Observation of Two-Magnon Bound States in the Two-Leg Ladders of $(Ca, La)_{14}Cu_{24}O_{41}$

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Phonon-assisted two-magnon absorption is studied in the spin-1/2 two-leg ladders of $(Ca, La)_{14}Cu_{24}O_{41}$ for $E \parallel c$ (legs) and $E \parallel a$ (rungs). We verify the theoretically predicted existence of two-magnon singlet bound states, which give rise to peaks at $\approx$2140 and 2800 cm^{-1}. The two-magnon continuum is observed at $\approx$4000 cm^{-1}. Two different theoretical approaches (Jordan-Wigner fermions and perturbation theory) describe the data very well for $J_\parallel \approx 1020-1100$ cm^{-1}, $J_\parallel/J_\perp \approx 1-1.2$. At high energies, the magnetic contribution to $\sigma(\omega)$ is strikingly similar in the ladders and in the undoped high-T_c cuprates, which emphasizes the importance of strong quantum fluctuations in the latter.

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Low-dimensional quantum spin systems display a fascinating variety of low-energy excitations. Prominent examples are the fractional quantum states of one-dimensional (1D) chains, the $S = 1/2$ spinons, or the variety of bound states in gapped spin liquids such as, e.g., dimerized chains or even-leg ladders. In 2D, the magnetic excitations of the undoped high-T_c cuprates are usually discussed in more conventional terms, namely, renormalized spin waves. But these fail to describe the high-energy excitations probed by optical two-magnon-plus-phonon absorption [1]. The nature of incoherent high-energy excitations is currently under intensive debate [2–5].

In this light, the study of other cuprates with related topologies is very instructive. As far as high-energy excitations are concerned, the Cu_2O_3 two-leg ladders realized in $(Ca, La)_{14}Cu_{24}O_{41}$ [6] provide a bridge between 1D physics and the 2D CuO_2 layers. The Hamiltonian of antiferromagnetic $S = 1/2$ two-leg Heisenberg ladders reads

$$\mathcal{H} = \sum_i \{J_\parallel(\mathbf{S}_{1,i}\mathbf{S}_{1,i+1} + \mathbf{S}_{2,i}\mathbf{S}_{2,i+1}) + J_\perp \mathbf{S}_{1,i}\mathbf{S}_{2,i}\},$$

where $J_\perp$ and $J_\parallel$ denote the rung and leg couplings, respectively. For $J_\parallel = 0$ one can excite local rung singlets to rung triplets which become dispersive on finite $J_\parallel$. For $J_\perp = 0$ the $S = 1$ chain excitations decay into asymptotically free $S = 1/2$ spinons. An intuitive picture of the "magnons" (elementary triplets) for $J_\perp, J_\parallel \neq 0$ can be obtained from both limits: The elementary excitations are either dressed triplet excitations or pairs of bound spinons with a finite gap Δ as long as $J_\perp > 0$. In a gapped system it is particularly interesting whether bound states occur. Theoretical studies of two-leg ladders show that both singlet and triplet two-magnon bound states always exist [7–12]. However, in the $S = 1/2$ cuprates their experimental observation is a difficult task. Inelastic neutron scattering directly probes the spin gap, but cannot determine the high-energy excitations to a sufficient extent due to the large exchange interactions [13]. Magnetic Raman scattering [14] is restricted to $k = 0$ excitations, but for the relevant values of $J_\parallel/J_\perp$ the singlet bound state appears only for $k \neq 0$ (see Fig. 1 and Ref. [12]). In this case, optical spectroscopy is the appropriate tool [10]. Two-magnon-plus-phonon absorption [15] is able to probe magnetic excitations throughout the entire Brillouin zone (BZ), since the simultaneous excitation of a phonon takes care of momentum conservation.

In this Letter, we present optical conductivity data of $Ca_{14-x}La_xCu_{24}O_{41}$ and identify the two-magnon singlet bound state by *two* peaks reflecting Van Hove singularities in the density of states (DOS) of the bound state. Our theoretical results for bound states in the experimentally relevant parameter range are based on two different approaches, namely, Jordan-Wigner fermions [16] and perturbation expansion about the strong rung coupling limit

