Dynamics of the two-dimensional $S = 1/2$ dimer system $(C_5H_6N_2F)_2CuCl_4$

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Inelastic neutron scattering was used to study a quantum $S = 1/2$ antiferromagnetic Heisenberg system—Bis(2-amino-5-ﬂuoropyridinium) Tetrachlorocuprate(II). The magnetic excitation spectrum was shown to be dominated by long-lived excitations with an energy gap of $\Delta = 1.07(3)$ meV. The measured dispersion relation is consistent with a simple two-dimensional square lattice of weakly-coupled spin dimers. Comparing the data to a random phase approximation treatment of this model gives the intra-dimer and inter-dimer exchange constants $J = 1.45(2)$ meV and $J' = 0.31(3)$ meV, respectively.

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Quantum spin liquids, where strong zero point fluctuation destroy magnetic long-range order even at $T = 0$, have been a subject of intense studies for over two decades. Of particular interest are two-dimensional systems of this type. In addition to their relevance to layered superconducting cuprates, they are of interest in the context of field-induced quantum phase transitions where, to date, most experimental work was performed on either spin chains or ladders or 3D systems. Several 2D spin liquids including BaCuSi$_2$O$_6$, SrCu$_2$(BO$_3$)$_2$ and PHCC have been studied in great detail, but show rather complex behavior due to geometrically frustrated interactions.

Recently, a new quantum antiferromagnet Bis(2-amino-5-ﬂuoropyridinium) Tetrachlorocuprate(II) (5FAP-CuCl$_4$, for short) has been discovered and characterized by bulk measurements. The ground state is a spin liquid. The energy gap $\Delta$ to the lowest excited (triplet) state was determined to be $0.97(4)$ meV from the high-field magnetization data. 5FAP-CuCl$_4$ ($\{C_5H_6N_2F\}_2CuCl_4$) crystallizes in a monoclinic space group $P2_1/c$ with lattice constants $a = 6.926(7)$ Å, $b = 21.73(2)$ Å, $c = 10.911(10)$ Å, and $\beta = 100.19(2)^\circ$. There are four inequivalent Cu atoms per unit cell as shown in Fig. (a). In view of crystal structure, 5FAP-CuCl$_4$ consists of CuCl$_4^{2-}$ anion layers separated by organic cations. Those CuCl$_4^{2-}$ anions form zigzag layers which are stacked along the crystallographic $a$ axis as shown in Fig. (b). Fig. (c) shows the arrangement of CuCl$_4^{2-}$ anions and organic cations viewing from the $a$ axis. The yellow and purple lines indicate the most plausible super-exchange interactions that could be carried across Cu-CI-CI-Cu bonds. The former involves the shortest CI-CI contact with a separation of 3.66 Å, while for the latter the relevant CI-CI distance is 4.07 Å. One can expect inter-layer coupling along the $a$ axis to be exponentially weak due to a much larger CI-CI separation 5.07 Å. Even with this in mind, it is not obvious which in-lane interactions are the most relevant. To better understand the spin Hamiltonian for 5FAP-CuCl$_4$, in this paper, we report inelastic neutron scattering (INS) measurements of magnetic excitations and their dispersion relation. We show that 5FAP-CuCl$_4$ can be adequately described by a minimal model that is equivalent to a square lattice of weakly interacting antiferromagnetic $S = 1/2$ dimers with no geometric frustration.

Small size fully deuterated single crystalline samples of 5FAP-CuCl$_4$ were prepared by the procedure described in Ref. 15. About twenty single crystals ($\sim 0.3$ g total) were co-aligned with a mosaic about 4° and used for INS measurements on the cold-neutron triple-axis spectrometer IN14 at Institut Laue-Langevin. Another assembly consisting of 20 single crystals ($\sim 0.5$ g) with a total 5° mosaic was used for the measurements on TASP$^{16}$ spectrometer at SINQ, Paul Scherrer Institute. Horizontal beam divergences were given by $^{58}$Ni guide-60°-open-open at IN14 and by 10°/Å-open-open-open at TASP. Both experiments were performed with the scattered wave vector $k_f$ fixed at 1.5 Å$^{-1}$ and Be filter placed after the sample was used to remove higher order beam contamination. The sample was oriented horizontally in a (0, k, l) reciprocal lattice plane and cooled in a standard He-4 cryostat.

The data were collected in a series of constant-$q$ scans at $T = 1.5$ K along the high symmetry directions in the (0, k, l) reciprocal plane. The inset of Fig. (a) shows the raw data of a typical scan performed at $q = (0,0,-1.5)$, where a sharp resolution-limited peak due to a magnetic excitation is clearly visible. The background (shown as a solid line) was determined by fitting the data over the range where no magnetic excitations are apparent, to a
FIG. 1: (color online) (a) Outline of a unit cell in 5FAP-CuCl$_4$. (b) View from the c axis, showing the zigzag layer structure. Only Cu and Cl atoms are shown, the organic cations have been removed for clarity. (c) View from the a axis, showing the arrangement of CuCl$_2^-$ anions and organic cations. Different color lines stand for the different magnetic interactions. Color coding is as follows: Cu, Cl, C, H, F, and N.

term linear in energy, plus a resolution-limited Gaussian peak at zero energy transfer. The latter accounted for incoherent elastic scattering. Background-subtracted data at several wave vectors are shown in Fig. 3. At certain wave vectors the observed signal has a distinct double-peak structure as shown in Figs. 3(c) and (d). Solid lines in Fig. 3 are fits to Gaussian profiles of fixed widths, determined by instrumental resolution, as calculated using the Cooper-Nathans approximation. Excitation energies (dispersion relation) obtained from such fits are summarized in Fig. 2. The spectrum appears to consist of two equivalent branches, an “optic” and an “acoustic” one, although the former is not visible at the majority of the wave vectors studied.

