Experimental Observation of the Crystallization of a Paired Holon State

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An exciton at 201 meV is observed in the doped-hole ladder cuprate Sr$_{14}$Ca$_2$Cu$_{24}$O$_{41}$, using ultraviolet resonance Raman scattering with incident light at 3.7 eV polarized along the rungs. The excitation is of charge nature, with a temperature independent excitation energy, and can be understood via an intraladder pair-breaking process. The intensity tracks closely the order parameter of the charge density wave in the ladder CDW, but persists above its transition temperature $T_{CDW}$, indicating a strong local pairing above the $T_{CDW}$. The 201 meV excitation vanishes in La$_5$Ca$_9$Cu$_{24}$O$_{41+\delta}$ and La$_5$Ca$_9$Cu$_{24}$O$_{41}$ which are samples with no holes in the ladders. Our results suggest that the doped holes in the ladder are composite bosons consisting of paired holons that order below $T_{CDW}$.

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Important physics in strongly correlated materials is driven by the nature of the pairing state of charges, i.e., holes in hole-doped materials such as high-temperature superconductor copper oxides (cuprates) [1]. The paired hole states are believed to be responsible for the mechanism of superconductivity and the formation of the related but insulating charge density wave (CDW) order. However, thus far the nature of the pair-breaking mechanism in both cases is still unclear.

An ideal system to study paired hole states is the two-leg “spin ladder” Sr$_{12}$Ca$_2$Cu$_{24}$O$_{41}$ (SCCO) which is believed to contain the basic physics of the cuprates [2–7]. SCCO is a self-doped material with 6 holes per formula unit and is a layered material consisting of two different cuprate structures: CuO$_2$ “chains” and Cu$_3$O$_5$ “ladders” (see Fig. 1 and Ref. [8] for the complete structure). Here, $x$ does not change the total number, but redistributes holes between chains and ladders [9]. SCCO has striking properties; it exhibits superconductivity for $x > 10$ under pressures above 3 GPa [10]. For $x = 0$, dc conductivity and low-frequency dielectric measurements [11,12] suggest the existence of unconventional CDWs which exhibit below $\sim 200$ K an energy gap of about $\sim 112$ meV ($= \Delta_{CDW}$).

The distribution of holes in the chains and ladder has been one of the central subjects as many interpretations depend on this distribution. For instance, neutron diffraction results by Matsuda et al. [13] were thought to be a signature of a superlattice reflection in the chain with periodicity $L_c = 0.25$ ($L_c$ is the indices Miller of the chain). The neutron diffraction result was interpreted as a hole modulation in the chain via a spin dimerization leading to 5 holes residing in the chains and 1 hole in the ladders. However, more recent neutron diffraction studies by Braden et al. [14], analysis of the crystal structure by van Smaalen [15], the hard x-ray diffraction result by Zimmermann et al. [16], and resonant soft x-ray scattering (RSXS) studies [17–19] have clearly shown that the $L_c = 0.25$ peak is a structural modulation driven by a misfit strain between the chains and ladders.

FIG. 1 (color online). (a) CuO$_2$ chain. The charge transfer (CT), O(ch) 2p $\rightarrow$ Cu 3d transition, is polarization independent along the a and c axis [9]. (b) Cu$_2$O$_3$ ladders consisting of paired hole “singlet” states and Raman active processes, i.e., [intermediate], and [final] states. (Zoom-in) Based on Wannier functions, the lowest energy state of holes in ladders is a Zhang-Rice singlet [33] and the weight of the orbital in the 4 oxygen atoms are different due to the geometry of the ladder. Thus, the CT excitation is polarization dependent in ac plane. In the [final] state, the energy cost of each broken bond with a bar is $J/4$ and each frustrated bond is $J/2$. The two new bonds in the left ladder give contributions that cancel with each other.
A direct way to measure the distribution of holes is x-ray absorption spectroscopy (XAS). However, this was also subject to interpretation because the model used previously had unexplained discrepancies with regard to the strong polarization dependence observed in XAS [20]. A recent polarization dependent XAS study on SCCO [9] has resolved these discrepancies and has accordingly revisited the number of holes in the chain and ladders in which for $x = 0$, there are 3.2 holes in the chain and 2.8 in the ladder. Furthermore, the combination of XAS and RSXS has revealed that (1) SCCO contains the unconventional CDWs, i.e., a hole Wigner crystal (HC) in the ladder or CDW$_L$ ($x = 0.10$, 11, and 12) [17,18], and a 4$f_p$ CDW in the chain or CDW$_C$ ($x = 0$) [19], and (2) suggesting the existence of paired hole states along the rung of the ladders [9]. It is concluded that the interplay of lattice commensuration, Coulomb repulsion, and geometric tiling of edge-shared ladders is responsible for the CDW$_L$ and enforces a unique environment for the holes to pair (see Fig. 1). In contrast, the misfit strain between the ladder and chain substructures is the driving force for the chain 4$f_p$ CDW.

