Eur. Phys. J. B **7**, 519–522 (1999)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Rapid Note

Magnetic excitations in the quantum spin system $KCuCl_3$

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Received: 6 August 1998 / Revised: 18 November 1998 / Accepted: 9 December 1998

Abstract. An inelastic neutron scattering study of the magnetic properties in the spin 1/2 double chain insulator $KCuCl_3$ is presented. Above a spin gap of $\sim$ 2.6 meV well-defined excitations are observed which are dispersive in all directions of reciprocal space. Both the energy and the spectral weight of the excitations can be quantitatively described by a model based on a singlet nonmagnetic ground state and dispersive singlet-triplet modes. The relevant feature in the model description are weakly coupled dimers. Confirmation of the triplet nature of the excitations and of the robustness of the theoretical approach is provided by the observed three-fold splitting of the modes in a magnetic field. The information deduced from the measurements is discussed and compared to earlier works on the subject.

PACS. 75.30.Et Exchange and superexchange interactions – 75.10.Jm Quantized spin models – 78.70.Nx Neutron inelastic scattering

1 Introduction

Recently considerable efforts, both experimentally and theoretically, have been devoted to quantum spin systems. Following Haldane's conjecture [1] that integer-spin antiferromagnetic Heisenberg chains (AFHC) have a spin gap, experiments were performed to verify this prediction [2,3], and to obtain the complete excitation spectrum in spin-1 AFHC [4]. These exciting results led to increased efforts to describe end explore the nature of the ground state and the excitations in other low-dimensional systems where quantum effects lead to spin-gaps, such as spin-Peierls systems [5], isolated dimers [6], alternating chains [7], and even-leg ladders (for a review, see [8]). In the study of these compounds, inelastic neutron scattering turned out to be the experimental method of choice. While magnetic susceptibility, nuclear magnetic resonance (NMR), and electron-spin resonance (ESR) experiments give important information on the spin gap, neutron scattering also explores the magnetic excitations above the gap, which allows to determine the dominant magnetic exchange couplings; without this knowledge, one can only speculate whether the material is a chain, a ladder, or a different type of quantum spin system.

Susceptibility [9] and ESR [10] experiments on $KCuCl_3$ led to the conjecture that this compound is such a spin 1/2 two-leg ladder material, exhibiting a nonmagnetic quantum ground state with a spin gap. Support in this sense is given by the arrangement of the magnetic Cu^{2+} ions, which are disposed along double chains. The susceptibility measurements were well-explained by quantum Monte-Carlo calculations with strong rung coupling between the double chains [11]. In recent neutron scattering experiments, the existence of dispersive modes along the chains as well as in one direction perpendicular to chains were observed [12], indicating that the coupling between the ladders is not negligible, and that the magnetism has at least two-dimensional character. However, due to the lack of a complete experimental and theoretical characterization of $KCuCl_3$, the question about the nature of the ground state and the dominant exchange couplings was not clearly solved.

In this work we present the first comprehensive study of the magnetic excitations spectrum in $KCuCl_3$. Our experiments reveal that the modes above the spin excitation gap are dispersive in all directions of reciprocal space, *i.e.* $KCuCl_3$ has to be considered as a three-dimensional magnetic system despite the lack of long-range magnetic order. We furthermore observe variations of the intensities which are in agreement with an antiferromagnetic dimerization of the spins along the rungs of the double chains. In the presence of an external field, we observe a three-fold splitting of the excitations, unambiguously characterizing

