High-Temperature Magnetic Correlations in the 2D $S = 1/2$ Antiferromagnet Copper Formate Tetradeuterate

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The temperature dependence of the structure factor $S(k)$ of the instantaneous magnetic fluctuations in copper formate tetradeuterate has been investigated using neutron scattering techniques. Our data extend to unprecedently high temperatures ($T \sim J$) compared to the 2D exchange coupling. The correlation length ξ and amplitude S_0 are in good agreement with the predictions for a 2D $S = 1/2$ Heisenberg antiferromagnet on a square lattice. [S0031-9007(98)07991-5]

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The study of quantum magnets remains at the forefront of condensed matter physics. Their importance stems mainly from the fact that spin models continue to be a productive arena in which to develop many-body methods that have far ranging applicability. In addition there is the specific need to understand the role played by magnetism in determining the basic physical properties of various classes of materials, such as the cuprate based high-temperature superconductors. The magnetism of these particular materials is characterized by strongly fluctuating antiferromagnetically coupled quantum ($S = 1/2$) spins on a (almost) square 2D lattice, and for this reason the study of the corresponding theoretical model has attained a particularly significant status. (For a comprehensive review, see [1].) Here we present experimental data on the correlation length ξ and amplitude S_0 of the magnetic fluctuations measured to unprecedently high temperatures in copper formate tetradeuterate (CFTD), a 2D $S = 1/2$ magnet.

Though no exact solution has been found, there is now a general consensus that the ground state of the 2D $S = 1/2$ Heisenberg antiferromagnet on a square lattice (2DQHAFSL) has long-range order (LRO). Using a spin-wave approximation the ground state properties have been calculated as staggered magnetization $N_0 = 0.307$, spin-wave stiffness $\rho_S = 0.181J$, and spin-wave velocity $c = 1.18\sqrt{2}\,Ja$, where J is the exchange coupling and a is the lattice constant [2].

The understanding of the system at finite T was greatly advanced by the work of Chakravarty, Halperin, and Nelson (CHN) [3]. For $T \ll J$, the behavior of the system was investigated by mapping it onto the quantum nonlinear sigma model (QNLσM). Depending on the coupling parameter g, which expresses the strength of the quantum fluctuations, the QNLσM will show LRO at $T = 0$ for $g < g_c$. As the 2DQHAFSL is believed to have LRO at $T = 0$, it must correspond to $g < g_c$. For low temperatures CHN found that the only effect of the quantum fluctuations is to renormalize the coupling constants. In this *renormalized classical* region the correlation length ξ has been calculated to 3-loop order by Hasenfratz and Niedermeyer [4] with the result that

$$\xi_{\mathrm{CHN}} = \frac{e}{8}\,\frac{\hbar c}{2\pi\rho_S}\,e^{2\pi\rho_S/T} \times \left[1 - \frac{1}{2}\,\frac{T}{2\pi\rho_S} + \mathcal{O}\left(\frac{T}{2\pi\rho_S}\right)^2\right]. \quad (1)$$

The structure factor has an almost Lorentzian line shape with an amplitude given by [5]

$$S_0 = 13.50 \times N_0^2 \xi^2 \,\frac{T^2}{(2\pi\rho_S)^2}\,. \quad (2)$$

At higher temperatures, the QNLσM exhibits a crossover to the so-called quantum critical (QC) region, where the proximity to the QC point $g = g_c$ dominates the behavior [6]. For the square lattice $S = 1/2$ system the crossover is predicted to be around $T \sim J/2$. Deep within the QC region, ξ becomes linear in $1/T$. Approaching the crossover, only the lowest order correction has been evaluated to give $\xi = 0.962\hbar c[T - 0.3098(2\pi\rho_S)]^{-1}$. However, this result is not expected to be valid down to the region where the crossover is expected. One important question is whether the mapping of the 2DQHAFSL onto the QNLσM is still valid at the temperatures where the latter exhibits the crossover to QC behavior.

Several other theoretical and computational methods have been applied to the 2DQHAFSL, including high-temperature expansion (HTE) [7], quantum Monte Carlo (QMC) [8–10], and the pure quantum self-consistent harmonic approximation (PQSCHA) [11]. An HTE series for $S(k)$ has been generated up to the 14th order in J/T. The series is believed to give reliable results for temperatures down to $T \sim 0.4J$. QMC calculations have been performed using several different algorithms [8–10]. The joint data cover $J/12 < T < 4J$, corresponding to $352000 > \xi > 0.289$. PQSCHA [11] has been found to perform well even in the $S = 1/2$ case down to $T \sim 0.4J$.

