Experimental report

20/02/2018

Proposal: 4-05-676 **Council:** 10/2016

Title: Magnetic dimerization in the new frustrated spin ladder Li2O(CuSO4)2

Research area: Physics

This proposal is a new proposal

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Samples: Li2O(CuSO4)2

Instrument	Requested days	Allocated days	From	To
IN4	6	5	24/02/2017	01/03/2017

Abstract:

Through this proposal, we want to study the magnetic excitations in a very rare realization of a frustrated two-leg ladder system Li2O(CuSO4)2 using inelastic neutron scattering. This compound displays an intriguing phase transition under the form of a weak and progressive distortion of the high-temperature tetragonal crystal at about 140 K, possibly driven by magnetic frustration. State-of-the-art density functional calculations reveal that this structural distortion is accompanied by a strong magnetic dimerization. Our main purpose is to assess the validity of this scenario by probing the temperature-dependent magnetic excitations in the compound: (i) through a measure of the evolution of the spin gap with the temperature across the phase transition and (ii) in the dimerized phase, through the extraction of the characteristic intradimer distance via constant energy transfer scan in wave vector Q. The experimental results will be confronted to other results obtained recently in infra-red spectroscopy and interpreted using exact diagonalization calculations.

TECHNICAL FORM

EXPERIMENT TITLE Magnetic dimerization in the new frustrated spin ladder $Li_2Cu_2O(SO_4)_2$ PROPOSAL NUMBER
(to be completed by ILL)

EXPERIMENTAL TEAM (names and affiliation)
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INSTRUMENT IN4

Abstract

The recently discovered $Li_2Cu_2O(SO_4)_2$ [1] appears as a very rare realization of a $S = 1/2$ two-leg ladder system, with a very peculiar frustrated geometry in its high-temperature tetragonal structure. X-ray diffraction measurements indicate that a tetragonal to triclinic structural phase transition takes place at $\sim T_c = 125$K [2]. Furthermore, Density Functional Theory (DFT) calculations show a strong magnetic dimerization associated to the triclinic distortion which partially lifts the geometric frustration [3]. Here we propose to measure the magnetic excitations in $Li_2Cu_2O(SO_4)_2$ using the time-of-flight spectrometer IN4 in order to get informations about the nature of the spin excitations in the system.

Report

The spin ladder compound $Li_2Cu_2O(SO_4)_2$ crystallizes in a tetragonal structure (Figure 1). The magnetic Cu^{+2} ions are localized in square planar environments grouped by two to form platelets. These platelets are connected one to each other at 90° through an oxygen atom. Moreover a sulphate group SO_4 creates a bridge between the copper in the platelets that point in the same direction. These environments form copper chains, well separated by lithium atoms. In this chain three principle interactions should occur, the near neighbour (NN) interaction between the copper in the same platelets $J_\perp$, the interplatelets interaction J and the longer ranged interaction through the SO_4 bridge J_2. These three magnetic couplings were calculated via DFT+U calculation (Broken symmetry formalism), funding the couplings J and J_2 antiferromagnetic and the intraplatelet coupling $J_\perp$ ferromagnetic. The frustration thus arises from competing NN and next near neighbour (NNN) interactions along the legs.
Temperature dependent magnetic susceptibility measurements show a behaviour typical for a 1D antiferromagnetic system, with a spin-singlet ground-state and a singlet-triplet spin-gap. In agreement with these results, powder neutron diffraction confirmed the absence of magnetic long-range order down to 2K, but also revealed the occurrence of a structural phase transition at about 125 K from the tetragonal to the triclinic symmetry. This transition is not accompanied by any volume discontinuity and only involves a very weak distortion in the structure. Combining experimental and theoretical approach, we demonstrate that this weak distortion involve a strong splitting in the interplatelets couplings, with a strong increase of one of the couplings along the legs. The triclinc phase can thus be described by a staggered $S = 1/2$ dimer structure, removing most of the magnetic frustration. Concomitantly with the structural transition, recent results obtained from infrared spectroscopy reveal an unusual softening of a mode measured for low temperature (10 K) at ~ 155 cm$^{-1} = 14.4$ meV that might no be attributed to a phonon mode and could be related to a magnetic excitation.