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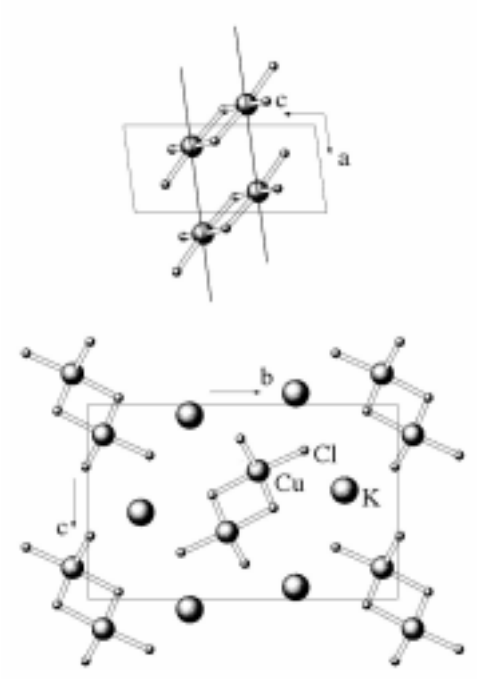

Fig. 1. Crystal structure of $KCuCl_3$ and arrangement of the Cu_2Cl_6 complexes. Top: projection on the *ac* plane, showing a Cu_2Cl_6 double chain. Bottom: projection on the *bc* plane, showing the chemical unit cell.

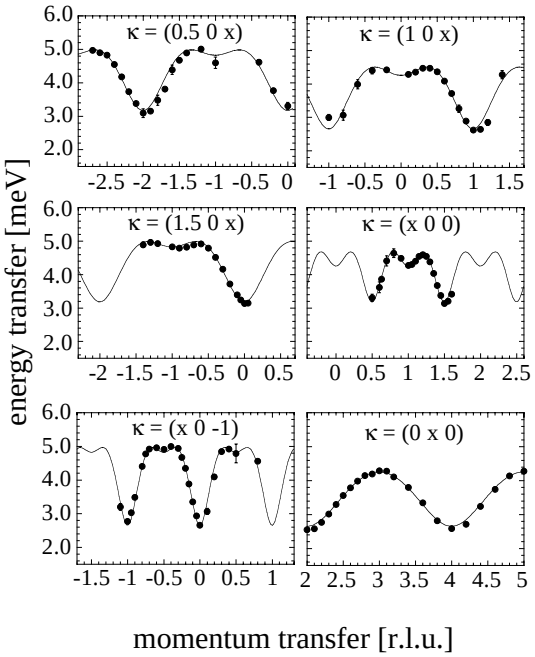

Fig. 2. Measured energy of the magnetic excitations in $KCuCl_3$ at $T = 5$ K (IN8). The momentum transfer $\hbar\kappa$ is given in chemical reciprocal lattice units, the lines correspond to the model calculation.

the triplet nature of the modes above the gap. A theoretical analysis based on a singlet dimer ground state and singlet-triplet dimer excitations accounts for the nonmagnetic ground state, for the spin excitation gap and for the observed field splitting. Weak three-dimensional effective exchange couplings between the dimers are shown to adequately describe the dispersion relation and the spectral weight of the modes above the gap.

2 Experiment and data evaluation

$KCuCl_3$ crystallizes in the monoclinic space group $P2_1/c$, with lattice parameters $a = 4.029$ Å, $b = 13.785$ Å, $c = 8.735$ Å, $\beta = 97.3°$ [13]. The magnetic properties in this compound are given by the spin 1/2 Cu^{2+} Jahn-Teller ions, which are disposed in double chains along the a direction (Fig. 1). A projection on the *bc* plane shows that the double chains are centered at the edges and in the center of the unit cell, and arranged differently (Fig. 1). For the experiments we used a $KCuCl_3$ single crystal with length $l \sim 10$ mm and diameter $d \sim 7$ mm. The excitations were measured on the triple-axis spectrometers IN14, IN8 and IN3 at the high flux reactor of the Institute Laue-Langevin (ILL) in Grenoble, France. Some additional measurements were performed on the triple-axis spectrometer Drüchal at the new spallation neutron source SINQ at the Paul Scherrer Institute in Villigen, Switzerland. The dependence of the excitation energy and intensity on the momentum transfer κ is shown in Figures 2 and 3, respectively. For reasons of clarity, we avoided a zone scheme representation.

