Collective Magnetic Excitations in the Spin Ladder $Sr_{14}Cu_{24}O_{41}$ Measured Using High-Resolution Resonant Inelastic X-Ray Scattering

J. Schlappa,[1] T. Schmitt,[1,*] F. Vernay,[1] V. N. Strocov,[1] V. Ilakovac,[2,3] B. Thielemann,[4] H. M. Rønnow,[5] S. Vanishri,[6] A. Piazzalunga,[7] X. Wang,[5,†] L. Braicovich,[7] G. Ghiringhelli,[7] C. Marin,[6] J. Mesot,[4,5] B. Delley,[1] and L. Patthey[1]

[1]*Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[2]*Université Pierre et Marie Curie—CNRS UMR 7614, LCP-MR, Paris, France*
[3]*Université de Cergy-Pontoise, Département de Physique, F-95000 Cergy-Pontoise, France*
[4]*Laboratory for Neutron Scattering, ETH Zurich and Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland*
[5]*Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*
[6]*INAC/SPSMS/DRFMC, CEA-Grenoble, 17, rue des Martyrs, 38054 Grenoble Cedex 9, France*
[7]*CNR/INFM Coherentia/Soft—Dip. Fisica, Politecnico di Milano, p. Leonardo da Vinci 32, 20133 Milano, Italy*

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We investigate magnetic excitations in the spin-ladder compound $Sr_{14}Cu_{24}O_{41}$ using high-resolution Cu L_3 edge resonant inelastic x-ray scattering (RIXS). Our findings demonstrate that RIXS couples to two-triplon collective excitations. In contrast to inelastic neutron scattering, the RIXS cross section changes only moderately over the entire Brillouin zone, revealing high sensitivity also at small momentum transfers, allowing determination of the two-triplon energy gap as 100 ± 30 meV. Our results are backed by calculations within an effective Hubbard model for a finite-size cluster, and confirm that optical selection rules are obeyed for excitations from this spherically symmetric quantum spin-liquid ground state.

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Collective excitations in strongly correlated electron materials remain a pivotal challenge in contemporary solid state physics. It is widely debated whether magnetic excitations provide the pairing interaction in the high-temperature and unconventional superconductors [1,2]. From that perspective quantum spin systems attract considerable interest. While most such materials, e.g., the cuprate superconductors, exhibit enormous complexity, the two-leg spin ladder is easier to tract theoretically [3–6]. It consists of two parallel chains (legs) with a transverse (rung) exchange coupling. This system features a singlet ground state and dispersive triplet excitations (*triplons*), that both have quantum mechanical origin without any classical counterpart. To date, mainly two techniques have been established as momentum- and energy-resolved probes of the dispersion of collective excitations: angle-resolved photoelectron spectroscopy and inelastic neutron scattering (INS) for charge and spin degrees of freedom, respectively [7,8]. Because of the latest instrumental improvements [9,10], the energy scale of magnetic exchange is becoming readily accessible for resonant inelastic x-ray scattering (RIXS) [11–14], which is promising to give information on both, spin and charge degrees of freedom, and in addition is an element-specific technique. Furthermore, RIXS requires only small sample volumes (<0.1 mm^3). Recent RIXS studies were performed on long-range ordered magnets with spin-wave excitations [15–17].

In this Letter, we report a study of the two-leg quantum spin ladder $Sr_{14}Cu_{24}O_{41}$ [18,19] by means of momentum-resolved high-resolution RIXS at the Cu L_3 edge. Given that Cu L_3 scattering experiments have been already shown to contain valuable information about the charge degrees of freedom [20], an outstanding question we would like to address here is: how can RIXS provide information on magnetic excitations from a quantum ground state. In the ladder system of $Sr_{14}Cu_{24}O_{41}$ no symmetry breaking occurs—neither in spin- nor in real-space—in contrast to, e.g., a magnetically ordered state, where both symmetries are broken and the direction of the ordered moments dictates the quantization axis for spin excitations. Symmetry breaking has drastic effects on the observed magnetic excitations in RIXS spectra as discussed in a recent publication [21]. In the present study we find well-defined excitations, which unambiguously match the predicted dispersion for the two-triplon spectrum [22]. Backed by a numerical Hubbard model investigation, we thereby confirm that the optical selection rules are obeyed for quantum ground states with no broken symmetry. While the INS cross section is inherently small around the Brillouin zone (BZ) center (small momentum transfers) [22,23], the observed RIXS signal is found to be intense all over the BZ, allowing us to determine directly the two-triplon energy gap in $Sr_{14}Cu_{24}O_{41}$ at zero momentum transfer as 100 ± 30 meV.

