Experimental evidence of paired hole states in model high-$T_c$ compounds

A. Rusydi, 1,2,3 P. Abbamonte, 1,4 M. Berciu, 5 S. Smadici, 1,4 H. Eisaki, 6
Y. Fujimaki, 7 S. Uchida, 7 M. Rübsamen, 3 and G. A. Sawatzky 5

1National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY, 11973-5000, USA
2Materials Science Centre, University of Groningen, 9747 AG Groningen, The Netherlands
3Institut für Angewandte Physik, Universität Hamburg, Janggissstraße 11, D-20355 Hamburg, Germany
4Physics Department and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL, 61801
5Department of Physics and Astronomy, University of British Columbia, Vancouver, B.C., V6T-1Z1, Canada
6Nanoelectronics Research Institute, AIST, 1-1-1 Central 2, Umezono, Tsukuba, Ibaraki, 305-8568, Japan
7Department of Superconductivity, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

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The distribution of holes in Sr$_{14-4x}$Ca$_x$Cu$_{24}$O$_{41}$ (SCCO) is revisited with semi-empirical reanalysis of the x-ray absorption (XAS) data and exact-diagonalized cluster calculations. A new interpretation of the XAS data leads to much larger ladder hole densities than previously suggested. These new hole densities lead to a simple interpretation of the hole crystal (HC) recently reported with 1/3 and 1/5 wave vectors along the ladder. Our interpretation is consistent with paired holes in the rung of the ladders. Exact diagonalization results for a minimal model of the doped ladders suggest that the stabilization of spin structures consisting of 4 spins in a square plaquette as a result of resonance valence bond (RVB) physics suppresses the hole crystal with a 1/4 wave vector.

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conductivity and the NMR data analysis at $x = 0$ are based on the neutron diffraction observation \cite{20} of what was thought to be a superlattice reflection corresponding to a chain charge density wave (CDW) consistent with the neutron diffraction observation \cite{20} of what was expected in the basic crystal structure and is therefore not evidence for a CDW.

The only direct measurement of the hole density distribution comes from polarization dependent XAS. This is also subject to interpretation, and the model used previously had unexplained discrepancies with regard to the polarization-dependence. In N"ucker \textit{et. al.}'s analysis \cite{17} of the XAS data it is concluded that the holes are mainly concentrated on the chains. Their interpretation assumes that there are only 2 distinct O 1s pre-edge absorption energies, one (H1) corresponding to holes in the chains and the other (H2) to holes in the ladders. The H1 peak should be independent of the ac-plane polarization since the lobes of the O 2p orbitals involved in the chain ZR singlets are oriented at 45$^\circ$ to the $a$- and $c$-axes (see Fig. 1a). The H2 peak should be strongly polarization dependent since the rung O and the leg O have different hole amplitudes. However, for $x = 0$, XAS data shows that H1 is as strongly polarized as H2. In Ref. \cite{17} it is argued that this effect is small and therefore is neglected.

Single crystals of SCCO were grown by travelling solvent floating zone techniques \cite{24}. The surfaces were prepared in the manner described in Ref. \cite{11}. Polarization-dependent XAS measurements in the fluorescence detection mode were carried out on the soft x-ray undulator line X1B at the National Synchrotron Light Source. The energy resolution in the range of interest was about 200 meV. The spectra were corrected for incident flux variations and were normalized at about 70 eV above and 10 eV below the edge where the absorption is atomic like and structureless.

The $x = 0$ spectrum shown in Fig. 1(b)\&(c) is identical to that published in Ref. \cite{17}. Like them, we assign the lowest energy structures to the holes doped in O 2p orbitals and the higher energy structure at about 530 eV to transitions to the upper Hubbard band (UHB) or Cu 3d orbitals. These are followed by a broader structure due to transitions to unoccupied bands hybridized with O 2p and 3p states. The UHB structure is only weakly polarization dependent, as expected given the symmetry of the empty $d_{z^2}$ orbital. Since the point group symmetry for the ladder is not quite $D_{4h}$ (the four O surrounding a Cu are not identical, see Fig. 1a) some polarization-dependence remains. In addition, there is a strongly polarization dependent feature at lower energies, composed of at least two components. In Ref. \cite{17}, XAS data for La$_3$Sr$_{11}$Cu$_{24}$O$_{41.02}$ (with only 3 holes per unit cell) shows only one nearly polarization independent structure at the lower energy. As concluded there, this strongly suggests that the holes involved are almost solely on the chains, where all O sites O(ch) are identical, and with 2p orbitals oriented to 45$^\circ$ (see Fig. 1a).

