to separate charge and spin degrees of freedom.[14] For a charged string propagating on such a chain, we can then write eigenstates with total wave vector k (measured in units $1/a$) as

$$|\Psi_k\rangle=\sum_{l,r}e^{ik(l+r)/2}e^{i\phi_k(l-r)}\Phi_k(l-r)\,|l,r\rangle\,,$$

where $l,r=0,\pm 1,\pm 2,\ldots$ ($l\leq r$) denote respectively, the left- and rightmost O^- or Cu^+ site in the ionic string state $|l,r\rangle$ with string length $L=r-l$. The wave amplitude $\Phi_k(r-l)$ describes the relative motion of the two ends of the string. The eigenenergies $\epsilon(k)$ are determined by the Schrödinger equation

$$\epsilon(k)\Phi_k(L)=-\tilde{t}(k)[\Phi_k(L+1)+\Phi_k(L-1)]+E_\pm(L)\Phi_k(L)\,, \tag{3}$$

where $\Phi_k(L)\equiv 0$ if $L<0$, and $\tilde{t}(k)=|2t\sin(k/2)|$ with an appropriately chosen phase $\phi_k=+\pi$ or $-\pi$ in $|\Psi_k\rangle$. Thus, in a single CuO chain, we obtain one 1D energy band $\epsilon(k)\equiv\epsilon_\nu(k)$ for each "internal" string eigenstate of (3), $\Phi_{k\nu}$, $\nu=0,1,\ldots$. In the 2D CuO_2 lattice, this leads to two 2D bands, $\epsilon_\nu^{(x)}(k_x,k_y)=\epsilon_\nu(k_x)$ and $\epsilon_\nu^{(y)}(k_x,k_y)=\epsilon_\nu(k_y)$ for each ν, corresponding to propagation along the x or y direction, respectively. If $\tilde{t}(k)\gg|E_\pm(L+1)-E_\pm(L)|\sim e_s$, $\Phi_k(L)$ varies slowly with L and (3) can be treated in a continuum approximation.[15] With $E_\pm(L)$ approximated by (2), the low-lying eigenenergies of (3)

are

$$\epsilon_\nu(k) \cong a \pm V - 2\tilde{t}(k)\{1 - \tfrac{1}{2}\alpha_\nu[e_s/\tilde{t}(k)]^{2/3}\} .$$

Here, α_ν, $\nu = 0,1,2,\ldots$, are the lowest, even-parity eigenvalues of a dimensionless continuum Hamiltonian $h \equiv (-d^2/dy^2 + |y|)$, of order unity. The corresponding $\Phi_{k\nu}$ are spread out over an average length $L_0 \sim (2t/e_s)^{1/3} \gg 1$. Notice that by delocalizing the two ends of the string relative to each other, the system (in its ground state) lowers its hybridization energy by an amount of order t, but increases its "potential" energy $E_\pm(L_0)$ only by an amount of order $L_0 e_s \sim (e_s/t)^{2/3} t \ll t$. Thus in a non-half-filled system, each doping-induced extra hole will spontaneously form a spatially extended charged string when $t \gg e_s$. The band minimum of $\epsilon_\nu(k)$ is at $k_0 = \pm\pi$ with an effective mass

$$m_\nu = (\partial^2 \epsilon_\nu/\partial k^2)^{-1} = (2t)^{-1}/[1 - \alpha_\nu/6)(e_s/t)^{2/3}]$$

parallel to the string direction. Thus, in the "large-string" limit, $t \gg e_s$, the string bandwidth is of order $2t$. However, the internal excitation energies near k_0,

$$\omega_{\nu\mu}^{(\pm)}(k_0) \equiv |\epsilon_\nu(k_0) - \epsilon_\mu(k_0)| = |\alpha_\nu - \alpha_\mu|(2e_s^2 t)^{1/3},$$

vanish at the instability $e_s \to 0$. In the "small-string" limit, defined by

$$t \ll \min|E_q(L+1) - E_q(L)| \equiv e_s' \lesssim e_s ,$$

we can treat $\tilde{t}(k)$ as a perturbation in Eq. (3).[15] The string bandwidth is then of order $t^2/e_s' \ll t$ (again with the band minimum at $k_0 = \pm\pi$), whereas the internal excitation energies are of order $\omega_{\nu\mu}^{(\pm)}(k) \sim e_s' \gg t$. Similar results can be obtained in these two limits for the bandwidth and internal energies $\omega_{\nu\mu}^{(0)}$ of a neutral string excitation, created with energies $\epsilon(k) \gtrsim e_s + (b-1)V$ from the vacuum.

A possible mechanism for attractive interactions between pairs of charged strings is indicated by the ionic states shown in Figs. 2(e) and 2(f). They consist of T-shaped clusters of two perpendicular, charged strings, which, for simplicity, have both the same length, typically $L \sim L_0$. The ionic ($t = 0$) energy of this state differs from that of two spatially well-separated charged strings (with the same lengths L) by an amount $U_s(L) = u_s(L)V$, where $u_s(L) = -1$ (for $L \geq 1$) if $\kappa \to \infty$, but $u_s(L) > 0$ for $\kappa \to 0$, with $u_s(L) \leq 0.159$ for $L \geq 1$. Thus, to obtain an attraction, $U_s \sim -V < 0$, in this pairing channel, it is crucial that the longer-range parts of V_{ij} be screened out. The superconducting order parameter will then consist primarily of terms $\Delta_{ij} \equiv c_{is}c_{js}$, where $i \neq j$ denote pairs of different oxygen sites on the T-shaped cluster.[8,16] This string-pairing mechanism is thus quite different from the charge-transfer-mediated pairing proposed in Ref. 7 which is based on a weak-coupling treatment and implies strong on-site ($i = j$) pairing contributions Δ_{ij} from the copper sites.