The present neutron scattering study was intended to investigate the magnetic excitations of the unconventional low dimensional spin system $Li_2Cu_2O(SO_4)_2$ in its low temperature phase (triclinic structure). Because of the quasi-1D nature of the system, any dispersive magnetic scattering is plausibly assumed to originate from the spin dynamics along the chain direction. We therefore performed neutron spectroscopic measurements on the thermal time-of-flight spectrometer IN4 to map the magnetic excitations of $Li_2Cu_2O(SO_4)_2$, employing a powder sample (6.8 g of $Li_2Cu_2O(SO_4)_2$) consisting of nonoriented single crystals. The powder sample was put in a flat plate holder ($4.0 \times 2.8 \times 0.2$ cm^3) made of aluminium and thermalized by a standard Orange cryostat. Spectra were recorded using neutrons with an incident energy $E_i = 31.5$ meV at different temperatures between $T = 1.5$ and 100 K for typical measuring times of 12h. Additionally, absorption corrections were applied taking into account the shape of the sample and the different absorption of the scattered neutrons depending on their angle and final energy. Moreover, a vanadium standard and an empty cell were measured to account for background and detector efficiency. The raw data have been corrected for background and neutron absorption and were normalised to vanadium employing the program package LAMP.

Figure 2 show the resulting $S(Q, E)$ as a function of energy transfer E (meV) and momentum transfer Q (Å^{-1}). Our data revels the emergence of an excitation at $Q \sim 2.0$ Å^{-1} and $E \sim 14$ meV. Its intensity decreases continuously in temperature till $T = 100K$, where the excitation completely disappears. While the intensity of the phonon scattering increase with Q^2, the magnetic contributions decrease with Q and vanish progressively in T [4]. These results mean that the observed excitation is dominated by those of magnetic origin.

As we have a powder (we have not mono-crystal), we cannot see the dispersions, but only the density of magnetic states. In order to better describe the magnetic excitation, we cut at fixed $Q = 2.0A^1$ the dynamic structure factor $S(Q, E)$ (Figure 3). The result shows a first broad peak in scattering intensity for an energy transfer $E = 11$ meV, corresponding to the predicted spin-gap energy $E = 11.6$ meV, extracting from the susceptibility by fitting the low-temperature pattern with $\chi(T) = \frac{A}{\sqrt{T}} \exp\left\{-\frac{\Delta}{k_B T}\right\}$. The energy of the second peak ($E = 14.7$ meV) corresponds to those of the unusual peak seen in the IR spectroscopy, which confirms that what we see should be a magnetic excitation.

In order to explain the excitations observed experimentally in the low-temperature range, we are solving a spin Hamiltonian parametrized ab-initio (DFT) implementing a perturbative approach to quantitatively calculate spectral densities of the excited (magnetic) states.

References: [1] Sun M., Rousse G., Abakumov A.M., Saubanre M., Doublet M.-L., Rodrguez-Carvajal J., VaN Tendeloo G. et Tarascon J.-Li2cu2o(so4)2: a possible electrode for sustainable li-based batteries showing a 4.7 v redox ac- tivity vs li+/li0, M., Chem. Mater., 27, 30773087 (2015); [2] G. Rousse, J. Rodrguez-Carvajal, C. Giacobbe, M. Sun, O. Vaccarelli, and G. Radtke, Low-temperature structural transition in the quasi-one-dimensional spin-1/2 compound Li2Cu2O(SO4)2, Phys. Rev. B, vol. 95, p. 144103, (2017); [3] O. Vaccarelli, G. Rousse, A. Saul, and G. Radtke, Magnetic dimerization in the frustrated spin ladder Li2Cu2O(SO4)2 , Phys. Rev. B, vol. 96, p. 180406, (2017); [4] H. F. Fong, B. Keimer, P. W. Anderson, D. Reznik, F. Dogan, and I. A. Aksay, Phonon and magnetic neutron scattering at 41 mev in yba2 cu3 o7 , Phys. Rev. Lett., vol. 75, pp. 316319, (1995).