The correlation length and structure factor amplitude from these three different approaches are compared with each other, and with the predictions of CHN in Fig. 1. It can been seen that the results from the HTE, QMC, and PQSCHA studies are in good mutual agreement. It

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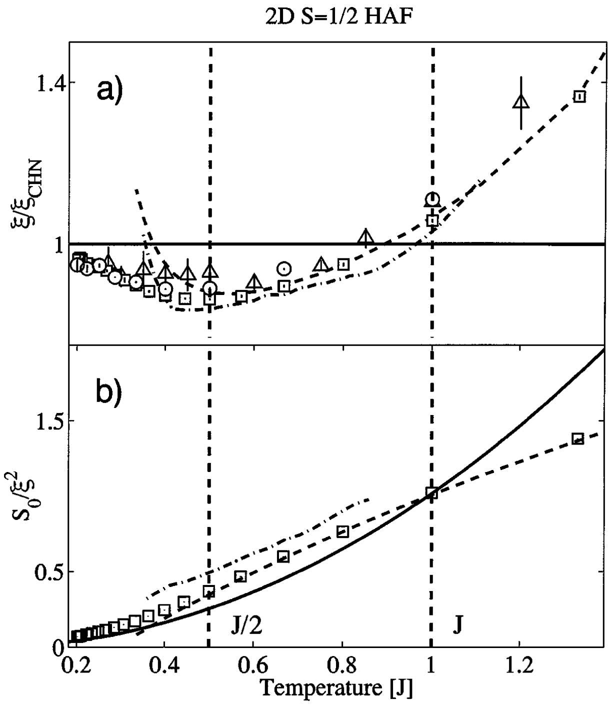

FIG. 1. Theoretical and numerical predictions for ξ and S_0. Lines are CHN [4] (solid), HTE [7] (dashed), and PQSCHA [11] (dot-dashed). The points are results of QMC: triangles [8], squares [9], and circles [10]. To address the questions raised in the text, we plot the ratio between ξ and the renormalized classical ξ_{CHN} and the ratio S_0/ξ^2.

is also apparent that there is a systematic trend for CHN to overestimate ξ at temperatures less than J, and to underestimate it for $T \geq J$. Indeed it has been argued by Beard *et al.* [10] that the mapping is only strictly valid for $\xi > 10^5$ and that the apparent agreement for higher T is perhaps coincidental.

While the theoretical behavior of the 2DQHAFSL has been comprehensively investigated over a large temperature range, relatively little is known from an experimental point of view of how the system behaves at temperatures comparable to or greater than J. For example, neutron scattering experiments that directly probe ξ and S_0 have been restricted to $T \approxeq J/2$ as we describe below. Another outstanding issue is the behavior of the ratio S_0/ξ^2, which for CHN scales with T^2, while experimental indications of a constant ratio have been reported [12]. In Fig. 1(b) it can be seen that the numerical data only follow T^2 at low T, but the ratio does not saturate. If the first order correction to the CHN result is included as a fitting parameter, the agreement between CHN and QMC can be extended up to $T < 1.3J$.

To date probably the best direct experimental data on the temperature dependence of ξ and S_0 are from the neutron scattering experiments of Greven *et al.* [12] on $Sr_2CuCl_2O_2$. Obviously, to compare the data with the theoretical predictions it is desirable to measure the scattering over as wide a temperature range as possible. The lower temperature limit T_N is set by the 3D Néel ordering which occurs in any real 2D system, and the upper limit is determined by the signal-to-noise ratio as the signal weakens at higher temperatures. Over the temperature range $0.21J < T < 0.39J$ in $Sr_2CuCl_2O_2$ ($J =$ 125 meV, $T_N = 256.5$ K), Greven *et al.* obtained excellent agreement with RC predictions for ξ, but found that their data for S_0 were proportional to ξ^2 rather than $\xi^2 T^2$ as given in Eq. (2). Two other systems have been studied using neutron scattering, with results that are in broad agreement with the RC results for temperatures up to $\approx 0.5J$. These are La_2CuO_4 ($J = 135$ meV, $T_N = 325$ K) [13] and $Cu(DCOO)_2 \cdot 4D_2O$ (CFTD) ($J = 6.3$ meV and $T_N = 16.5$ K) [14–17]. We note that in none of these experiments was it possible to follow the scattering up to temperatures where the QC regime could be probed. To our knowledge the only experiments that have probed the QC regime are the NMR experiments of Imai *et al.* [18] on La_2CuO_4. The inverse relaxation rate $1/T_1$ was found to saturate for $T > 600$ K, which was interpreted as a crossover to the QC region. The correlation length was also extracted from T_{2G} measurements [19] and found to be inversely proportional to temperature above 600 K in accordance with the predicted behavior of the QC region. However, subsequent attempts to reproduce these latter results were unsuccessful [20].