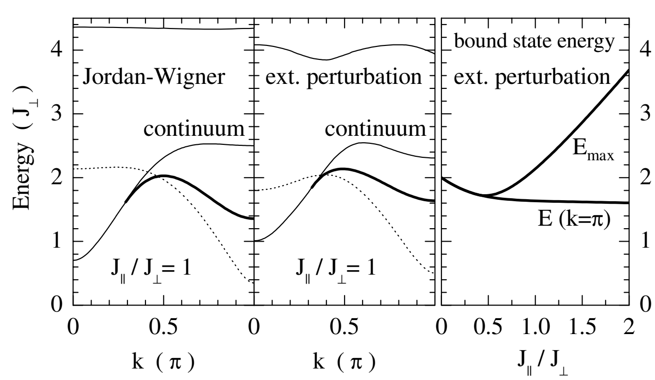

FIG. 1. One-magnon dispersion (dotted lines), band edges of the two-magnon continuum (thin solid lines), and bound singlet dispersion (thick lines) for $J_\parallel/J_\perp = 1$ obtained from Jordan-Wigner fermions (left) and extrapolated perturbation (middle panel). Right: Energy of the Van Hove singularities of the bound singlet at $k = \pi$ and at the dispersion maximum as a function of $J_\parallel/J_\perp$.

up to 13th order using unitary transformations [17,18]. Both yield an excellent description of the optical data for $J_\parallel \approx 1020-1100$ cm^{-1} and $J_\parallel/J_\perp \approx 1-1.2$.

Single crystals with $x = 5$ and 4 were grown by the traveling solvent floating zone method [19]. Their single phase structure and stoichiometry have been verified by x-ray, energy dispersive x-ray, and thermogravimetric analyses [19]. The La content x determines the average oxidation state of Cu. A nominally undoped sample is obtained for $x = 6$, which probably is beyond the La solubility limit [19]. Single phase crystals could be synthesized only for $x \leq 5$. The samples with $x = 5$ and 4 on average contain $n = 1/24$ and $2/24$ holes per Cu, respectively. But x-ray absorption data show that at least for $n \leq 4/24$ the holes are located within the chains [20], which agrees with previous considerations [21,22]. Thus we consider the ladders to be undoped which is supported by the similarity of our results for $x = 5$ and $x = 4$.

The optical conductivity $\sigma(\omega)$ was determined by collecting both transmission [23] and reflection data between 500 and 12 000 cm^{-1} on a Fourier spectrometer. In Fig. 2 we show $\sigma(\omega)$ at $T = 4$ K for polarization of the electrical field parallel to the legs, $E \parallel c$, and to the rungs, $E \parallel a$. Phonon and multiphonon absorption dominates $\sigma(\omega)$ below $\approx$1300 cm^{-1} (see inset). A steep increase of the electronic background, probably due to interband excitations of charge-transfer type, is observed above 6000 cm^{-1} for $E \parallel a$ (3000 cm^{-1} for $E \parallel c$). Our analysis focuses on the two peaks between 2000 and 3000 cm^{-1} and the broad feature at 4000 cm^{-1}. Also plotted in Fig. 2 is $\sigma(\omega)$ of $YBa_2Cu_3O_6$ [1], a typical example of the two-magnon-plus-phonon absorption spectrum of the undoped 2D cuprates [15]. This comparison gives a first motivation to interpret the peaks in $\sigma(\omega)$ of the ladders as magnetic excitations. Note that in the ladders both the exchange constants and the relevant Cu—O bond stretching phonon frequencies are comparable to those found in the 2D cuprates. Since the exchange in the chains is much smaller, $J_{\text{chain}} \approx -14$ cm^{-1} [22], their magnetic excitations do not contribute to $\sigma(\omega)$ in this frequency range. Reducing the La content x from 5 to 4 causes a slight *blueshift* of the magnetic peaks that is opposite to the *redshift* of the electronic background. We attribute the blueshift to an increase of the exchange constants caused by the reduction of the lattice parameters (Ca is smaller than La), and the redshift of the background to an increased hole density in the *chains*.

