Spin dynamics of the model 2D quantum antiferromagnet CFTD

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(October 24, 2018)

The magnetic exciton spectrum in the two-dimensional (2D) $S = 1/2$ Heisenberg antiferromagnet copper deuterofomate tetradeuterate (CFTD) has been measured for temperatures up to $T \sim J/2$, where $J = 6.31 \pm 0.02$ meV is the 2D exchange coupling. For $T \ll J$, a dispersion of the zone boundary energy is observed, which is assigned to a wavevector dependent quantum renormalization. At higher temperatures, spin-wave-like excitations persist, but are found to broaden and soften. By combining our data with numerical calculations, and with existing theoretical work, a consistent description of the behaviour of the model system is found over the whole temperature interval investigated.

While at the atomic level, magnetism is a quantum phenomenon, the collective behavior of magnets can be largely understood using classical concepts. This can even be true for antiferromagnets with low spin and spatial dimensionality, where quantum fluctuations are sizable. A famous example is the 2D quantum magnetic copper deuteroformate tetradeuterate (CFTD) has been measured for temperatures up to $T = 0$.

With the exception of the spin dynamics at $T = 0$, where $J = 6.31 \pm 0.02$ meV is the 2D exchange coupling, for $T \ll J$, a dispersion of the zone boundary energy is observed, which is attributed to a wavevector dependent quantum renormalization. At higher temperatures, spin-wave-like excitations persist, but are found to broaden and soften. By combining our data with numerical calculations, and with existing theoretical work, a consistent description of the behaviour of the model system is found over the whole temperature interval investigated.

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Though experiments on the dynamics of the 2DQHAFSL are relatively scarce, considerable theoretical work exists. Time dependent information is contained in the dynamical structure factor $S(Q, \omega) = \int d\omega e^{-i\omega t} \sum \sum e^{iQr} \langle \langle S_i(0) S_j(t) \rangle \rangle$, which is a function of wavevector $Q$ and energy $h\omega$, and is measured directly in neutron scattering experiments. The $T = 0$ properties can be described by classical SW theory, but with quantities such as the SW velocity $v_s = Z_c \sqrt{2} J_a$, spin stiffness $\rho_s = Z_p J/4$, and susceptibility $\chi_\perp = Z_\perp/(8 J)$ renormalized by quantum corrections. Consistent values for the renormalization constants $Z_c = 1.18$, $Z_p = 0.72$ and $Z_\perp = 0.51$ have been obtained using the SW expansion to order $1/(2S)^2$ and series expansion from the Ising-limit. However, these two approaches to the $T = 0$ spin dynamics disagree in detail, in that the SW expansion predicts a constant energy at the zone boundary (ZB), whereas the Ising-limit expansion predicts a $\sim 7\%$ dispersion.

On warming, scattering from thermally excited magnons, and a variation of the order parameter on a length scale set by $\xi$, will limit the lifetime of the excitations. Correspondingly, the inverse magnon lifetime, $\Gamma$, will increase, while the dispersion softens to lower...
energies. Various theoretical studies \[13-20\] and QMC calculations in the limited temperature range \(0.35J < T < 0.5J\) \[21\] have addressed the dynamic structure factor of the 2DQHAFSL at finite \(T\). Most approaches agree on the existence of well-defined excitations, but few experimental data are available to test the various quantitative predictions. Much of the experimental work on the 2DQHAFSL has focussed on \(La_2CuO_4\) \[7\] and \(Sr_2CuCl_2O_2\) \[22\], both of which contain the \(CuO_2\) planes that are the building blocks of the cuprates. These materials have the drawback that their large coupling constant \(J \sim 1500\) K makes studies on temperature and energy scales comparable to \(J\) technically challenging. Another realization of the 2DQHAFSL is \(Cu(DCOO)_{2} \cdot 4D_2O\) (CFTD), where the \(S = 1/2\) \(Cu\) moments are coupled through formate groups, leading to an exchange energy \((J = 73.2\) K) which is more amenable to experiments. The correlation length \(\xi(T)\) in CFTD has recently been measured up to temperatures of \(T \sim J\) \[14\], and found to be in good agreement with theory and computations.