We chose to reinvestigate CFTD to obtain data on ξ and S_0 to much higher temperatures. CFTD has certain advantages over the cuprate compounds in that the energy scale of the interactions are better matched to the energy scale of neutrons from a thermal or cold source at a reactor, and large single crystals are available. CFTD crystalizes in a monoclinic structure [15] which below an antiferroelectric transition at 236 K has the $P2_1/n$ space group symmetry with lattice parameters $a = 8.113$ Å, $b = 8.119$ Å, $c = 12.45$ Å, and $\beta = 101.28°$. The almost square a-b planes contain face centered $S = 1/2$ Cu ions separated by formate groups and with an in-plane distance of 5.74 Å, while the distance between the Cu ions in adjacent planes separated by the crystal bound water is 6.23 Å.

The magnetic interactions in CFTD are dominated by an isotropic coupling $J = 6.3$ meV in the a-b plane, which has been determined by inelastic neutron scattering measurements of the spin-wave dispersion [16] and by bulk magnetization measurements [17]. It should be noted that due to the strong quantum fluctuations even in the ordered phase, the zone boundary energy is $\hbar\omega_{\mathrm{ZB}} = 1.18 \times 4SJ$. The same experiments estimate the interplanar coupling $J' \sim 5 \times 10^{-5} J$, and a Dzyaloshinsky-Moriya interaction $J_D = 0.46$ meV $= J/14$. Thus CFTD is close to the ideal 2D Heisenberg antiferromagnet, but due to the weak interplanar coupling it orders three dimensionally at $T_N =$ 16.5 K. The sublattice magnetization reaches only 48% of its classical value [15], reflecting the importance of quantum fluctuations.

The neutron scattering experiments were performed at Risø National Laboratory using the RITA spectrometer [21], which incorporates several novel features that make it particularly suitable for the study of fluctuations in low-dimensional systems. These include a large (17×12 cm^2) position sensitive detector and a neutron velocity selector. The former allowed us to optimize effectively the signal-to-noise ratio during the data analysis, and the latter to check the validity of the energy integration at any desired incident energy without the need to worry about $\lambda/2$ contamination. A single crystal of dimensions $12 \times 12 \times 4$ mm^3 prepared by slow dehydration of $Cu_2CO_3(OD)_2 \cdot D_2O$ in a solution of d_2-formic acid in D_2O was mounted in a helium flow cryostat with the reciprocal axes b^* and c^* in the scattering plane. We estimate that the sample was deuterated to approximately 98%.

The spectrometer was configured in a 2-axis mode with the wave vector of the outgoing neutron perpendicular to the 2D magnetic sheets. This is the standard configuration for the study of 2D magnets, and ensures that the measured intensity is proportional to $\int_{-\infty}^{E_i} S(k,\omega)\,d\omega \simeq S(k)$ where E_i is the incident energy [22]. Most of our data were taken with $E_i = 10$ meV $\sim 4/3J$, but the energy integration was checked experimentally by varying E_i up to 19 meV. (For comparison, the experiments on La_2CuO_4 and $Sr_2CuCl_2O_2$ used incident energies up to J [13] and $J/3$ [12], respectively.)

At higher temperatures ($T > 0.6J$) the signal became too weak relative to the elastic incoherent background from the residual hydrogen in the sample, and a second configuration had to be employed. A set of graphite crystals was inserted after the sample in order to reflect out of the exit beam those neutrons which were elastically scattered by the sample including the unwanted incoherent background. This elastic filter had a transmission given by $T(\omega) = 0.9 - 0.85 \times \exp(-\omega^2/2\sigma^2)$ where $\sigma = 0.665$ meV. This approach is justified in part by the fact that the fluctuations are spread out in energy, while the incoherent scattering is elastic and confined to zero energy transfer. Moreover the characteristic energy of the fluctuations increases with T, so that at higher T the use of a filter has less influence. As will be explained later, considerable care was taken to ensure that the data taken with and without the filter could be included in an overall comparison with theory.