RIXS experiments were performed at the Advanced Resonant Spectroscopies (ADRESS) beamline [10], at the Swiss Light Source (SLS), Paul Scherrer Institut, using the Super Advanced X-ray Emission Spectrometer (SAXES) [9]. A flux of 10^{13} photons/sec/0.01% bandwidth was focused to a spot size below 6×80 μm^2 (vertical $\times$ horizontal). RIXS spectra were recorded in typically 1 h acquisition time, achieving a statistics of 50–200 photons (per energy channel of ~28 meV) at the peak maxima. The combined energy resolution was 120 meV at the Cu L_3 edge (~930 eV). The $Sr_{14}Cu_{24}O_{41}$ single crystal was grown with the traveling-solvent floating zone method. Samples were cleaved *ex situ*, producing a mirrorlike surface with ***b***-orientation. The sample was mounted with ***b***- and ***c***-direction in the scattering plane, as depicted in the sketch of the experimental geometry in Fig. 1. Two geometries were used: $\Psi = 90°$ and 130°. For the second, one can cover up to 90% of the BZ along the ladder-legs ($c_L = 3.93$ Å) at the Cu L_3 edge. Incident light was linearly polarized either out of the scattering plane ($\boldsymbol{\sigma}$-polarization, $E \parallel a$) or in the plane ($\boldsymbol{\pi}$-polarization, $E \perp a$). Despite the high photon flux we did not observe any evolution with time in the spectra, confirming that the system is not susceptible to beam damage over our experimental time, in contrast to, e.g., organic semiconductors [24].

Figure 1(a) shows an x-ray absorption spectrum (XAS) acquired in TFY mode with a photodiode. Cu L_3 RIXS spectra were measured at the incident photon energies indicated by lines *A*-*D*, and off resonance. Previous Cu *K* RIXS investigations reported on charge excitations in the energy range of 2–6 eV [25,26]. In Fig. 1(b) and in the whole present study we concentrate on the response below 1 eV. Off resonance, only weak elastic scattering occurs. In the resonant excitation region, two peaks arise, which sharpen with lower temperature as expected for correlated systems [Fig. 1(b)]. The peak around zero energy loss contains the elastic signal plus unresolved low-energy contributions from phonons and presumably magnetic excitations from the chains. The second peak occurs at finite energy loss in the range of the intraladder exchange coupling. Figure 1(c) displays a series of spectra as the incident photon energy is tuned through the resonance. Below resonance, spectra *A*-*C* show essentially smooth evolution, suggesting a simple universal coupling to this excitation. Above resonance, in spectrum *D*, the high-energy tail of the excitation appears enhanced, suggesting that above resonance the coupling becomes more complex, which upon further investigation could lead to additional information. For the remainder of this work, all measurements were taken at 15 K with the incident photon energy *C* and, if not mentioned otherwise, with σ-polarized light.