Several studies have found the intimate connection between the local physics of the quasi-one-dimensional (quasi-1D) two-leg spin ladders and two-dimensional (2D) cuprates [21]. Studies of the two-magnon (2M) excitation in SCCO using Raman scattering in visible have suggested that the nearest-neighbor exchange coupling $J$ (∼100 meV) in the ladder is isotropic [22]. A similar observation was found in 2D cuprates [21]. An inelastic neutron scattering study found a spin-liquid state with a spin gap of 40 meV for $x = 0$ [13]. This spin-gap energy is also similar to the spin-resonance mode seen in the 2D cuprates [21]. However, it is unclear whether the spin gap is directly relevant to the energy of the paired holes. Recently, a pair-density wave consisting of a hole pair was proposed to exist in 2D cuprates [23,24]. This has also been followed by recent evidence for paired charges in underdoped cuprates using a scanning tunneling microscope [25]. The suggested pair-density wave scenario is in fact very similar to a quasi-1D system [2,3]. Thus, the understanding of the quasi-1D–two-leg spin ladder is of fundamental importance to understand the physics of the cuprates. Here, we study a pair-breaking excitation of holes at 201 meV (∼2$\Delta_{CDW}$), the intimate relationship between the paired hole states and the ladder CDW, and the existence of preformed hole pairs by using ultraviolet resonance Raman scattering (UVRRS) and RSXS [26].

Figure 2 shows inelastic light Raman scattering spectra with an incident photon energy, $h\nu$, of (a) 2.7 and (b) 3.7 eV for (aa) and (cc) polarizations of Sr$_{12}$Cu$_{23}$O$_{41}$ (SCO), La$_6$Ca$_8$Cu$_{24}$O$_{41}$ (L6C8CO$_{41}$), La$_8$Ca$_8$Cu$_{24}$O$_{41,056}$ (L6C8CO$_{41,056}$), and La$_3$Ca$_6$Cu$_{22}$O$_{41}$ (L5C9CO). [The (xy) polarization geometry in Raman means that the incoming (out going) photons are polarized along $x(y)$.] $h\nu = 2.7$ eV, our Raman result is similar to Ref. [22]. We have observed a two-phonon excitation at ∼138 meV and a three-phonon excitation at ∼207 meV. These excitations are the second and third order of a one-phonon excitation (∼69 meV), respectively, that is Raman active oxygen Ag modes and gets enhanced by Fröhlich interaction [27]. 2M excitations are observed in (cc) and weaker in (aa) geometry with an energy of 375 meV yielding an isotropic $J$ of 100–120 meV. They are strong in the (cc) polarization and weaker in the (aa). We have also observed sharp and strong 2M excitation in (cc), however, weaker in (aa). The energy of the 2M excitation is nearly isotropic at ∼375 meV Raman shift yielding an isotropic $J$ of ∼100–120 meV.

Our central observation is a new electronic excitation at 201 meV Raman shift of SCO using UVRRS measured at $h\nu = 3.7$ eV [Fig. 2(b)]. The polarization dependence shows that the intensity of the 201 meV peak in (aa) is at least 10 times higher than the intensity in (cc). In cross polarization, the 201 meV feature is nearly invisible. The energy of this excitation is about twice the value of the CDW gap measured by dc conductivity and low-frequency dielectric measurements [11,12].

Another striking evidence that the 201 meV is directly related to the presence of holes comes from a doping dependent study. Reference samples which contain no holes in the ladder but nearly identical magnetic structures as seen by NMR and neutron measurements, do not show the 201 meV peak [28,29]. If the 201 meV feature would be related to the spin, then it should also appear in the reference samples. However, we have found that the 201 meV peak vanishes in L6C8CO$_{41}$, L6C8CO$_{41,056}$, and L5C9CO, i.e., samples without holes in the ladders [see Fig. 2(b)].

Furthermore, we have studied a complete resonance profile (RP) of 201 meV, 375 meV, and 140 meV excitations which are shown in Figs. 3(a) and 3(b). The RP of
large spin/orbit coupling, which is small for the netic excitation would require, due to spin conservation, a that the $2M$ and the 201 meV excitation have different ma-

d next to an existing singlet state ($S$). The intermediate state is a many-body state consisting of multiple determinants, including $\langle S \rangle$ and $\langle S \rangle$ for both polarizations. This shows that these features are weaker at higher $h\nu$. Open blue circles and open green circles are $\langle a \rangle$ and $\langle c \rangle$ polarizations of $2M$ from Ref. [22], respectively, however corrected for the appropriate dielectric function [34]. The data all are taken at 20 K.

