Collective spin excitations in a quantum spin ladder probed by high-resolution Resonant Inelastic X-ray Scattering

J. Schlappa,1 T. Schmitt,1,3 F. Vernay,1 V. N. Strocov,1 V. Ilakovac,2,3 B. Thielemann,4 H. M. Rønnow,5 Vanashri S.,6 A. Pizzalunga,7 X. Wang,5 L. Braicovich,7 G. Ghiringhelli,7 C. Marin,6 J. Mesot,4,5 B. Delley,1 and L. Patthey1

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/INFN 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 collective spin excitations from a quantum spin-liquid ground state. In contrast to Inelastic Neutron Scattering (INS), the RIXS cross section changes only moderately over the entire Brillouin Zone (BZ), revealing a high sensitivity also at small momentum transfers. The two-triplon energy gap is found to be $100\pm30$ meV. Our results are supported by calculations within an effective Hubbard model for a finite-size cluster.

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Collective excitations in strongly correlated electron materials remain a pivotal challenge in contemporary solid state physics. Magnetic excitations are heavily debated to 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, 4, 5, 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, 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 (ARPES) and inelastic neutron scattering (INS) for charge and spin degrees of freedom, respectively [7, 8]. Due to the latest instrumental improvements [9, 10], the energy scale of magnetic exchange is becoming readily accessible for resonant inelastic x-ray scattering (RIXS) [11, 12, 13, 14], which is promising to give information on both, spin and charge degrees of freedom, and in addition is a element-specific technique. Furthermore, RIXS requires only small sample volumes ($<0.1$ mm$^3$). Recent RIXS studies of magnetic systems focussed on spin excitations in long-range ordered magnets [15, 16, 17].

In this letter, we report our 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. One important question is how RIXS, which also couples to charge, can provide information on magnetic excitations from such a quantum ground state. We demonstrate unambiguously that this technique couples to purely quantum mechanical excitations from a singlet ground state. While the INS cross section is inherently low around the Brillouin zone (BZ) center (small momentum transfers) in a similar compound [20], the observed RIXS signal is found to be intense all over the BZ. A numerical investigation of a Hubbard model as well as the optical transition selection rules leads us to conclude that the response is due to two-triplon excitations. We demonstrate that in the case of a gapped spin liquid, RIXS is particularly sensitive to these excitations. We thus are in position to directly evaluate the two-triplon energy gap in Sr$_{14}$Cu$_{24}$O$_{41}$ at zero momentum transfer as $100 \pm 30$ meV.

RIXS experiments were performed at the Advanced Resonant Spectroscopies (ADRESS) beamline [10] at the Swiss Light Source (SLS), Paul Scherrer Institut, Switzerland, using the Super-Advanced X-ray Emission Spectrometer (SAXES) [3]. A flux of $10^{13}$ photons/sec/0.01% bandwidth was focused to a spot size below $8 \times 100$ μm (ν×H). RIXS spectra were recorded in typically 1 hour acquisition time, achieving a statistics of 50-200 photons in peak maxima. The combined energy resolution was 120 meV at the Cu $L_3$ edge ($\sim$930 eV). The Sr$_{14}$Cu$_{24}$O$_{41}$ single crystal was grown with the traveling-solvent floating zone method. Samples were cleaved ex-situ, producing a mirror-like surface with b-oration. The sample was mounted with b- and c-direction (leg-direction) in the scattering plane, as depicted in the sketch of the experimental geometry in Fig. 1. Two geometries were used with the angle between the incident ($k$) and scattered ($k'$) light being 90° (up-
per part) and 130° (lower part). With this setup one can cover at the Cu L$_3$-edge up to 90% of the BZ in Sr$_{14}$Cu$_{24}$O$_{41}$ (the lattice constant of the ladder system is $c_L = 3.93$ Å). Incident light was linearly polarized either out of the scattering plane ($\sigma$-polarization) or in the plane ($\pi$-polarization).

The left panel in Fig. 1 displays Cu L$_3$ RIXS spectra of Sr$_{14}$Cu$_{24}$O$_{41}$ measured at room temperature (RT) and at 15 K. Spectra were obtained with $\sigma$-polarized light at 20° grazing incidence in 90° geometry. The excitation energy was detuned by $\sim 0.2$ eV from the resonance maximum to reduce the elastic contribution, indicated in the x-ray absorption data (XAS) in the inset (acquired in TFY mode with a photodiode). Both RIXS spectra reveal two intense well-separated structures. One peak at zero energy loss consists of the elastic signal with unresolved low-energy contributions from phonons and presumably magnetic excitations of the chains. The second peak at final energy loss represents a low-energy excitation. The position at around 270 meV corresponds to the energy range of intra-ladder exchange coupling. Previous Cu K RIXS investigations reported on charge excitations in the energy range of 2-6 eV [21, 22]. The spectrum at RT is slightly broader than at 15 K, which is the expected temperature dependence of spin excitations.

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 around $a$. Momentum transfer dispersion was measured at 15 K using the same photon energy and polarization as in Fig. 1. RIXS data for different $q_c$ transfer are presented in Fig. 2. The upper panel displays raw spectra normalized with acquisition time and a geometry-dependent factor accounting for variations in scattering volume [23]. Spectra for $|q_c| < 0.21 \times 2\pi/c_L$ were obtained in 90° geometry (black) and for higher momentum transfer in 130° geometry (gray). All spectra reveal the same pronounced magnetic mode as in Fig. 1, dispersing strongly across the BZ [24].

