Quantum spin correlations in an organometallic alternating sign chain

M. B. Stone, W. Tian, M. D. Lumsden, G. E. Granroth, D. Mandrus, J.-H. Chung, N. Harrison, and S. E. Nagler

1Neutron Scattering Science Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831 USA
2Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA
3Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
4Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
5NCNR, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
6Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA
7Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA

High resolution inelastic neutron scattering is used to study excitations in the organometallic magnet DMACuCl₃. The correct magnetic Hamiltonian describing this material has been debated for many years. Combined with high field bulk magnetization and susceptibility studies, the new results imply that DMACuCl₃ is a realization of the $S = 1/2$ alternating antiferromagnetic-ferromagnetic (AFM-FM) chain. Coupled-cluster calculations are used to derive exchange parameters, showing that the AFM and FM interactions have nearly the same strength. Analysis of the scattering intensities shows clear evidence for inter-dimer spin correlations, in contrast to existing results for conventional alternating chains. The results are discussed in the context of recent ideas concerning quantum entanglement.

PACS numbers: 75.10.Jm, 75.40.Gb, 75.30.Et

Low dimensional, dimerized quantum spin systems exhibit diverse physics ranging from simple spin gaps to exotic spin liquids. A prototypical example is the $S = 1/2$ Heisenberg alternating chain (HAC), defined by the Hamiltonian $H = \sum_n J_1 S_{2n-1}S_{2n} + J_2 S_{2n}S_{2n+1}$. The HAC has been widely studied theoretically and experimentally. Considering $J_1 > 0$ antiferromagnetic (AFM), ground state behavior of the HAC depends on the ratio $\alpha = J_2/J_1$. $\alpha = 1$ corresponds to the quantum critical pure AFM chain. When $|\alpha| \ll 1$ the system behaves as nearly independent dimers, and perturbation theory in $\alpha$ provides a straightforward approach to calculate physical properties of the spin gap system. For $\alpha < 0$, one has a realization of the antiferromagnetic-ferromagnetic (AFM-FM) HAC. For $\alpha \ll -1$, the HAC maps onto the $S = 1$ AFM Hal- dane chain with the dimer viewed as a composite object and the regime $\alpha \approx -1$ is particularly interesting since the system exhibits intermediate behavior between dimer and Haldane physics. Calculating physical properties must be done carefully since perturbation theory from the dimer limit is not a good approximation here.

We report new inelastic neutron scattering (INS) results for (CH₃)₂NH₂CuCl₃ [DMACuCl₃ or MCCL]. We use state of the art linked-cluster calculations and bulk measurements to show DMACuCl₃ contains a realization of the AFM-FM HAC with $\alpha = -0.92(4)$. Moreover, in contrast to results on existing AFM-AFM HACs, there is evidence for spatially extended entanglement of the principle dimers via the FM coupled spins.

DMACuCl₃ is monoclinic at room temperature with $\beta = 97.5^\circ$ with copper-halide planes separated along c by methyl groups, such that magnetic coupling is only expected in the ab-plane as shown in Fig. 15. Thermodynamic and structural considerations were used to identify DMACuCl₃ as an AFM-FM HAC along the a-axis with $\alpha \approx -1$ and, attracting interest since other experimental realizations of AFM-FM HACs have $\alpha \ll -1$. Further measurements were interpreted as independent FM and AFM dimers with evidence for a transition to long range order below $T = 0.9 K$. Preliminary INS in the disordered phase eliminated both independent dimer and a-axis chain models. Recently, it was shown that the low-temperature (LT), $T < 285 K$, structure is triclinic with two independent chains along...
The high-temperature (HT) b-axis [24, 25], cf. Fig. 1. Bond lengths in the LT structure favor HAC Cu-halide-halide-Cu or Cu-halide-Cu exchange paths, found to be relevant in other low-d magnets [2, 3, 4].

Deuterated samples were obtained by slow evaporation of a D$_2$O solution of CuCl$_2$ and (CD$_3$)$_2$ND-HCl. A 2.23 g single crystal mounted in the (hk0) plane was examined using the SPINS spectrometer at NIST configured with 80’ collimation before and after the sample and a cooled Be filter in the scattered beam. A flat PG(002) analyzer selected scattered neutrons at 5 meV. Constant wavevector, Q, scans were performed at $T = 1.8$ K indexing Q in the HT monoclinic notation with LT lattice constants, $a=12.05$ Å and $b=8.43$ Å [13].

Representative scans are shown in Fig. 2. Energy transfers were scanned up to $\hbar \omega \approx 4.5$ meV. A single peak disperses along $k$ between $0.95(2) \leq \hbar \omega \leq 1.66(2)$ meV as shown in Fig. 2(a)-(d). The mode is only weakly dispersive along $h$ at the bottom (Fig. 2(e) and (f)) and top (Fig. 2(g) and (h)) of the band with $\approx 0.2(1)$ meV dispersion along ($h$ 1.5 0). Intensity reduction for temperatures large compared to the energy scales of excitations indicates a magnetic origin, cf. Fig. 2(c). The intrinsic peak width is small compared to the instrumental resolution of $\approx 0.25$ meV FWHM. We do not see any reasonable evidence for gapless excitations or magnetic continuum scattering.