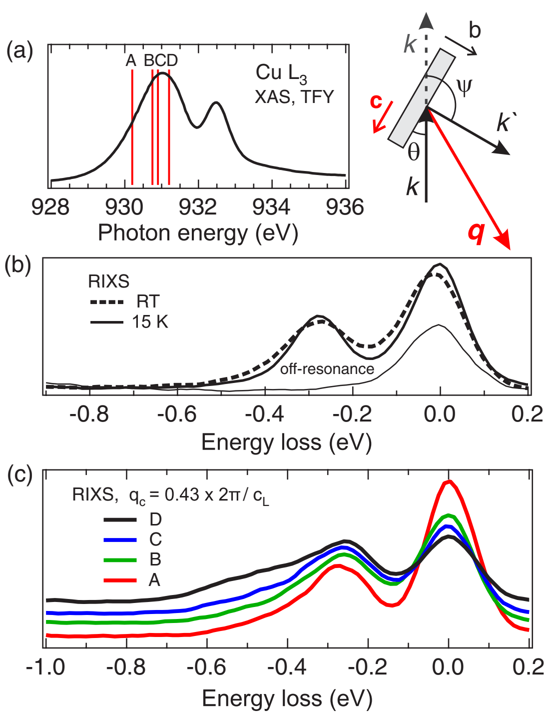

FIG. 1 (color online). Cu L_3 XAS and RIXS data from $Sr_{14}Cu_{24}O_{41}$: (a) XAS (left) measured in total fluorescence yield (TFY) mode at 15 K; Right: sketch of the experimental setup and definition of symbols: $\boldsymbol{k}$ ($\boldsymbol{k}'$) wave vector of the incident (scattered) light, θ incidence angle, Ψ scattering angle, $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$ transferred momentum; (b) RIXS for energy *C*—at 15 K (solid line) and room temperature (RT) (dashed line)—and off-resonance; (c) RIXS energy series (*A*-*D*) at 15 K. All data were measured at $\Psi = 90°$, $\theta = 20°$ using σ-polarized light.

To understand the local vs collective character of this excitation we studied its dispersion upon q_c, momentum transfer along the leg-direction. Since $Sr_{14}Cu_{24}O_{41}$ is a low-dimensional system, where we expect no dispersion along ***b***, we could map out q_c by simply rotating the sample and varying θ. RIXS data for different q_c transfer are presented in Fig. 2. The raw spectra were normalized with acquisition time and a geometry-dependent factor accounting for variations in scattering volume [27]. Data for $|q_c| < 0.21 \times 2\pi/c_L$ were obtained at $\Psi = 90°$ (black) and for higher momentum transfer at 130° (gray). All spectra show the same pronounced magnetic mode as in Fig. 1, which disperses strongly across the BZ revealing its collective character [28].

Each spectrum was fitted by two Gaussians. The first, representing the elastic contribution was subtracted to yield the RIXS intensity map versus momentum and energy transfer shown in Fig. 3(a). From the second Gaussian, we extracted the center of mass of the magnetic

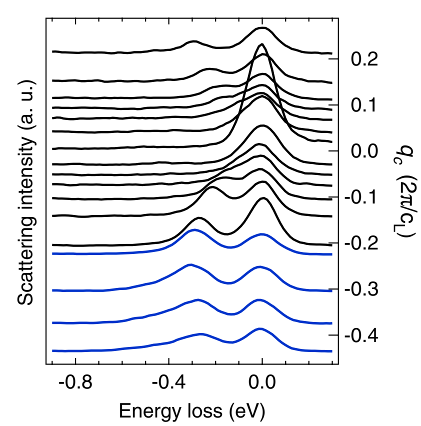

FIG. 2 (color online). Dispersion of magnetic excitations in Cu L_3 RIXS: black (blue) corresponds to $\Psi = 90°$ (130°).

excitation as a function of momentum transfer, also shown in Fig. 3(a). The excitation is seen to disperse symmetrically around the BZ center ($q_c = 0$), where it also reaches its minimum. With larger $|q_c|$ it moves first towards a maximum of 320 meV close to $q_c = 0.3 \times 2\pi/c_L$, beyond which it decreases slightly towards the BZ edge. The width of the peak increases continuously from the BZ center to the edge.