Below \(236\) K, CFTD has the \(P2_1/n\) space group with lattice parameters \(a = 8.113\) \(\AA\), \(b = 8.119\) \(\AA\), \(c = 12.45\) \(\AA\), and a monoclinic angle \(\beta = 101.28^\circ\). The \(ab\) plane contains face centred \(S = 1/2\) \(Cu^{2+}\) ions, forming an almost square lattice. The SW dispersion along \(a^*\) and \(b^*\) measured by neutron scattering is well described by an isotropic nearest-neighbour coupling \(J = 6.31\) meV, and a small anisotropy induced gap of \(0.38\) meV at the zone centre \[23\]. The inter-layer coupling is estimated to be less than \(10^{-4}J\), while a Dzyaloshinskii-Moriya term \(J_D = 0.46\) meV has been inferred from magnetization measurements \[21\]. Below \(T_N = 16.54\) K the system orders three-dimensionally due to the inter-layer coupling \[24\].

Our neutron inelastic scattering experiments using the direct geometry time-of-flight (TOF) spectrometer HET at ISIS, UK. The incident energy \(E_i = 25\) meV gave an energy resolution of FWHM 1.64 meV at zero energy transfer. A 3.71 g single crystal of CFTD was aligned with the 2D planes normal to the incident beam. In the geometry used the horizontal and vertical detector banks measured scattering along the \([1,1]\)-type direction, while the diagonal banks collected data along the \([1,0]\) directions. The measured intensities were corrected for detector efficiency, and converted to absolute units by normalising to the incoherent scattering from a vanadium standard.

Data were collected at several temperatures between 8 K and 150 K with typically 24 hours of counting per temperature. The data at 8 K (within the 3D ordered phase) provide a precise determination of the spin Hamiltonian, and allow characterization of the phonon background. For example, the band at 20 meV is probably due to the localised motion of the crystal bound water, which freezes in an anti-ferroelectric transition at 236 K \(\sim 20.3\) meV \[25\], while the extra scattering around 7 meV is due to acoustic phonons emerging from the (1,0,1) type reciprocal lattice points, see Fig. 1(a).

\[FIG. 1.\] Inelastic TOF data in CFTD with \(Q_{2D}\) in units of \((\pi, \pi)\). (a) Raw data at 8 K. (b) Representative cuts along energy (b1) and \(Q\) (b2) as indicated by the windows in panel (a). The vertical scales cover 0 to 100 m barn/steradian/meV/spin, and the solid lines are fits to the resolution convoluted cross-section described in the text. (c)–(d) Background subtracted data at 16 K and 36.2 K respectively. The pseudo-colour scale (from blue to dark red) range from 0 to 50 m barn/steradian/meV/spin.

At 8 K, the magnetic signal is concentrated along a sharp SW dispersion curve. The data were analysed by taking cuts along \(Q\) and \(\omega\), as illustrated in Fig. 1(b), allowing the phonon contribution to be dealt with as a local background. Each cut was fitted with a parameterized model for the scattering obtained by convolving the full instrumental resolution with the linear SW theory form \(S(Q, \omega) = \frac{2}{\pi} \sqrt{1 - \gamma_Q} \delta(\omega - \omega_Q); \omega_Q = 2J_{\gamma_\gamma} \sqrt{1 - \gamma_Q^2}; \gamma_Q = \frac{1}{2}(\cos Q_x + \cos Q_y)\), multiplied by the magnetic form factor of free \(Cu^{2+}\) and the Bose population factor. Since the parameterization is only applied locally (the parameters \(A\) and \(J\) were allowed to vary for each cut), it imposes no constraints on the global form of \(S(Q, \omega)\) or on the extracted dispersion, shown in Fig. 2. It is evident that along \([1,1]\) the dispersion is well described by a uniform renormalization of the linear SW theory result. A fit gave \(J = J/Z_e = 6.31 \pm 0.02\) meV, in good agreement with previous neutron scattering \[24\] studies.
and the value derived from high-temperature susceptibility [24]. The present data can be combined with the susceptibility data to give a value of the renormalization factor \( Z_c = 1.21 \pm 0.05 \), within error the same as the theoretical value 1.18 [1,2].