Representative data sets recorded by scanning the neutron wave vector transfer through the 2D rods are shown in Fig. 2. To extract ξ and S_0 from the data we assumed a Lorentzian line shape which was convoluted with the full experimental resolution function using an adaptive integration procedure to ensure convergence. As illustrated in Fig. 2(a) the data taken with the standard 2-axis setup were well described by Lorentzians. The experimental statistics were insufficient to distinguish between different possible line shapes. A representative data set taken with the elastic filter is shown in the lower panel of Fig. 2(b), where it is compared to data taken at the same temperature using the standard configuration. It is evident that the use of the filter has improved the signal-to-noise ratio from approximately 1/20 to 1.

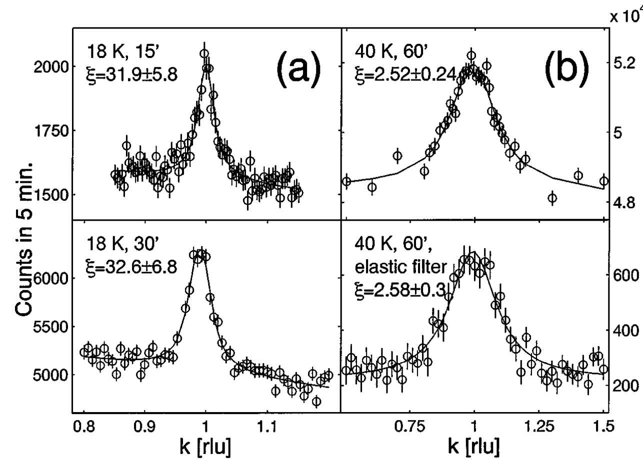

FIG. 2. Typical data illustrating how different spectrometer configurations gave consistent values of ξ. (a) Data taken at 18 K with $15'$ and $30'$ collimation, respectively. (b) Data taken at 40 K with $60'$ collimation with and without an elastic filter.

In the case of the elastic filter data an extra correction to the extracted parameters had to be made to allow for the fact that with the filter we do not measure the full energy integrated structure factor $S(k) = \int S(k,\omega)\,d\omega$ but rather $S_T(k) = \int S(k,\omega)T(\omega)\,d\omega$. Estimates of the correction factor were obtained by numerically integrating both a low-temperature form of $S(k,\omega)$ [23] and one that has been proposed to hold in the QC region [24]. At intermediate temperatures ($40\text{ K} < T < 70\text{ K}$), the correction factors agreed within 12%. The correction factor by which the experimentally determined ξ was multiplied ranged between 1.08 and 0.64 in the interval between 40 and 90 K. Once the correction factor had been applied to ξ, good agreement between the data taken with and without the filter was found, as shown in Fig. 2(b). The correction factor for the amplitude was found to be larger, varying between 1.31 and 1.83 with temperature.

The main results of this Letter are shown in Fig. 3 where we plot ξ (inverse Lorentzian half-width) as a function of T. The first thing to note is that the data for ξ taken with and without the elastic filter are in excellent agreement in the temperature range in which they overlap ($25 \le T \le 55$ K). The results cover a large temperature range $0.2J < T < 1.25J$, and are generally consistent with the CHN prediction. In view of the difference between the CHN and the QMC-HTE results, we show in the inset of Fig. 3 our data normalized to the CHN result together with the QMC data. Our data are indeed consistent with the QMC deviation from CHN, albeit with unsatisfactory large error bars below $T \sim 0.4J$.

In Fig. 4 we show the data for S_0 normalized to each other in the regions of overlap and compared to the predictions by theory and calculations. The data which cover almost 3 orders of magnitude are in relatively good agreement with the theoretical curves.