We observe a dispersive behaviour of the modes along all directions in reciprocal space, above a spin gap of the order 2.6 meV. Also, the dispersion relation is found to be commensurate with the chemical reciprocal lattice. The doubling of the period along the b^* and along the c^* directions is ascribed to a cell centered in the *bc* plane. This shows that there are three-dimensional magnetic exchange couplings, and that these exchange couplings connect different double chains (Fig. 1). We also observe a strong modulation of the intensity of the excitations, which in contrast to the energy bears no particular relationship with the chemical reciprocal lattice. This is a manifestation of the correlation between spins separated by an incommensurate distance with respect to the chemical lattice units. In particular, zeros of the intensity turn out to correspond to the destructive interference of spins antiferromagnetically coupled along the rungs of the double chains. This exchange coupling is thus expected to dominate the spin system. As we will demonstrate, a model based on weakly coupled dimers located at the rungs of the double chains accounts for the experimental observations.

We model the system with the isotropic spin 1/2 Heisenberg Hamiltonian

$$H = -\frac{1}{2} \sum_{i,j,\mu,\nu} J_{i\mu,j\nu} S_{i\mu} S_{j\nu} \qquad (1)$$

where i, j designate the dimers and $\mu = 1, 2$, $\nu = 1, 2$ the individual ions on the dimers i and j, respectively. The dimers are formed by two Cu^{2+} ions which are separated by $R_1 = 0.48a + 0.10b + 0.32c$ for dimers at the edges and $R_2 = 0.48a - 0.10b + 0.32c$ for dimers in the center

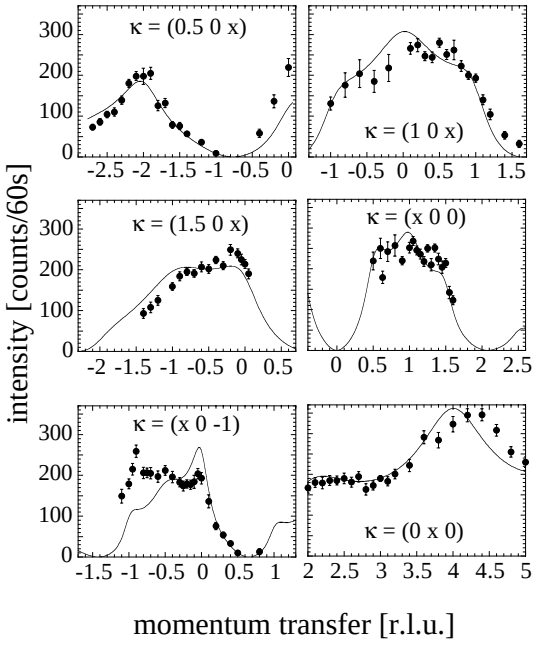

Fig. 3. Measured intensity of the magnetic excitations in $KCuCl_3$ at $T = 5$ K (IN8). The momentum transfer $\hbar\kappa$ is given in chemical reciprocal lattice units, the lines correspond to the model calculation.

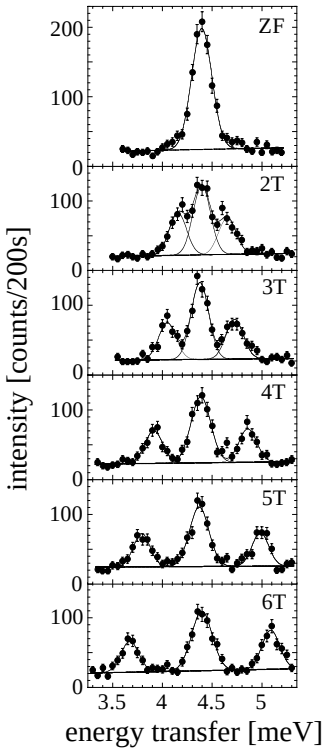

Fig. 4. Measured splitting of the magnetic excitations in $KCuCl_3$ at $T = 1.5$ K and $\kappa = (0.7\ 0\ 0)$ [r.l.u.] up to 6 T (IN14). The external field is perpendicular to the scattering plane.