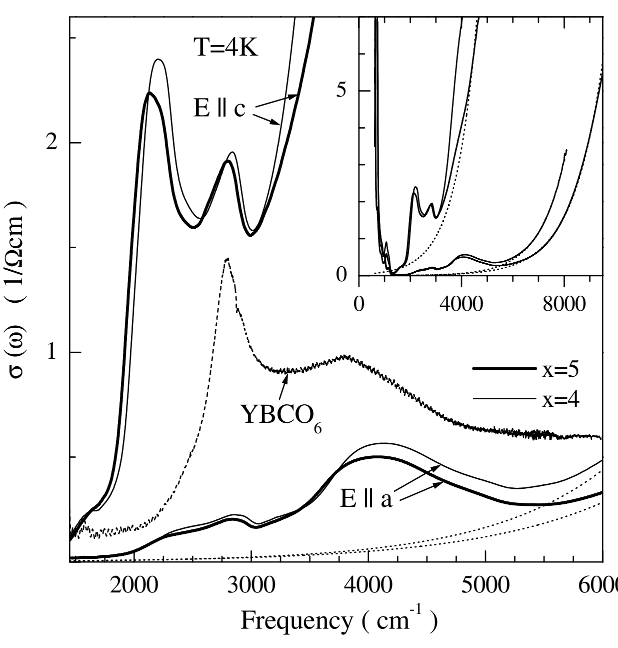

FIG. 2. Optical conductivity $\sigma(\omega)$ of $Ca_{14-x}La_xCu_{24}O_{41}$ (thick lines: $x = 5$; thin solid lines: $x = 4$) for $E \parallel c$ (legs) and $E \parallel a$ (rungs) at 4 K. Dashed lines: Bimagnon-plus-phonon absorption of $YBa_2Cu_3O_6$ is given for comparison [1]. Inset: $(Ca,La)_{14}Cu_{24}O_{41}$ data on a larger scale. Dotted lines: estimate of the electronic background (exponential fits for $\omega > 6500$ cm^{-1} for $E \parallel a$; $\omega > 4500$ cm^{-1} for $E \parallel c$).

Since spin is conserved, $\sigma(\omega)$ reflects $\Delta S = 0$ excitations, e.g., the excitation of two $S = 1$ magnons coupled to $S_{\text{tot}} = 0$. Direct excitation of two magnons is Raman active [14] but infrared forbidden due to symmetry. We can effectively avoid this selection rule by simultaneously exciting a Cu—O bond stretching phonon that breaks the symmetry [15]. Hence, the lowest order infrared-active magnetic absorption is a two-magnon-plus-phonon process. The low values of $\sigma(\omega) \lesssim 2\Omega^{-1}$ cm^{-1} indeed indicate a weak higher-order absorption process.

The two-magnon-plus-phonon contribution to $\sigma(\omega)$ was evaluated to first order in $J_\parallel$ by Jurecka and Brenig [10] in the case of strong rung coupling. They found a single sharp peak reflecting the singlet bound state. In order to gain quantitative control over the experimentally relevant regime of $J_\parallel/J_\perp \approx 1$ we use two different approaches to calculate the dynamical four-point spin correlation function, namely, Jordan-Wigner fermions and perturbation theory [25]. In the former, we make use of the Jordan-Wigner transformation [16] to rewrite the spins as fermions with a long-ranged phase factor. Expanding the phase factor yields new interaction terms between the fermions which we treat in random phase approximation. The second approach is perturbative in nature. It is performed by a continuous unitary transformation [17,18]. The one-particle energies and the two-particle bound state energies are extrapolated by standard techniques (Padé and Dlog-Padé); the spectral densities are computed by optimized perturbation [26]. Details will be given elsewhere. The magnon (elementary triplet) dispersion, the two-particle continuum, and the dispersion of the singlet bound state obtained for $J_\perp = J_\parallel$ are given in the two left panels of Fig. 1. The results of the two techniques agree well even though there is a quantitative discrepancy ($\lesseqgtr$10%–20%) in some energies (dispersion at $k = 0$ and π, bound state energy). The magnon dispersion of extrapolated perturbation (middle panel) reproduces previous results very well [27,28]. We focus on the singlet bound state which shows a considerable dip at $k = \pi$. This has gone unnoted thus far because it occurs only for $J_{\parallel}/J_{\perp} \gtrapprox 0.5$ (see right panel in Fig. 1 and Ref. [11]).

To compare with experiment we consider the effect of the phonons. The total spectral weight is obtained by taking into account a dependence of the exchange constants on the external electric field $\mathbf{E}$ and the displacements of O ions $\mathbf{u}$, $J_{\parallel,\perp} \equiv J_{\parallel,\perp}(\mathbf{E},\mathbf{u})$ [1,15]. The phonons modulate the intersite hopping and the on-site energies on both Cu and O sites. We expand $J(\mathbf{E},\mathbf{u})$ to order $d^2J/d\mathbf{u}d\mathbf{E}$ which entails the coupling of a photon to a phonon and two neighboring spins. This determines how to integrate the spin response in the BZ. Here, the weight factor is a mixture of $\sin^4(k/2)$ [29] and of a k-independent term. For simplicity, we consider only the dominant term $\sin^4(k/2)$ [30] and Einstein phonons with $\omega_{\mathrm{ph}} = 600\ \mathrm{cm}^{-1}$ as is common for the cuprates. Our findings depend only very weakly on the precise phonon energy.