In ladders, things are more complicated. There are two types of O sites: the rung sites, O(r), coordinated by 2 Cu ions, and the leg sites, O(l), coordinated by 3 Cu ions (see Fig. 1(a)). The different coordination numbers result in different binding energies for the core 1s and valence 2p orbitals. Higher values are expected for the orbitals of O(l), while those of O(r) should be close to O(ch) which is also coordinated by 2 Cu ions. Moreover, each ladder ZR singlet involves one O(r)$_a$, two O(l)$_c$ from the leg, and one O(l)$_a$ from the leg of a neighboring ladder. The subscripts $a$ and $c$ refer to the polarization needed to observe O 1s to 2p transitions. For $a$-polarization, transitions are possible for O(r)$_a$ and O(l)$_a$ at different energies, while for $c$-polarization, transitions are only possible from 2 identical O(l)$_c$, with energy close to that of O(l)$_a$. We performed a simultaneous least-square fit to all the measured spectra. Outputs of the fits, namely the spec-
tral weight (SW), full width at half maximum (FWHM) and various energies are shown in Fig. 2(a)-(c). The number of holes $\delta_L = (3 - 5\delta_e)/7$ are determined from the spectral weights of the various absorption lines:

$$\delta_L = \frac{3(SW_{O(ch)} + SW_{O(\perp)} + SW_{O(\parallel)})}{7(SW_{O(ch)} + SW_{O(\perp)} + SW_{O(\parallel)} + SW_{O(ch)})}$$

where $SW_{O(ch)}$ is the total SW for both polarizations.

We start with $x = 0$. XAS data and theoretical fits are shown in Figs. 1(b),1(c). For $E||c$, the doped hole region has at least two structures. In our interpretation this is due to the energy difference between $O(ch)$ and $O(\perp)$. For $E\parallel a$, the contribution of $O(\perp)$ should be replaced with that of $O(\parallel)$ and $O(a)$, thus shifting more weight to the lower energy. This is indeed consistent with the data. In our fitting results, shown in Fig. 2, the energy of $O(\parallel)$ is about 0.2 eV higher than that of $O(ch)$, while the energy of $O(\perp)$ and $O(a)$ are roughly equal and about 0.5 eV higher than that of $O(ch)$. The SW of the UHB is almost polarization independent. This shows that the ladder holes are distributed nearly isotropically amongst the 4 O involved in the ZR singlet, even though the symmetry is not the full $D_{4h}$. (If large deviations were found, the $Z$R picture would not be valid for the ladder holes). The FWHM of $O(ch)$, which is about 0.62 eV, is about 5% larger than the ones in the ladders. From Eq. (1), we find $\delta_L = 2.8/14$ and $\delta_e = 3.2/10$.

We continue the analysis for $x = 4$. In Figs. 1(d),1(e) we show the fitting for $E\parallel c$ and $E\parallel a$ data, respectively. Again, the SW in the UHB is almost polarization independent (Fig. 2(a)) while the energies of the various O sites are close to the $x = 0$ values (Fig. 2(c)), consistent with our understanding of the polarization dependent XAS. From Eq. (1) we find $\delta_L = 3.4/14$ and $\delta_e = 2.6/10$.

Figs. 1(f) and 1(g) show our XAS data for $x = 11$. (The maximum HC intensity occurs at $x = 11$ where the wave vector is closest to $3\delta_L$ (11)). In Ref. 17 it is claimed that here, the UHB is strongly polarization dependent while the O doped hole pre-edge region is almost polarization independent. Our results show an opposite behavior, like for samples with smaller $x$. In fact, the shape and the intensity of the hole-doped and UHB peaks of Ref. 15 are similar to ours, and can be made to coincide by rescaling. We conclude that the difference is due to the method used in the normalization of the data.