of the bc plane of the unit cell. We only consider κ vectors which either lie in the a^*c^* plane, or are parallel to the b^* direction; therefore we do not distinguish between the two types of dimers: the projection of the dimers on the ac plane is identical, and $R = R_1 = R_2 = 0.48a + 0.32c$. The same holds for the projection of the dimers on the b direction, however the individual ions of the dimers are then interchanged, and $R = R_1 = -R_2 = 0.10b$.

The Hamiltonian in equation (1) is rewritten in the singlet-triplet basis introducing the total dimer spin $K_i = S_{i,1} + S_{i,2}$ and the Néel dimer spin $L_i = S_{i,1} - S_{i,2}$ [14], and assuming $J_{ij,11} = J_{ij,22} = J_{ij,\parallel}$ and $J_{ij,12} = J_{ij,21} = J_{ij,\times}$. It follows

$$H = H_0 + H_K + H_L \tag{2}$$

where

$$H_0 = -\frac{1}{4} J \sum_i K_i K_i - L_i L_i \tag{3}$$

$$H_K = -\frac{1}{4} \sum_{i,j} J^K_{ij} K_i K_j \tag{4}$$

$$H_L = -\frac{1}{4} \sum_{i,j} J^L_{ij} L_i L_j \tag{5}$$

with $J^K_{ij} = J_{ij,\parallel} + J_{ij,\times}$, and $J^L_{ij} = J_{ij,\parallel} - J_{ij,\times}$. J denotes the intradimer exchange. H_0 can readily be diagonalized, which gives for a negative J an energy spectrum with a singlet ground state, separated by an energy $|J|$ from an excited triplet. Assuming that J is the most dominant exchange coupling, H_0 is expected to be a valid approximation for the ground state of $KCuCl_3$. Since K_i is diagonal in the singlet-triplet space and vanishes for a singlet, the H_K part does not contribute to the energy unless two or more neighboring dimers are excited. On the contrary, L_i is completely off-diagonal in the singlet-triplet space, which implies that the low energy spectrum given by the dispersion relation of the singlet-triplet modes is solely determined by H_L. H_L has the form of a Heisenberg Hamiltonian, but the spins are now replaced by singlet-triplet dimer excitations, which propagate from one dimer site to another. The fact that along b the individual ions of the two differently oriented dimers are interchanged in comparison to the ac plane implies that in the description of the excitations with κ along b^* the effective exchange couplings connecting these dimers have a negative sign compared to the a^*c^* plane. Starting from the noninteracting H_0 dimer limit, the random phase approximation is applied (see [15,16] for a recent application). At $T = 0$ K, the imaginary part of the wave-vector dependent susceptibility in the positive energy transfer range is then given by

$$\chi''_{\alpha\beta}(\kappa,\omega) = \frac{1}{2}\pi \frac{-(1-\cos(\kappa R))JM}{\sqrt{J^2 + 2MJJ^L_{int}(\kappa)}} \times \delta(\hbar\omega - \sqrt{J^2 + 2MJJ^L_{int}(\kappa)})\delta_{\alpha\beta} \tag{6}$$

where M denotes the singlet-triplet transition matrix element, and $J^L_{int}(\kappa)$ the Fourier transformed interdimer coupling exchange constants J^L_{ij}. Note the intrinsic $1 - \cos(\kappa R)$ structure factor which reflects the antiferromagnetic dimer character of the excitations. $\chi''(\kappa,\omega)$ can directly be determined by neutron scattering, because the cross section is proportional to

$$\frac{d^2\sigma}{d\Omega d\omega} \sim \sum_{\alpha\beta} (\delta_{\alpha\beta} - \frac{\kappa_\alpha \kappa_\beta}{\kappa^2}) |f(\kappa)|^2 \chi''_{\alpha\beta}(\kappa,\omega) \tag{7}$$

Table 1. Values of the interdimer exchange coupling constant J and the effective exchange coupling constants $J_{0i}^{L} = J^{L}(r_i - r_0)$ between the dimers in $KCuCl_3$, where r_i denotes the center of gravity of the dimers, with $r_0 = (000)$.