If we take into account admixtures from the "virtual" higher-energy states, several new effects arise. Namely, as t becomes comparable to V, the Cu^{2+} vacuum and charged strings will be "dressed" by virtual neutral string excitations (Fig. 1). Also, the restriction of the string propagation to 1D CuO chains will be largely removed, which leads to a mixing of the two sets of bands $\epsilon_\nu^{(x)}$ and $\epsilon_\nu^{(y)}$. With strings propagating in two dimensions, their charge and spin degrees of freedom[12] are intimately coupled.[14(b)] Finally, as a result of virtual double occupancy (with finite U_d, U_p), superexchange couplings[8-10] arise which are responsible for antiferromagnetic order in the Cu^{2+} vacuum[11] and lead to string-spin interactions in the doped systems. While the foregoing effects contribute to string mass renormalizations, damping processes, and effective string-string interactions, they will not affect the main conclusions of this paper, namely, that near the valence instability ($t \gg e_s$), (a) doping-induced extra holes form spatially extended, stringlike, charged quasiparticles of a characteristic size $L_0 \sim (2t/e_s)^{1/3}$, (b) the string quasiparticles exhibit low-energy internal excitations, typically of order $\omega_{0\mu}^{(\pm)} \sim (e_s^2 t)^{1/3} \ll t$, and (c) in the presence of screened intersite Coulomb repulsions $V > t$ attractive interactions exist between pairs of charged strings.[16]

With regard to the high-T_c materials,[1,2] specifically the La_2CuO_4 system, the foregoing results have several important experimental implications. First, inelastic scattering or optical-absorption experiments in an ideal half-filled system at temperature $T = 0$ should *not* detect any charge-transfer-related excitations below the threshold energy $\omega_0 \sim E_0(1) = e_s + (b-1)V \gtrsim 1-3$ eV for creating neutral strings from the Cu^{2+} vacuum, even though the system may be very close to the $Cu^{2+} \to Cu^{+}$ valence instability ($e_s \to O^{+}$).[17,18] "Soft" excitations below ω_0, associated with the incipient instability, should manifest themselves only in the non-half-filled (doped) system. They correspond to the low-lying internal excitations $\omega_{\nu\mu}^{(\pm)}$ of the doping-induced charged strings and their intensity should thus increase (linearly, at first) with dopant concentration.[17] Internal excitations of the neutral strings should lead to high-energy sidebands, roughly at energies $\omega_0 + \omega_{0\mu}^{(0)}$, slightly above ω_0. Second, an additional absorption threshold should be observable, roughly at the ionization energy, $\omega_I \sim e_I = e_s + bV \gtrsim 4$-$6$ eV, corresponding to the creation of charged string ($q = +$)-antistring ($q = -$) pairs. Thus, optical absorption at the upper threshold, ω_I, in a half-filled system at $T = 0$ should be accompanied by observable photoconductivity, whereas at the lower threshold ω_0 no such effect should be found. Third, the creation of strings (by doping or photoexcitation) is accompanied by transfer of positive charge and spin density from the copper to the (in-plane) oxygen sites. This should be observable in core-hole spectroscopies and, respectively, in magnetic neutron scattering and magnetic resonance measurements.

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[16]J. E. Hirsch, in Proceedings of the Workshop on Mechanisms of High-T_c Superconductors, Minnesota, 1987 (unpublished); J. E. Hirsch, S. Tang, E. Loh, and D. J. Scalapino (unpublished) have recently reported exact diagonalization data for model (1) (near $e_s=0$, with $\kappa\rightarrow\infty$) from which they infer the existence of attractive interactions between extra holes occupying different oxygen sites, consistent with the mechanism proposed here.
[17]Close proximity to the valence instability is thus not inconsistent with recent optical absorption data on undoped single-crystal La_2CuO_4 which do not appear to exhibit any strong electronic excitations below ~ 2 eV; J. Orenstein *et al.*, Phys. Rev. B **36**, 8892 (1987). Recent work by Tanner and coworkers on $La_{2-x}Sr_xCuO_4$, on the other hand, seems to indicate that presence of a broad "mid-infrared" absorption continuum in the energy range 0.1–0.5 eV with an integrated intensity that increases with dopant concentration $x\sim 0.0$–0.2; D. Tanner, presented at the Aspen Winter Physics Conference, Aspen, Colorado, 1988 (unpublished); D. Tanner *et al.* (unpublished). With $e_s\sim 0.1$–0.2 eV and $t\sim 1$–2 eV, this mid-infrared continuum could be tentatively assigned to the internal excitations $\omega_0^{(+)}_{\mu}$ of doping-induced charged strings, which are broadened into a continuum by the various damping mechanisms discussed.
[18]Similarly, the energy $\Delta\sim E_0(1)\sim e_s+(b-1)V$ for a Cu–O NN hole transfer [shown in Figs. 1(a) and 1(b) and referred to as $3d^9\rightarrow 3d^{10}L$ in Refs. 3 and 4] does *not* vanish at the instability but rather becomes of order V. Thus, V should be taken into account in the interpretation (Refs. 3 and 4) of core-hole spectra when $e_s,\Delta\lesssim V$.