The fit of the polarization dependent XAS for $x = 11$ is more difficult than for $x = 0$ or 4. The problem is not statistical noise, but rather the structural peaks themselves. We see in Fig. 1(f) & (g) that there is no clear evidence for multiple peaks in the doped hole regime because the energy resolution is too poor to resolve the peaks. We therefore use the $x = 0$ results as input for the fitting. The fits are shown in Figs. 1(f), 1(g). As before, we find that the SW of UHB is almost polarization independent and the energies of the various O sites remain close to the $x = 0$ values (see Fig 2), validating our interpretation. We find $\delta_L = 4.4/14$ and $\delta_e = 1.6/10$. It is important to mention that these results depend strongly on the energy of $O(ch)$. For example, varying it by 0.05 eV changes $\delta_L$ by about 0.5/14. This is due to an instability in the fitting process caused by the close proximity of peaks in the pre-edge region (the energy of $O(ch)$ falls close to the leading edge of the hole-doped peak). This is why the $x = 0$ spectrum provides an important reference.

We now analyze some possible scenarios of the hole distribution in the ladder, for these new $n_L$ values. We also consider the connection to the wavelengths $\lambda_{HC} = 3c_L$ ($x = 11$) and $5c_L$ ($x = 0$) of the recently discovered HC [11]. First, DMRG calculations for a single ladder [16] found that holes prefer to pair along the rungs, resulting in a charge density wave shown pictorially in Fig. 3(a-i). For periodicity $\lambda_{HC} = Nc_L$, the doped hole density in ladder $\delta_L$ should be $1/N$, i.e. $\delta_L = 0.2$ if $N = 5$, $\delta_L = 0.25$ if $N = 4$ and $\delta_L = 0.35$ if $N = 3$. These values are very close to our new XAS estimates, as shown in Fig. 3(b). Surprisingly, however, the $\lambda_{HC} = 4c_L$ HC, which is predicted by DMRG, to be a stable phase, is not observed in RSXS [11]. While the study of this discrepancy is on going, a possible explanation is proposed below. Another hole distribution consistent with these $\lambda_{HC}$ values, not involving pairing, and also discussed in Ref. 15, is single rung bond-centered holes which is shown in Fig. 3(a-ii). Since $\delta_L$ for this case is halved, this model does not match our XAS results. In
a third scenario proposed in Ref. [3], the holes could be site centered, alternating between the two legs as shown in Fig. 3(a-iii). While this matches the $\delta_n$ values, it requires an odd number of undoped rungs in the HC unit cell and is therefore inconsistent with the observed $N = 3$ and $N = 5$ HC. We conclude that our results support the scenario of holes paired along the rungs.

Assuming rung-paired holes, a minimal model of the doped ladder is an antiferromagnetic Heisenberg Hamiltonian plus a cyclic four spin exchange term $[26, 27]$

$$\mathcal{H} = J_{\parallel} \sum_{\alpha=1}^{N_R} S_{\alpha,n} \cdot S_{\alpha,n+1} + J_{\perp} \sum_{n=1}^{N_R} S_{1,n} \cdot S_{2,n} + \mathcal{H}_{\text{ring}}$$

Here, $N_R = N - 1$ is the number of undoped rungs per HC unit cell, $\alpha = 1, 2$ indexes spins on the two legs, and $J_{\parallel}$ and $J_{\perp}$ are exchange couplings along the rung and leg, respectively. We assume no coupling between spins on opposite sides of rungs occupied by paired holes. $\mathcal{H}_{\text{ring}} = J_{\text{ring}} \sum_{n=1}^{N_R} S_{1,n} \cdot S_{1,n+1} + S_{2,n} \cdot S_{2,n+1} + S_{1,n} \cdot S_{2,n-1} + S_{1,n+1} \cdot S_{2,n} + S_{1,n} \cdot S_{2,n+1} + S_{1,n+1} \cdot S_{2,n-1} + 4 \{ (S_{1,n} \cdot S_{2,n+1})(S_{1,n+1} \cdot S_{2,n}) - (S_{1,n} \cdot S_{2,n+1} - S_{1,n+1} \cdot S_{2,n}) \}$ is a four-spin cyclic exchange.