In Fig. 3 we compare the theoretical results with the experimental data. For the former, an artificial broadening of $J_{\perp}/20$ is used. For the latter, the magnetic part of $\sigma(\omega)$ was obtained by subtracting the electronic background (dotted lines in Fig. 2). For $E \parallel a$, the background was determined unambiguously by an exponential fit for $\omega > 6500\ \mathrm{cm}^{-1}$. The $\sigma_a(\omega)$ curves for $x = 5$ and 4 nearly coincide after subtraction of the background. This corroborates the assumption that the ladders are undoped. For $E \parallel c$, the measurable range of transmission was limited to below $\approx 5000\ \mathrm{cm}^{-1}$ by the higher absorption, and the precise shape and spectral weight of the highest peak at $\approx 4000\ \mathrm{cm}^{-1}$ cannot be determined unambiguously.

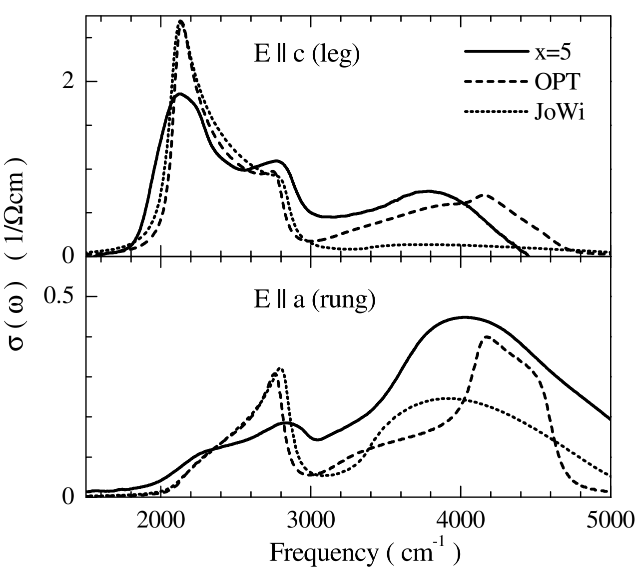

FIG. 3. Comparison of experiment (solid lines for $x = 5$) and theory for $J_{\perp} = J_{\parallel} = 1020\ \mathrm{cm}^{-1}$ (OPT: optimized perturbation) and $1100\ \mathrm{cm}^{-1}$ (JoWi: Jordan-Wigner fermions), with $\omega_{\mathrm{ph}} = 600\ \mathrm{cm}^{-1}$. The exponential fits of the electronic background have been subtracted from the experimental data (dotted lines in Fig. 2).

The two peaks at 2140 and 2800 cm^{-1} ($x = 5$) can be identified with the 1D Van Hove singularities in the DOS of the singlet bound state. The lower peak corresponds to the singlet energy at the BZ boundary, $E(k = \pi)$, the higher one to the maximum of the singlet dispersion $E_{\max}$ at about $k \approx \pi/2$ (see Fig. 1). These two energies determine the two free magnetic parameters $J_{\perp}$ and $J_{\parallel}$. The experimental $\sigma(\omega)$ is well described by both theories for $J_{\parallel} \approx 1020{-}1100\ \mathrm{cm}^{-1}$ and $J_{\parallel}/J_{\perp} \approx 1$ (see Fig. 3) providing an unambiguous identification of the experimental features. The quantitative analysis can be pushed a step further [31] based on the values of $E_{\max}$ and $E(k = \pi)$ computed by extrapolated perturbation (right panel of Fig. 1). The strong dependence of $E_{\max}$ on $J_{\parallel}/J_{\perp}$ allows one to pinpoint $J_{\parallel}$ and $J_{\perp}$, yielding the same value for $J_{\parallel} \approx 1080\ \mathrm{cm}^{-1}$ and a slightly larger ratio of $J_{\parallel}/J_{\perp} \approx 1.15$. Our interpretation of the experimental features is confirmed by the good agreement between theory and experiment concerning the line shape of the bound states. Excellent justification for this interpretation is also provided by the selection rule stemming from reflection symmetry about the a axis (RSa). Both theories show that the bound singlet at $k = \pi$ is *even* under RSa. But the excitations at $k = \pi$ are *odd* under RSa for $E \parallel a$ and *even* for $E \parallel c$. Thus, the weight of the bound state varies as $(k - \pi)^2$ for $E \parallel a$, whereas it is prevailing for $E \parallel c$. This explains the low spectral weight of the lower peak for $E \parallel a$. It is reduced to a weak shoulder.