Comparing the extracted dispersion curve in Fig. 3(a) to the spectral-density calculations for multitriplon contributions by Schmidt and Uhrig [22], reveals that the dominating magnetic mode observed in our Cu L_3 RIXS data matches very closely the lower boundary of the two-triplon continuum (solid black line), which disperses in complete antiphase with the single-triplon excitation (dashed red line). We therefore unambiguously assign the magnetic excitation in the RIXS spectra to the two-triplon channel. The two-triplon channel has been partially measured with INS from $La_4Sr_{10}Cu_{24}O_{41}$ [23]. However, while INS intensities are high in the region $q_c > 0.25$ and low for small momentum transfer, our RIXS data display roughly uniform intensity of the excitation throughout the BZ. In particular, we can track it to the BZ center, and determine directly the minimum gap for two-triplon excitations to

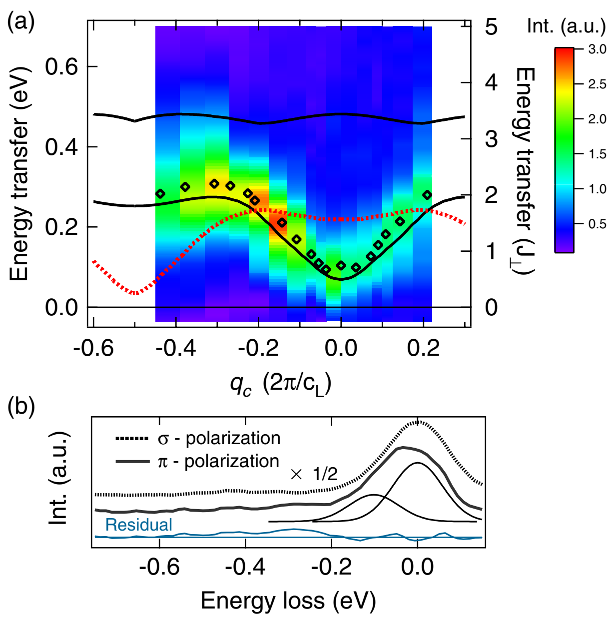

FIG. 3 (color online). (a) RIXS data as intensity map vs momentum and energy transfer after subtraction of the elastic signal. We overlay the extracted dispersion curve of the lower boundary of the two-triplon continuum with open black diamond symbols. For comparison we plot calculated one- (red dashed line) and two-triplon (black full lines) dispersion curves from *K*. Schmidt *et al.* [22]. The right axis is scaled in units of J along the rungs ($J_\perp$), extracted from the theoretical model below. (b) RIXS spectra measured close to the BZ center point for $q_c = -0.04 \times 2\pi/c_L$, using σ- and π-polarized light. The π-polarized spectrum is fitted by two Gaussians, the residual is represented by the thin blue line.

100 ± 30 meV. Values close to $q_c = 0$ ($q_c < 0.05 \times 2\pi/c_L$) were obtained from π-polarized data to suppress contribution from the elastic channel. Figure 3(b) shows a representative fit, revealing an additional weak residual between 200 and 600 meV, which represents scattering from the two-triplon continuum.

We now compare the assignment of the magnetic excitation to what can be expected on theoretical grounds. The simplest approach is to neglect spin-orbit coupling, in which case L and S remain good quantum numbers, and to use the electric dipole approximation by which only transitions with $\Delta L = \pm 1$ and $\Delta S = 0$ will be allowed. In the present system the elementary magnetic excitation (*triplon*) consists in promoting a spin-singlet into a triplet, which clearly leads to $\Delta S = 1$ and not to a dipole-allowed transition. Having a $\Delta S = 0$ excitation necessarily means exciting an even number of these triplons together, the leading process being thus a two-triplon excitation. Since this agrees with our experimental observation, we reach the important conclusion that the above-described simplest scenario for the RIXS process is valid. For instance, if spin-orbit coupling of the Cu $2p$ shell had been relevant, it would allow local spin flips.