These excitations is shown in Figs. 3(a) and 3(b), which identify the involved Raman matrix elements. The 201 meV resonates at $\sim 3.7$ eV. This is in contrast to the RP of the 2M which is in resonance at $\sim 2.5$ eV and is off-resonance at $\sim 3.7$ eV for both polarizations. This shows that the 2M and the 201 meV excitation have different matrix elements. Furthermore, a novel unconventional magnetic excitation would require, due to spin conservation, a large spin/orbit coupling, which is small for the Cu$_3$Au$^0$ ion [30]. On the other hand, the RP of the multiphonon excitation is also very different compared to the RP of 201 meV excitation. The intensity of 140 meV gets weaker with increasing incident photon energy. Thus, the 201 meV feature is neither of magnetic nor of phonon origin.

The matrix element of the 201 meV excitation with a resonance at 3.7 eV can be well explained in a two-step pair-breaking process illustrated in Fig. 1(b). First, in the ladder next to an existing singlet state ($S$) of paired holes, $d^\uparrow L(S)d^\downarrow L(S)$, the $a$-polarized 3.7 eV photon creates a charge transfer, $d^\uparrow d^\downarrow L(T)$, along the $a$-direction, leading to an virtual intermediate state. (Here $T$ indicates triplet state, as 3.7 eV is typical energy for creation of a triplet state.) The intermediate state is a many-body state consisting of multiple determinants, including $d^\uparrow L(S)d^\downarrow L(S)$, $d^\uparrow d^\downarrow L(T)$, $d^\uparrow L(S)d^\downarrow L(T)$, and $d^\uparrow d^\downarrow L(S)$, and other permutations of the holes that are strongly mixed due to their nearly identical energy. Second, the intermediate state releases the energy via an interladder charge transfer, leaving one singlet on each ladder. The Raman shift of this pair-breaking process is $7\nu/4$ (ignoring Coulomb repulsion and interchain magnetic coupling), in reasonable agreement with current lore of the strength of intraladder magnetic coupling $J$ [cf. 2(b)]. The pair-breaking excitation is absent in undoped LCCO where no paired holes reside and should be $a$ polarized in the Raman experiment.

The observed resonant Raman process has strong implications to the electronic structure of the CDW$_L$ phase and more generally of the doped holes in the ladder. Specifically, it indicates that the CDW$_L$ phase consists of paired holes residing across the rungs. Furthermore, across the paired holes the antiferromagnetic spin configurations are antiphased, i.e. $\pi$-phase shifted, similar to those in the “stripe” phase of perovskite cuprates [31]. It is straightforward to verify that initial states without this phase shift would have different excitation energies by at least $J$. In the ladder, this $\pi$-phase shift is apparently driven by the kinetic energy of the holes, similar to the holon propagation in a pure 1D system, as only with the $\pi$-phase shift the paired holes can move freely along the ladder without causing magnetic frustration. In essence, the paired holes in the ladder can be regarded as a composite boson consisting of a pair of holons at low temperature.

Further insights can be obtained from the temperature dependence of the pair-breaking excitation and its contribution to the formation of the CDW$_L$. Figure 4(a) shows the Raman scattering spectra for selected temperatures. The reduction of the intensity at higher temperatures is apparent, as well as the constant energy of the pair-breaking excitation. This indicates strongly that the energy scale of the local pairing is much larger than that of the CDW$_L$ ordering, and is not temperature dependent. Interestingly, when comparing [cf. Fig. 4(b)] the intensity of the pair-breaking excitation with the CDW$_L$ order parameter, as measured by the integrated intensity of the RSXS CDW Bragg peak, both track each other very closely below $T_{CDW}$. This observation confirms the intimate dependence to the phase coherence of the CDW$_L$ order parameter and the $\pi$-phase shifted antiferromagnetic background. Furthermore, above $T_{CDW}$ where the CDW$_L$ order vanishes, but the intensity of the pair-breaking excitation remains finite and almost temperature independent. In consequence this has to be seen as evidence for the existence of disor-
dered paired hole states above $T_{CDW}$, and the short-range antiferromagnetic order with a $\pi$-phase shift [cf. 4(c)]