The lower panel of Fig. 2 displays an intensity map of the RIXS data plotted vs. momentum and energy transfer. The elastic contribution has been subtracted, after fitting each experimental spectrum with two Gaussians. The magnetic excitation is seen here to disperse around the BZ center ($q_c = 0$), where it also reaches its minimum in energy loss. With larger $|q_c|$ it moves first towards higher energy losses and is then folding back close to $q_c = 0.3 \times 2\pi/c_L$ towards the BZ edge. The width increases slightly towards BZ edge.

This dispersing behavior reveals the collective character of the observed magnetic mode. Similar dispersion has been partially observed in INS from La$_4$Sr$_{10}$Cu$_{24}$O$_{41}$ [20]. Our dispersion curve revealed by the Cu L$_3$ RIXS data matches well with the two-triplon mode measured...
with INS, however, the observed intensity vs. momentum dependence is different. While INS intensities are high in the region $q_x > 0.25$ and low for small momentum transfer, our RIXS data reveals uniform intensity of the excitation over the BZ. The magnetic excitation can be detected close to the BZ center, where it approaches a finite energy loss value.

Using the procedure described above, we extracted from our data the center of mass of the magnetic excitation for the different points in the BZ. The resulting dispersion curve is presented in upper graph of Fig. 3. Data points corresponding to spectra measured in $130^\circ$ geometry have been mirrored upon the BZ center. Values close to $q_x = 0$ ($q_x < 0.05 \times 2\pi/c_L$) were obtained from $\pi$-polarized data to suppress contribution from the elastic channel. We can follow for the observed energy gap the energy loss of $100 \pm 30$ meV and for the maximum loss value $320$ meV. The lower panel of Fig. 3 presents fit of a $\pi$-polarized spectrum (thick solid line). Interestingly, the residual reveals weak intensity in the energy range between -0.2 and -0.6 eV.

To assign the magnetic excitation which we observe in our RIXS data, we take a look at the electrical dipole transition selection rules. We confine our considerations to collective excitations and neglect in a first approximation the spin-orbit coupling [23]. As a consequence L and S remain good quantum numbers and in the electric dipole approximation 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. We simulate which kind of magnetic excitations will occur in the ladder system in the Cu $L_3$ RIXS process by confining our considerations to the optical selection rules. As a minimal model an effective Hubbard Hamiltonian downfolded from a multi-band Hubbard model is used [26, 27]:

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} (d_i^\dagger d_j + \text{h. c.}) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

with $n_{i,\sigma} = d_i^\dagger d_i$ and $d_i^\dagger$ the hopping parameters in (1) are taken as $t_{\perp} = 0.35$ eV, $t_{\parallel} = 0.3$ eV while the on-site Coulomb repulsion is $U = 3.5$ eV. According to results of XAS, the concentration of holes in the ladder system is smaller than 10% [28]. We consider therefore that we are at half-filling (1 hole per Cu-site). From the above parameters we extract $J_{\perp} \sim 140$ meV, which is close to the experimental value measured with INS or Raman scattering [20, 29, 30]. In this picture the experiment can be considered as a coherent process of two optical transitions: promoting a Cu-2$p$ electron to the 3$d$-band and the recombination of the 2p-hole with an electron from the 3$d$ band. In essence, this can be rationalized as having a non-magnetic impurity in the 3$d$-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 8-site cluster and 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: $O_k = \sum_{j,\sigma} p_j^\dagger d_j e^{i k \cdot r_j}$, $d$ creating one in the Cu-2$p$ shell. Presence of a Cu-2$p$ core-hole in the intermediate states was accounted for by an on-site Coulomb interaction [31]. 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 $\sim 100$ 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 in the $\Delta S = 0$
channel and that the main contributions are two-triplon excitations in the ladder subsystem. The observed energy gap of 100 ± 30 meV in our our experimental data is attributed to the two-triplon energy gap.

These results are in contrast to RIXS observations from a 3-dimensional antiferromagnet NiO, where it was found that the main contribution to magnetic excitations are in the local spin-flip channel 13. On the other hand, our interpretation is inline with observations of low-energy excitation spectra from IR spectroscopy, INS and with spectral-density calculations on cuprate ladder-systems 20, 29, 32, 33, 34. Comparing the data with spectral density calculations for multi-triplon contributions by Schmidt and Uhrig 29 indicates that the dominating magnetic mode observed in our Cu $L_3$ RIXS data corresponds to the lower boundary of the two-triplon continuum.

To summarize, we have investigated the two-leg spin ladder compound Sr$_{14}$Cu$_{24}$O$_{41}$ using RIXS at the Cu $L_3$ edge. Our data reveal that the dominant signal in the RIXS process in this system is due to two-triplon excitations. Therefore we prove that this technique is able to probe purely quantum mechanical fluctuations, in addition to spin-wave excitations in a long-range ordered magnet. The experimental results are supported by simulations based on optical selection rules and an effective Hubbard model for a finite-size cluster. Uniform RIXS cross-section over the BZ allows us to trace these collective modes down to zero momentum transfer, where a two-triplon spin gap of 100 ± 30 meV is found. We demonstrate that RIXS is emerging as a powerful probe of magnetic excitations, complementary to INS with respect to accessible energy and momentum transfer.

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* Electronic address: thorsten.schmitt@psi.ch

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