$J^{L}(r_i - r_0)$	r_i [r.l.u.]	[meV]
J_{a1}	$\pm(1\ 0\ 0)$	0.242(6)
J_{a2c}	$\pm(2\ 0\ 1)$	0.401(7)
J_{bc}	$\pm(0\ 1/2\ 1/2)$	0.016(2)
	$\pm(0\ \bar{1}/2\ 1/2)$	
J_{abc}	$\pm(1\ 1/2\ 1/2)$	−0.356(4)
	$\pm(1\ \bar{1}/2\ 1/2)$	
J	$(0\ 0\ 0)$	−4.247(6)

where $f(\kappa)$ denotes the Cu^{2+} magnetic form factor [17]. The lines in Figures 2 and 3 correspond to the calculated energies and intensities of the excitations. Given the Fourier transformed $J_{int}^{L}(\kappa)$ from Table 1, the exchange coupling constants are uniquely determined by the dispersion relation from equation (6), and correspond to the minimal effective coupling scheme which fits the measured data. For $M = 1$, which holds for spin 1/2, the intradimer exchange coupling constant J has a value of −4.25 meV, one order of magnitude bigger than the interdimer exchange couplings. In the intensity fit, the only free parameter is a scaling factor which accounts for the sample volume seen by the neutrons. Considering the simple nature of the dimer model, Figures 2 and 3 show that in general there is good agreement between measurements and model calculation.

The characterization of $KCuCl_3$ as a weakly coupled dimer system with dispersive singlet-triplet excitations is supported by investigations in a magnetic field. In Figure 4 the progressive three-fold splitting of the excitations in a field perpendicular to the scattering plane is shown. From the model description, an overall splitting of 0.23 meV/T is expected. Also, the intensity of the $\Delta S^z = 0$ transition is expected to be twice as strong as the intensity of the $\Delta S^z = \pm 1$ transitions. Both features are confirmed with good accuracy by the experimental results. In particular, the $\Delta S^z = 0$ transition is observed at the unshifted zero-field energy.

3 Conclusions

To conclude, we presented an experimental and theoretical study of the magnetic excitations in the insulator $KCuCl_3$. Spins 1/2 reside at the Cu^{2+} ion sites, and are arranged in double chains. Despite the quasi one dimensional geometry, we showed that $KCuCl_3$ is a three-dimensional magnetic system. A simple model derived from the isotropic spin 1/2 Heisenberg Hamiltonian characterizes $KCuCl_3$ as a weakly coupled dimer compound, and quantitatively explains the experimental observations, which are:

- The presence of well-defined excitation modes above a spin gap, and their three-dimensional dispersion relation $\hbar\omega(\kappa)$;
- The three-fold Zeeman splitting of these excitations under the influence of an external field;
- The strong spectral weight dependence of the excitations on the momentum transfer $\hbar\kappa$.

The question about the origin of the spin gap in $KCuCl_3$ can be answered within the treatment given as a dimer gap. We determined that the dimers are built along the rungs of the double chains, and that the spins 1/2 within the dimers are antiferromagnetically coupled, forming a singlet nonmagnetic ground state. Weak effective interdimer exchange couplings account for the dispersion relation of the singlet-triplet excitations above the gap.

Although the dimer model provides a complete description of the measurements, this study will hopefully lead to additional efforts to understand the exact nature of the ground state and excitations in three-dimensional quantum spin systems.

It is a pleasure to thank B. Braun, O. Fritz, S. Haas, T. Kato and B. Normand for stimulating discussions. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

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