The most comprehensive method of determining the relevant exchange parameters in a gapped system with weakly dispersive excitations is based on the application of the first-moment sum rule for the magnetic dynamic structure factor. This procedure involves quantitative measurements of inelastic intensities as a function of wave vector and was successfully applied to the rather complex interaction geometry in CuHpCl. Due to technical complications, associated with the sample fracturing upon cooling, and the data being collected in several disjoint experiments, in the present study we adopted a simpler approach. Only the measured excitation energies were analyzed. A parameterized model was refined to reproduce the experimental dispersion relations. The proposed minimal model is visualized in Fig. 4 which shows the exchange constants a single layer of magnetic Cu$^{2+}$ ions. The dimers are formed by the stronger antiferromagnetic bonds $J$, which ensures a spin-singlet ground state and an energy gap. The dispersion of singlet-triplet dimer excitations is due to the weaker inter-dimer exchange constant $J'$. Topologically, this spin network can be viewed as a square lattice of $S = 1/2$ dimers. Nevertheless, its actual realization in the crystal has two dimers per crystallographic unit cell. This leads to a folding of the Brillouin zone and the appearance of two excitation branches. As shown below, this minimal model seems to be fully consistent with experimental observations.

We can treat the weak inter-dimer coupling $J'$ at the Random Phase Approximation (RPA) level. This method has been applied to numerous spin systems,
FIG. 3: Representative background-subtracted INS data for 5FAP-CuCl$_4$ at $T = 1.5$ K. The solid lines are fits Gaussian profiles of instrumental width. The shaded area in (a) is excluded due to a contamination by “accidental Bragg” spurious scattering.

FIG. 4: (color online) Minimal model for magnetic interactions in 5FAP-CuCl$_4$, shown in projection onto the $(b,c)$ plane. Dimer singlets are formed by antiferromagnetic exchange $J$. Dispersion of singlet-triplet excitations is due to inter-dimer interaction $J'$. Including Cs$_3$Cr$_2$Br$_9$, BaCuSi$_2$O$_6$, BaCuSi$_2$O$_7$, Ba$_3$Mn$_2$O$_8$, and Ba$_3$Cr$_2$O$_8$ in application to 5FAP-CuCl$_4$, we can treat two decoupled dimers in a unit cell as the basic spin cluster (tetramer). These tetramers will then form a Bravais lattice. With four sites in each tetramer, their bare susceptibilities are written as a $4 \times 4$ matrix, the indexes enumerating the four spins in each unit:

$$
\chi_0(\omega) = \frac{J}{2J^2 - 2(\hbar\omega)^2} R(T) \begin{pmatrix} 1 & -1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & -1 & 1 \end{pmatrix}.
$$

(1)

Here $R(T) = \frac{1 - e^{-J/(kB T)}}{1 + 3e^{-J/(kB T)}}$ is the difference in population of the excited and ground states of the dimers. The weak interaction $J'$ couples adjacent tetramers, but also dimers within each tetramer. Its effect is taken into account within the RPA. The corresponding RPA equation is written as:

$$
\chi^{RPA}(q, \omega) = \chi_0(\omega)[1 - \chi_0(\omega)J'(q)]^{-1}.
$$

Here $J'(q)$ is the Fourier transform of exchange interactions due to $J'$. It is also written as a $4 \times 4$ matrix:

$$
J'(q) = J' \begin{pmatrix} 0 & 0 & 0 & e^{-i\pi(k+l)} + e^{-i\pi(k-l)} \\ 0 & 0 & 1 + e^{-i\pi(k+l)} & 0 \\ e^{-i\pi(k+l)} + e^{-i\pi(k-l)} & 0 & 0 \\ 0 & 0 & 0 & 1 + e^{-i\pi(k+l)} \end{pmatrix}.
$$

(3)

The dispersion relation is then readily obtained from the location of poles in $\chi^{RPA}(q, \omega)$:

$$(\hbar\omega_q)^2 = J^2 \mp JJ'(q)R(T)[\cos \pi(k+l) + \cos \pi(k-l)].
$$

(4)

The solid and dashed lines in Fig. 2 are fits of this dispersion relation to the experimental data. A good agreement is obtained with $J = 1.45(2)$ meV and $J' = 0.31(3)$ meV.

In summary, 5FAP-CuCl$_4$ can be described as a simple 2D network of weakly interacting spin dimers, which is topologically equivalent to a dimer square lattice. The magnon dispersion bandwidth is 0.70(4) meV, smaller than gap energy $\Delta = 1.07(3)$ meV, but still substantial. Future work will focus on the high-field study of quantum phase transition and critical phenomena in 5FAP-CuCl$_4$.