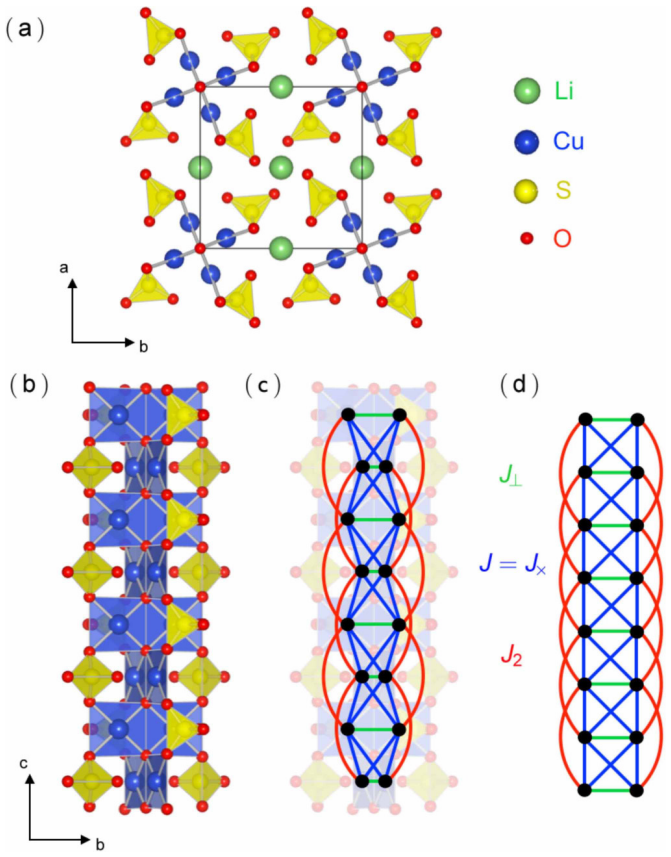

Figure 1: (a) Tetragonal crystal structure of $Li_2Cu_2O(SO_4)_2$ at room temperature. Cu are in blue, O in red, S in yellow, and Li in green. (b) Detail of the atomic structure of the chains running along the c axis. (c) Magnetic model deduced from the atomic structure, with the three dominant interactions along the chain: $J_\perp$ in green, $J = J_\times$ in blue, and J_2 in red. (d) Topologically equivalent frustrated two-leg spin ladder. [2]

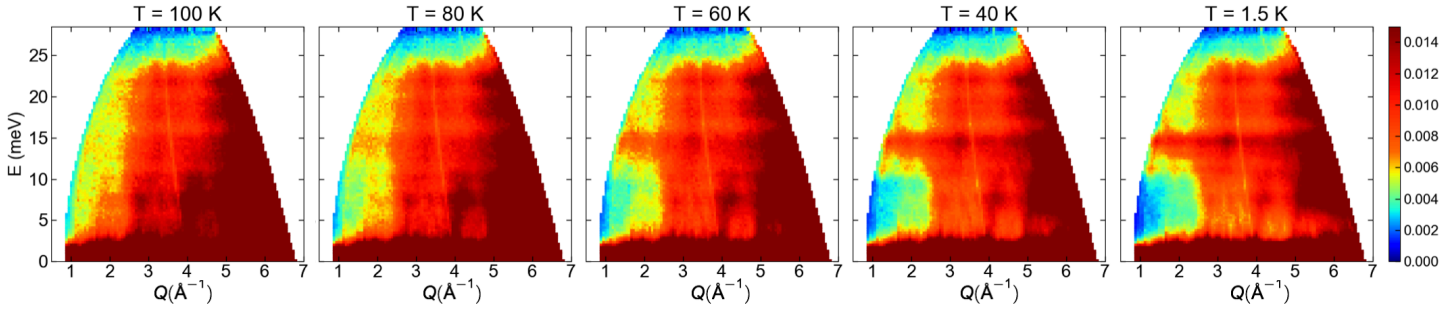

Figure 2: Measured $S(Q, E)$ plots for $Li_2Cu_2O(SO_4)_2$ at various temperatures T.

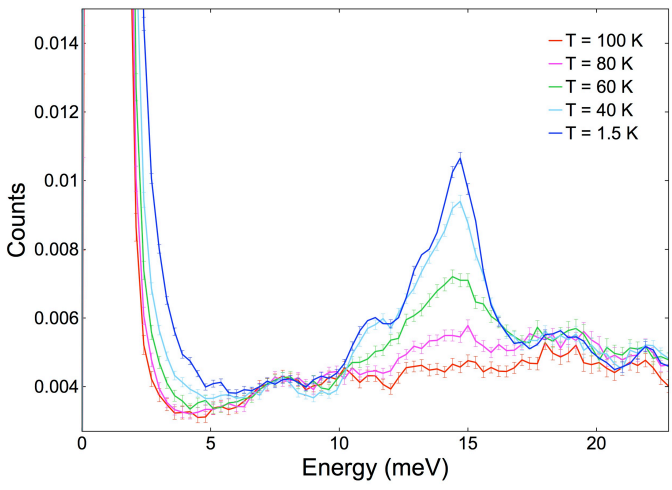

Figure 3: $S(Q, E)$ from Fig. 2 at fixed $Q = 2.0$ A^{-1}.