In this context it is important to outline the connection between the energy scales of the 201 meV excitation, the dc conductivity, the low-frequency dielectric measurements [11,12], and angle-resolved photoemission in 2D cuprates [21]. First, the dc conductivity and the low-frequency dielectric measurements show that the activation energy of SCO is $\sim 112$ meV ($\Delta_{CDW}^L$), which is half of the energy of the pair-breaking excitation ($\sim 2\Delta_{CDW}^L$). In some theories the energy of the paired hole state would be identical to the spin-gap energy [32]. However, here we find that the local pairing energy of the holes is 5 to 6 times higher than the spin gap. Moreover, it is also remarkable that the pair-breaking energy of 201 meV is about twice of
In conclusion, we have observed the pair-breaking excitation of holes at the 201 meV Raman shift along the rung of the ladder of SCO. Below $T_{\text{CDW}_L}$, the paired hole states are crystallized and responsible for formation of the CDW$_L$ long range order. Above $T_{\text{CDW}_L}$, the paired hole states exist as preformed states, however they are disordered. The CDW$_L$ and paired holes states occur in a unique environment of $\pi$-phase shifted antiferromagnetic spins similar to stripe phase in 2D cuprates. Our results open a possibility to study paired hole states in systems close to the instability towards the formation of the CDW$_L$ and to understand competing order parameters in correlated materials such as the high-temperature superconductors.

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[1] S. A. Kivelson et al., Rev. Mod. Phys. 75, 1201 (2003).
[2] E. Dagotto, J. Riera, and D. Scalapino, Phys. Rev. B 45, 5744 (1992).
[3] M. Sigrist, T. M. Rice, and F. C. Zhang, Phys. Rev. B 49, 12058 (1994).
[4] S. R. White, L. Affleck, and D. J. Scalapino, Phys. Rev. B 65, 165122 (2002).
[5] S. T. Carr and A. M. Tsvelik, Phys. Rev. B 65, 195121 (2002).
[6] S. Nishimoto, E. Jeckelmann, and D. J. Scalapino, Phys. Rev. B 66, 245109 (2002).
[7] K. Wohlfeld, A. M. Oles, and G. A. Sawatzky, Phys. Rev. B 75, 180501(R) (2007).
[8] E. M. McCarron, III et al., Mater. Res. Bull. 23, 1355 (1988).
[9] A. Rusydi et al., Phys. Rev. B 75, 104510 (2007).
[10] K. M. Kojima et al., J. Electron Spectrosc. Relat. Phenom. 117, 237 (2001).
[11] G. Blumberg et al., Science 297, 584 (2002).
[12] T. Vuletic et al., Phys. Rev. Lett. 90, 257002 (2003).
[13] M. Matsuda et al., Phys. Rev. B 54, 12 199 (1996).
[14] M. Braden et al., Phys. Rev. B 69, 244426 (2004); J. Etrillard et al., Physica (Amsterdam) 403C, 290 (2004).
[15] S. van Smaalen, Phys. Rev. B 67, 026101 (2003).
[16] M. v. Zimmermann et al., Phys. Rev. B 73, 115121 (2006).
[17] P. Abbamonte et al., Nature (London) 431, 1078 (2004).
[18] A. Rusydi et al., Phys. Rev. Lett. 97, 016403 (2006).
[19] A. Rusydi et al., Phys. Rev. Lett. 100, 036403 (2008).
[20] N. Nücker et al., Phys. Rev. B 62, 14 384 (2000).
[21] T. P. Devereaux and R. Hackl, Rev. Mod. Phys. 79, 175 (2007).
[22] A. Gozar et al., Phys. Rev. Lett. 87, 197202 (2001).
[23] H.-D. Chen et al., Phys. Rev. Lett. 89, 137004 (2002).
[24] Zlatko Tesanovic, Phys. Rev. Lett. 93, 217004 (2004).
[25] Y. Kohsaka et al., Science 315, 1380 (2007).
[26] See supplementary material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.105.026402 for detail samples and experimental method.
[27] Z. V. Popovic et al., Phys. Rev. B 62, 4963 (2000).
[28] R. S. Eccleston et al., Phys. Rev. Lett. 81, 1702 (1998).
[29] K. Kumagai et al., Phys. Rev. Lett. 78, 1992 (1997).
[30] A. Gozar et al., Phys. Rev. Lett. 93, 027001 (2004).
[31] J. M. Tranquada et al., Nature (London) 375, 561 (1995).
[32] G. Roux et al., Phys. Rev. B 72, 014523 (2005).
[33] F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).
[34] In the previous studies, all Raman spectra were corrected for the room temperature dielectric function only, which was assumed to be nearly temperature independent.