We use exact diagonalization to find the ground state for various $N_R$ values. The ground-state (GS) energy per rung, $e_{GS}(N_R) = E_{GS}(N_R)/N_R$, is shown in Fig. 3 (d) for various ratios of $J_{\perp}/J_{\parallel}$ and $J_{\text{ring}}$. The value of $J_{\perp}/J_{\parallel}$ is not known accurately, but is believed to be between 0.5 and 1.13 [18, 21, 30, 31, 32, 33]. An even/odd oscillation is observed for small $N_R$ and $J_{\perp}/J_{\parallel} < 1$, favoring $N_R = 2$ and 4 ($\lambda_{HC} = 3, 5c_L$). The origin of this oscillation is simple. The limit $J_{\parallel} \gg J_{\perp}$ corresponds to two AFM chains weakly coupled along the rungs. For even $N_R$, spins on each leg pair in a RVB-like state, and $E_{GS}$ is low. For odd $N_R$, each leg has an unpaired spin, significantly increasing $E_{GS}$. In the limit $J_{\parallel} \gg J_{\perp}$, the GS consists of spin-singlets along the rungs and the parity of $N_R$ is irrelevant. At large $N_R$, $e_{GS}$ converges to the bulk value. This even/odd oscillation provides a possible explanation for the absence of a HC with $N_R = 3$ ($\lambda_{HC} = 4c_L$). This HC costs an energy $e_{\text{ord}} = 6e_{GS}(3)$ per two unit cells (see Fig. 3(c-ii)). A disordered phase, at the same doping, has equal numbers of $N_R = 2$ and $N_R = 4$ plaquettes and an energy $e_{\text{dis}} = 2e_{GS}(2) + 4e_{GS}(4)$ for the same length (see Fig. 3(c-i)). If $e_{\text{dis}} < e_{\text{ord}}$, the HC phase is unstable. For $J_{\perp} = 130$ meV, we plot $e_{\text{dis}} - e_{\text{ord}}$ in Fig. 3(e), showing that the disordered phase is energetically favorable, especially for lower values of $J_{\parallel}/J_{\parallel}$.

We have also studied the effect of $\mathcal{H}_{\text{ring}}$ on $E_{GS}$. Such terms appear in 4th order perturbation expansions in the strong coupling limit of the Hubbard model [28] and are known to play an important role for Wigner crystals and $^3$He solid. Typical results for $e_{GS}(N_R)$ are shown in Fig. 3(f), for $J_{\parallel}/J_{\parallel} = 0.56$ [25] and $J_{\text{ring}}/J_{\parallel} = -0.1, 0, 0.1$. Since the sign of the ring exchange and superexchange should be the same [25], it follows that a large $J_{\text{ring}}$ suppresses the even-odd effect. For example, for $J_{\parallel}/J_{\parallel} = 0.56$, $e_{\text{dis}} - e_{\text{ord}}$ increases from -20.8 meV if $J_{\text{ring}} = 0$, to -12.5 meV if $J_{\text{ring}}/J_{\parallel} = 0.1$. We conclude that for reasonable values of $J_{\parallel}/J_{\parallel}$, $J_{\text{ring}}$ and $J_{\text{ord}}$ this simple model offers a possible explanation for the absence of the $\lambda_{HC} \sim 4c_L$ HC. An accurate determination of the exchange couplings is needed before the issue can be settled.

In conclusion, we propose a new interpretation of polarization dependent XAS for SCCO. Based on our analysis combining the XAS and RSXS data, we find strong support for a pairing of holes in the rungs of the ladders. We also give a possible explanation for the absence of the HC with 1/4 periodicity in terms of RVB physics.

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