The CHN prediction for S_0 has recently been questioned on the basis of data from $Sr_2CuCl_2O_2$ [12]. To address this

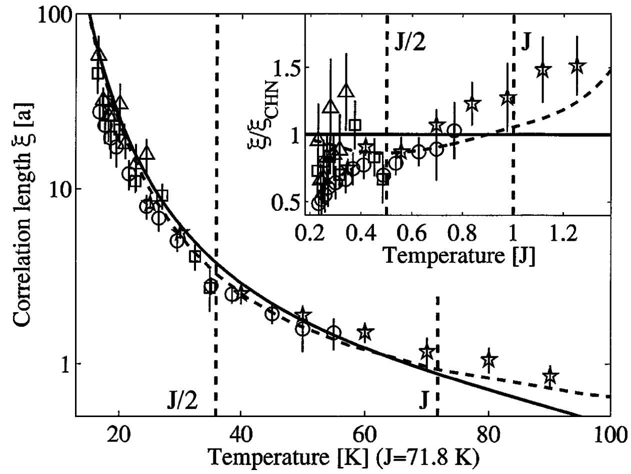

FIG. 3. The measured ξ in CFTD compared to the predictions by CHN [4] (solid) and the QMC [9] (dashed) results. The symbols indicate the collimation $\alpha = 15'$ (triangles), $30'$ (squares), and $60'$ (circles and stars). The stars were measured using an elastic filter.

question we show in the inset of Fig. 4 our experimental data for $S(k)/\xi^2$. Though insufficient to distinguish between the QMC and the CHN result, our data clearly show a T dependence of the ratio S_0/ξ^2.

Experimental tests of the proposed crossover to QC behavior are limited. The saturation of $1/T_1$ in NMR is consistent with the QC prediction, but cannot be considered to represent a verification of the existence of a crossover. In their work, Kim and Troyer [9] observe a linear T dependence of the uniform susceptibility χ_u in the range $0.3J < T < 0.5J$ in agreement with the QC prediction. In the range $0.3J < T < 0.8J$, $1/\xi$ does become linear, but the offset and the slope were found to be inconsistent with the QC prediction and hence the conclusion was that no QC behavior could be observed for ξ. The deviation

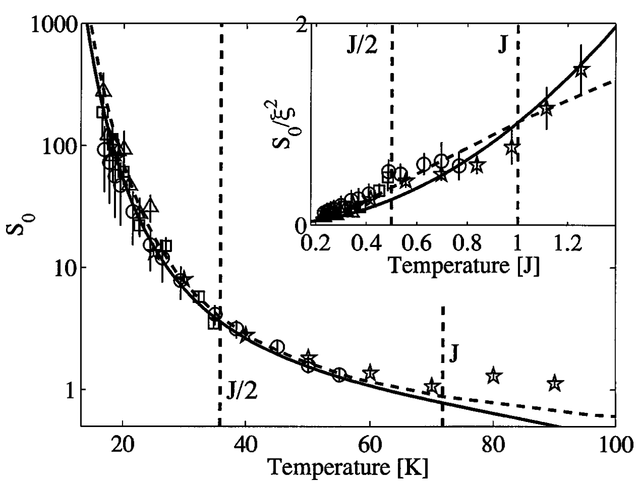

FIG. 4. The temperature dependence of S_0 in CFTD compared to the CHN [4] and QMC [9] predictions. The symbols indicate the collimation (cf. Fig. 3). The inset shows S_0/ξ^2 and addresses the question of the preexponential factor to the amplitude as discussed in the text.

between our data and the CHN result is consistent with the QMC result, and we therefore conclude that no sign of the crossover has been observed in CFTD. Combined with the findings by Beard *et al.* [10], this leads us to believe that the mapping of the 2DQHAFSL onto the QNLσM becomes invalid before the latter exhibits a crossover to the QC region.

In summary we have performed neutron scattering experiments on CFTD which is an excellent realization of the $S = 1/2$ 2D Heisenberg antiferromagnet on a square lattice. By utilizing a better optimized spectrometer we have been able to cover a large temperature range up to $T \gtrsim J$. Over the full temperature range, we observe generally good agreement with the predictions for the *renormalized classical* region for both the correlation length ξ and the amplitude S_0. For the correlation length, our data do deviate slightly from the CHN result in a way that is consistent with the QMC, HTE, and PQSCHA calculations.

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[24] $S(k,\omega)$ for the QC region was calculated from a $1/N$ expansion which gives only reliable results for $0.45 < J/T < 0.8$. A new method is being developed which should extend the results to higher temperatures. S. Sachdev (private communication).