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1 P. W. Anderson, Mater. Res. Bull. 8, 153 (1973).

2 P. W. Anderson, Science 235, 1196 (1987).
P. A. Lee, N. Nagaosa, and X.-G. Wen, Rev. Mod. Phys. 78, 17 (2006).

S. Sachdev, Quantum Phase Transition, Cambridge University Press (1999).

T. Giamarchi, Ch. Rüegg, and O. Tchernyshyov, Nature Phys. 4, 198 (2008).

M. B. Stone, D. H. Reich, C. Broholm, K. Lefmann, C. Rischel, C. P. Landee, and M. M. Turnbull, Phys. Rev. Lett. 91, 037205 (2003).

T. Hong, R. Custelcean, B. C. Sales, B. Roessli, D. K. Singh, and A. Zheludev, Phys. Rev. B 80, 132404 (2009).

T. Masuda, A. Zheludev, H. Manaka, L.-P. Regnault, J.-H. Chung, and Y. Qiu, Phys. Rev. Lett. 96, 047210 (2006); V. O. Garlea, A. Zheludev, T. Masuda, H. Manaka, L.-P. Regnault, E. Ressouche, B. Grenier, J.-H. Chung, Y. Qiu, K. Habicht, K. Kiefer, and M. Boehm, Phys. Rev. Lett. 98, 167202 (2007); T. Hong, A. Zheludev, H. Manaka, and L.-P. Regnault, Phys. Rev. B 81, 060410(R) (2010).

T. Hong, Y. H. Kim, C. Hotta, Y. Takano, G. Tremelling, M. M. Turnbull, C. P. Landee, H.-J. Kang, N. B. Christensen, K. Lefmann, K. P. Schmidt, G. S. Uhrig, and C. Broholm, Phys. Rev. Lett. 105, 137207 (2010).

M. B. Stone, Y. Chen, J. Rittner, H. Yardimci, D. H. Reich, C. Broholm, D. V. Ferraris, and T. Lectka, Phys. Rev. B 65, 064423 (2002).

Ch. Rüegg, N. Cavadini, A. Furrer, H.-U. Güdel, K. Krämer, H. Mutka, A. Wildes, K. Habicht, and P. Vorderwisch, Nature 423, 62 (2003).

S. E. Sebastian, N. Harrison, C. D. Batista, L. Balicas, M. Jaime, P. A. Sharma, N. Kawashima, and I. R. Fisher, Nature 441, 617 (2006); Ch. Rüegg, D. F. McMorrow, B. Normand, H. M. Ronnow, S. E. Sebastian, I. R. Fisher, C. D. Batista, S. N. Gvasaliya, Ch. Niedermayer, and J. Stahn, Phys. Rev. Lett. 98, 017202 (2007).

B. D. Gaulin, S. H. Lee, S. Haravifard, J. P. Castellan, A. J. Berlinsky, H. A. Dabkowska, Y. Qiu, and J. R. D. Copley, Phys. Rev. Lett. 93, 267202 (2004).

M. B. Stone, I. Zaliznyak, D. H. Reich, and C. Broholm, Phys. Rev. B 64, 144405 (2001); M. B. Stone, I. A. Zaliznyak, T. Hong, C. L. Broholm, and D. H. Reich, Nature 440, 187 (2006); M. B. Stone, C. Broholm, D. H. Reich, P. Schiffer, O. Tchernyshyov, P. Vorderwisch, and N. Harrison, New J. Phys. 9, 31 (2007).

L. Li, M. M. Turnbull, C. P. Landee, J. Jornet, M. Deumal, J. J. Novoa, and J. L. Wikaira, Inorg. Chem. 46, 11254 (2007).

F. Semadeni, B. Roessli, and P. Boeni, Physica B 297, 152 (2001).

M. J. Cooper and R. Nathans, Acta Cryst. 23, 357 (1967).

P. C. Hohenberg and W. F. Brinkman, Phys. Rev. B 10, 128 (1974).

S. B. Haley and P. Erdös, Phys. Rev. B 5, 1106 (1972).

B. Leuenberger, A. Stebler, H. U. Güdel, A. Furrer, R. Feile, and J. K. Kjems, Phys. Rev. B 30, 6300 (1984).

Y. Sasago, K. Uchinokura, A. Zheludev, and G. Shirane, Phys. Rev. B 55, 8357 (1997).

A. Zheludev, M. Kenzelmann, S. Raymond, T. Masuda, K. Uchinokura, and S.-H. Lee, Phys. Rev. B 65, 014402 (2001).

M. B. Stone, M. D. Lumsden, Y. Qiu, E. C. Samulon, C. D. Batista, and I. R. Fisher, Phys. Rev. B 77, 134406 (2008).

M. Kofu, J.-H. Kim, S. Ji, S.-I. Lee, H. Ueda, Y. Qiu, H.-J. Kang, M. A. Green, and Y. Ueda, Phys. Rev. Lett. 102, 037206 (2009).