Shortcomings of the theory are the overestimation of the spectral weight of the 2800 cm^{-1} peak for $E \parallel a$ and that the onset of $\sigma(\omega)$ around 2000 cm^{-1} is too sharp. However, the agreement is better than one may have expected since we neglected both the frustrating coupling between neighboring ladders and the ring exchange. A finite interladder coupling will produce a dispersion of the bound state along k_a and thereby broaden the features in $\sigma(\omega)$, which can explain a smearing out of the onset at 2000 cm^{-1}.

Without the ring exchange, the analysis of experimental data of various other techniques suggested a larger ratio $J_{\parallel}/J_{\perp} \gtrapprox 1.5$ (for a detailed discussion, see Ref. [27]). One finds a one-magnon gap of $\Delta \approx 280\ \mathrm{cm}^{-1}$ and a dispersion extending up to $\approx 1550\ \mathrm{cm}^{-1}$ [13]. For $J_{\parallel}/J_{\perp} = 1$ the dispersion extends from $\Delta \approx 0.5J_{\perp}$ up to $\approx 2J_{\parallel}$ (see Fig. 1). One obvious way [32] to reduce Δ with respect to the maximum is to increase the ratio $J_{\parallel}/J_{\perp}$, in this case to $\gtrapprox 1.5$. Such a large value is difficult to reconcile with the microscopic parameters, in particular with the similar Cu—O bond lengths along the legs and the rung which has provoked a controversial discussion [27]. Our analysis shows that $J_{\parallel}/J_{\perp} > 1.2$ can be excluded. Recently, it was pointed out that the neutron data are also consistent with $J_{\parallel}/J_{\perp} \approx 1{-}1.1$ and $J_{\parallel} \approx 900\ \mathrm{cm}^{-1}$, if a ring exchange of $\approx 0.15J_{\parallel}$ is taken into account [13]. Considering the fact that the ring exchange will renormalize $J_{\parallel}$ and $J_{\perp}$, this is in perfect agreement with our findings.

Finally, we address the broad peak at about 4000 cm^{-1} which is identified unambiguously as the two-magnon continuum by comparison with the theoretical results. The position, spectral weight, and shape of this ladder feature bears a striking similarity with the high-energy band observed in the undoped 2D cuprates (see Fig. 2). The 2D case does not show a truly bound state, the sharp peak at 2800 cm^{-1} in $\sigma(\omega)$ of $YBa_2Cu_3O_6$ is caused by a resonance, an *almost* bound state lying within the continuum [15]. This main peak is well described in terms of two-magnon-plus-phonon absorption, but the high-energy peak at 3800 cm^{-1} is absent in spin-wave theory [1]. Note that this discrepancy is particular for the 2D $S = 1/2$ case; the high-energy excitations are absent in the comparable $S = 1$ system La_2NiO_4 (Refs. [15,33]). In the cuprates, the magnetic origin of both peaks has been confirmed by absorption and Raman measurements under high pressure [34]. It has been suggested [1] that the high-energy weight in 2D $S = 1/2$ compounds is due to strong quantum fluctuations that go *beyond* spin-wave theory. Lorenzana *et al.* [35] argued that ring exchange increases the spectral weight at high energies. The intriguing similarity of the two-particle continuum of the $S = 1/2$ quasi-1D ladder $(Ca, La)_{14}Cu_{24}O_{41}$ with the 3800 cm^{-1} peak of $YBa_2Cu_3O_6$ strongly indicates that the high-energy spectral weight is indeed a signature of strong quantum fluctuations in this compound. The high-energy magnetic excitations in both systems are very well characterized as strongly quantum fluctuating and do *not* reflect the presence or absence of long-range order. This close resemblance between the experimental data of the quasi-1D and the 2D cuprates presented here is particularly interesting since the possible relevance of 1D physics such as spin-charge separation or the concept of spinons is one of the key issues in high-T_c superconductivity.

In conclusion, the existence of the singlet bound state and of the two-particle continuum was demonstrated experimentally in the optical conductivity of the $S = 1/2$ two-leg ladder $(Ca, La)_{14}Cu_{24}O_{41}$. By two independent theoretical approaches we confirmed that the two sharp peaks plus the important broad continuum seen in experiment are the unambiguous signature of a 1D dispersive bound singlet with strong incoherent quantum fluctuations. The experimental spectral weight distribution reflects the theoretical selection rules perfectly. Quantitative analysis yields $J_\parallel \approx 1020$–$1100\ \mathrm{cm}^{-1}$ and $J_\parallel/J_\perp \approx 1$–$1.2$. Our findings indicate that the similar experimental results for the high-energy excitations of the undoped high-T_c materials are also due to strong quantum fluctuations.

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