Along [1,0] there is a pronounced dip in energy around \((\pi, 0)\), indicating a dispersion of \( 6 \pm 1\% \) along the zone boundary (ZB) from \((\pi/2, \pi/2)\) to \((\pi, 0)\). Such a ZB dispersion has also been observed in \( \text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2 \) [24], where it was explained in terms of the Ising-limit expansion [2]. Indeed, the Ising-limit expansion accounts perfectly for our data without any additional parameters (dashed line in Fig. 3). However, our data can equally well be modelled within SW theory by introducing an antiferromagnetic next-nearest-neighbour coupling of \((0.067 \pm 0.007) \times J\), and \( a \) priori the experimental data cannot be used to discriminate between these two possibilities. To help resolve this issue we have undertaken numerical computations on finite sized systems, and do indeed find a ZB dispersion for pure nearest-neighbour coupling [27]. QMC on lattices up to \(32 \times 32\) spins and temperatures down to 0.3\(J\) extrapolate to about 6% ZB dispersion [24]. Exact diagonalisation of an \(8 \times 8\) system display a ZB dispersion of 4.8%. Both techniques yield no ZB dispersion in the \(4 \times 4\) system, which indicate that a significant number of spins are involved in this effect. We conclude that the experimentally observed ZB dispersion is indeed an intrinsic quantum effect on the \(T = 0\) spin dynamics of the pure 2DQHAFSL model with nearest-neighbour interactions. Recently a ZB dispersion of \(-13\%\) (i.e. opposite sign) has been found in \(\text{La}_2\text{CuO}_4\), which is attributed to higher-order spin couplings [28].

Above \(T_N\), the magnetic excitation spectrum broadens, making it more difficult to distinguish from the phonon scattering. To determine the phonon scattering, the SW contribution was simulated by convolving the linear SW result with the experimental resolution. When subtracted from the 8 K data the remaining intensity is dominated by phonon scattering. This was scaled to the thermal population factor and subtracted from the remaining \(T > T_N\) data. As this method assumes a uniformly renormalised SW dispersion, it obviously does not apply to \(Q||[1,1]\), and hence only the \(Q||[1, 1]\) data were analysed in this way. Fig. 1(c)-(d) shows examples of data sets where the phonon contributions have been removed. The background corrected data were analysed by fitting cuts along energy to the same parameterization as for the 8 K data, but with the delta function replaced by the damped harmonic oscillator (DHO) line shape \(\delta(\omega - \omega_Q) \rightarrow \frac{1}{\pi} \left( \frac{\omega_Q}{\omega_Q^2 + \omega^2 + \Gamma^2} \right)\). No clear trends could be found within error for the \(Q\) dependence of the fitting parameters \(A\), \(J\) and \(\Gamma\). In the following we therefore choose to discuss the \(Q\) averaged values \(\bar{A}(T), \bar{J}(T)\) and \(\bar{\Gamma}(T)\).

The amplitude, \(\bar{A}(T) = \frac{2}{\pi} \left( \frac{\omega_Q}{\omega_Q^2 + \omega^2 + \Gamma^2} \right) \bar{Z}(S)\), can be used to extract the renormalization \(\bar{Z}(S)\) of the susceptibility. (The factor \(\frac{2}{\pi}\) becomes \(\frac{\bar{A}(T)}{\bar{J}(T)}\) for the horizontal banks below \(T_N\) where the moments order almost vertically.) The temperature dependence of \(\bar{Z}(S)\) is listed in Table 1. At low \(T\), the experimental value is in perfect agreement with the predicted value of 0.51 [1]. At higher \(T\), \(Z_c\) appears to decrease, but no clear predictions for the \(T\) dependence of this quantity have yet been reported.