We extend this analysis using as the minimal model an effective Hubbard Hamiltonian, downfolded from a multiband Hubbard model [29,30]:

$$\mathcal{H} = \sum_{\langle i,j\rangle,\sigma} t_{ij}(d^\dagger_{i,\sigma} d_{j,\sigma} + \text{H.c.}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow} \qquad (1)$$

with $n_{i,\sigma} = d^\dagger_{i,\sigma} d_{i,\sigma}$. The hopping parameters in (1) are taken as $t_\perp = 0.35$ eV, $t_\parallel = 0.30$ eV while the on-site Coulomb repulsion is $U = 3.5$ eV, corresponding to $J_\perp \sim 140$ meV, which is close to the experimental value measured with INS or Raman scattering [22,23,31]. According to results of XAS, the concentration of holes in the ladder system is smaller than 10% [32]. We consider therefore that we are at half-filling (1 hole per Cu-site). In this picture the experiment can be considered as a coherent process of two optical transitions: promoting a Cu $2p$ electron to the $3d$ band and the subsequent recombination of the $2p$ hole with an electron from the $3d$ band. In essence, this can be rationalized as having a nonmagnetic impurity in the $3d$ band for the intermediate state. In the lower energy-loss region, this will naturally lead to magnetic rearrangements and finite overlaps with final excited states in different symmetry sectors than the ground-state. The Hamiltonian in Eq. (1) was fully diagonalized for an eight-site cluster. The eigenvalues and eigenvectors were obtained for the ground and final states at half-filling (8 particles) and for the intermediate states (7 particles). Spectral intensities were calculated using the Kramers-Heisenberg formula [11] with the optical transition operator expressed in the hole representation: $\mathcal{O}_{\boldsymbol{k}} = \sum_{j,\sigma} p^\dagger_{j,\sigma} d_{j,\sigma} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_j}$, d removing a hole in the $3d$ band and $p^\dagger$ creating one in the Cu $2p$ shell. The presence of a Cu $2p$ core-hole in the intermediate states was accounted for by

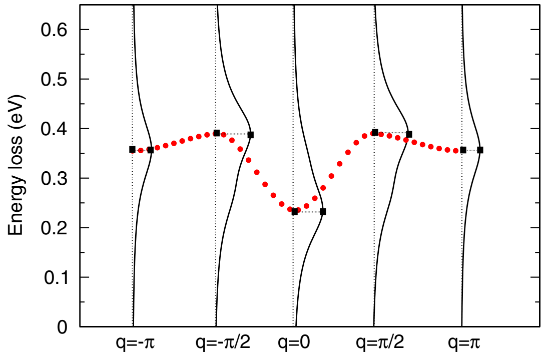

FIG. 4 (color online). Cu L_3 RIXS simulation for an effective Hubbard model on an eight-site ladder cluster.

an on-site Coulomb interaction [33]. The calculated RIXS profiles for the accessible k points are displayed in Fig. 4. These spectra show a dispersive low-energy excitation of energy loss $\leq$400 meV. Comparison of the energy position in the simulated and the experimental data reveals an offset of ~100 meV between them, which can be ascribed to finite-size effects. Nevertheless, despite the finite cluster-size, the excitation disperses in qualitatively the same way as in the experiment. We therefore conclude that the observed mode in our RIXS data is indeed the above described process in the $\Delta S = 0$ channel, the main contribution being to create a two-triplon excitation in the ladder subsystem.

Our interpretation is inline with IR-, Raman-spectroscopy, INS, and spectral-density calculations from the cuprate ladders [22,23,31,34–36]. On the other hand, our results are clearly in contrast to RIXS cross-sections for higher-dimensional antiferromagnets, where symmetry breaking occurs [21]. A recent three-dimensional example is NiO, where the main contribution to the magnetic RIXS signal was found in the local spin-flip channel [15].

To summarize, we have investigated the spin-ladder compound $Sr_{14}Cu_{24}O_{41}$ using RIXS at the Cu L_3 edge. Our data reveal that the dominant signal is due to two-triplon excitations. The finite RIXS cross section across the BZ allows us to trace these collective modes down to zero momentum transfer, and thereby determine the two-triplon spin gap to be 100 ± 30 meV. We show the observation of two triplons to be consistent with treating the RIXS process using optical selection rules and an effective Hubbard model for a finite-size cluster. Our findings show that in addition to spin-wave precessions around long-range ordered moments [17], RIXS can be used to study magnetic excitations from a nonsymmetry broken quantum ground state, and as such is emerging as a powerful probe, complementary to INS with respect to accessible energy and momentum transfer.

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*thorsten.schmitt@psi.ch
†Present address: Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.

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