The uniform SW renormalization of \(\omega_Q\) found along [1,1] at 8 K justifies the use of the average \(\bar{J}(T)\), which divided by \(J\) gives the temperature dependent SW renormalization \(Z_c(T)\) as shown in Fig. 3. Kaganov and Chubukov [30] have calculated the temperature dependence of the higher-order quantum corrections to SW theory, obtaining \(\nu_s(T) = \nu_s(0) \left( 1 + \frac{\zeta(3)}{4 \pi} \left( \frac{T}{T_N} \right)^3 \right)^{-1}\), where \(\zeta(3) \approx 1.231\). This result is represented by the solid line and is in good agreement with our data. The new QMC results are indicated by triangles and are also consistent with the data.
Spin waves are eigenmodes with respect to antiferromagnetic order and vary on a length scale set by the correlation length \( \xi(T) \). The most naive way to estimate the lifetime of a SW would be to divide \( \xi(T) \) by the SW velocity \( v_s(T) \). In Fig. 4 the solid line is the inverse lifetime \( \Gamma(T) = v_s(T)/\xi(T) \) obtained in this way, and is seen to be in surprisingly good agreement with the data.

In summary, we have measured the excitation spectrum of CFTD, which is an excellent physical realization of the 2DQHAFSL. Combining our data and numerical calculations, the existence of a quantum induced ZB dispersion has been unambiguously established. The finite temperature behaviour has been probed up to \( T > J/2 \), where well-defined SW like excitations persist. The temperature dependence of the SW softening and damping in this strongly quantum mechanical system are remarkably well described, without any adjustable parameters, by existing theories based on a quantum renormalization of the classical system.

We gratefully acknowledge Rajiv R. P. Singh for useful discussions. This work was supported by the Danish Research Academy, the UK EPSRC and the EU through its TMR and IHP programmes. ORNL is managed for the US DOE by UT Battle, LLC, contract DE-AC05-00OR22725.

Various calculations of the SW damping all predict a \( Q \) dependence with a minimum at \( (\pi, \pi) \). Around this point, the value of \( \Gamma \) is quite dependent on the definition of the line shape. This complication is irrelevant for the experimental data, where due to the large incoherent background, the fits were restricted to \( \omega > 2 \text{ meV} \approx J/3 \). The experimentally determined SW damping is shown in Fig. 3. QMC results for the damping have been reported for \( 0.35 < T/J < 0.5 \) \cite{21}. We find that these overestimate the experimental values of \( \hat{\Gamma} \) by almost a factor of two. To resolve this discrepancy, we have repeated the QMC calculations \cite{27}. If the same maximum entropy (ME) method is used for analytic continuation of the imaginary time MC data, then the results of Ref. 21 are reproduced. We found, however, that it is more robust to impose the same DHO line shape as used to analyse our experimental data. When this is done the QMC values shown in Fig. 3 are obtained which are in good agreement with the experimental data. Scaling arguments have also been used to calculate the SW damping \cite{13}. Since this approach mainly applies to the low-energy, long-wavelength behaviour of the system which was not probed in our experiments, we believe that it is not appropriate to compare it with our data. We do note, however, that for \( T < J/2 \) the data lie above the prediction for \( Q = (\pi, \pi) \), and below the prediction extrapolated to \( Q = (\pi/2, \pi/2) \). Our result for \( \Gamma(T) \) differ from those extracted from NMR in \( \text{Sr}_2\text{CuCl}_2\text{O}_2 \) \cite{22}. This may be because NMR is a local probe in the low energy limit, and the result for \( \Gamma(T) \) relies on a global assumption for \( S(Q, \omega) \). In contrast, our data give a direct and assumption free measurement of \( \Gamma(T) \).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{The SW softening \( Z_c = J/J \) and damping \( \Gamma/J \) as functions of temperature. The experimental data (circles) and new QMC results (triangles) are averages for \( \omega > 2 \text{ meV} \). The solid lines are respectively the prediction of Kaganov and Chubukov \cite{31,30} for \( Z_c \) and the relation \( \Gamma(T) = v_s(T)/\xi(T) \) for the damping.}
\end{figure}
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