We fit the constant Q scans with Gaussian peaks to determine dispersion and intensity variation in the (hk0) plane as summarized in Fig. 3. Lack of dispersion along $h$ excludes the proposed $\omega$-axis as the chain axis, and significant dispersion along $k$ excludes non-interacting dimer models. The $k$ dispersion has periodicity $2\pi/\alpha$ in reduced units, a quantum effect showing a lack of AFM order. The FM-FM HAC is ruled out by the absence of a second dispersive mode [26]. Notably, the band maximum or minimum is at $Q = 2m\pi/\alpha$ for integer $m$. This is unusual and rules out a HAC with $\alpha > 0$. Models that can produce such dispersion include the AFM-FM HAC and the AFM-AFM spin-ladder (SL) with the HAC favored due to structural arguments.

The dispersion for the HAC and SL models can be

### FIG. 2: $T = 1.8$ K constant Q scans of DMACuCl$_3$. (c) includes data at $T = 40$ K. Lines are based upon a global fit to the AFM-FM HAC model described in the text. Dashed lines are fitted backgrounds.

### FIG. 3: (a) Scattering intensity vs. $\hbar \omega$ along (0k0). Solid lines are fits to dispersion based upon linked-cluster models. Dotted line is dispersion based upon perturbation theory for weakly coupled dimers. (b) Integrated intensity vs. $Q$. (c) Dispersion based upon Gaussian peak approximation. Lines in (b) and (c) are based upon a global fit to the AFM-FM HAC model described in the text.

### TABLE I: Resulting exchange parameters from fitting dispersion to AFM-FM HAC and AFM-AFM SL models using linked-cluster expansions (E) and perturbation theory (PT).

| model (method) | $J_1$ or $J_\perp$ (meV) | $J_2$ or $J_\parallel$ (meV) |
|----------------|--------------------------|-----------------------------|
| AFM-FM HAC (E) | 1.406(8) | -1.30(5) |
| AFM-FM HAC (PT) | 1.319(8) | -0.68(2) |
| AFM-AFM SL (E) | 1.194(6) | 0.376(5) |
| AFM-AFM SL (PT) | 1.319(8) | 0.34(1) |
calculated using perturbation theory, with an identical form to first order, \( \hbar \omega(Q) = \epsilon_1 + \epsilon_2 \cos(Q \cdot u) \) [2, 4, 11, 27], where \( \epsilon_1 = J_1|J_\perp| \) and \( \epsilon_2 = \frac{|J_\perp|}{2} |J_\parallel| \) for the HAC [SL] models. It is more accurate to use state of the art linked-cluster expansion methods [12, 14]. Parameters obtained from fits of the data to these models are summarized in Tab.I. Dispersion alone cannot differentiate between the HAC and SL models. Solid lines in Fig. 3(a) show the fit to the linked cluster calculation and the dotted line a fit to the perturbation theory. Perturbation theory is clearly inadequate to describe the AFM-FM HAC as evidenced by the large difference in fitting parameters relative to the linked cluster method. Although fits to the AFM-FM HAC dispersion characterize the magnitude of FM exchange, this comparison does not include structural information determining which bond in Fig. 1(a) is FM or AFM.

In principle, high field INS can be used to determine absolute values of exchange parameters assuming they are field independent [28]. Unfortunately, to characterize DMACuCl\(_3\) accurately in this manner would require INS at magnetic fields well over \( \mu_0 H = 20 \) T; not possible at the present time. However, it is practical to examine high field bulk thermodynamic properties. Figure 4(a) shows pulsed field magnetization of DMACuCl\(_3\) up to 20 T at \( T = 1.6 \) K. The upper critical field where all spins are FM aligned is in the vicinity of 16 T. We also plot Quantum Monte-Carlo (QMC) calculations of the magnetization for 100 spins using exchange constants determined from cluster-expansion fits of \( \hbar \omega(Q) \) [29]. The AFM-FM HAC model reproduces the upper critical field indicating that the determined energy scales are more appropriate, but neither model accounts for the linear magnetization at low-field.

Recall that the LT structure has two types of bonding, i.e. two sets of exchange parameters for quasi-1d chains along the monoclinic \( b \)-axis. However, our INS measurements indicate only a single mode. The energy scale of the second set of quasi-1d chains is either much higher, lower or identical to that of the excitation we observe. Higher energy excitations would manifest a higher energy gap in the spectrum, not seen in thermodynamic measurements. It is most reasonable that these excitations are at lower energies. The present experiment sets an upper limit of \( J' \approx 0.2 \) meV for this energy scale, indistinguishable from the incoherent elastic scattering. In the absence of a measured exchange for the weakly coupled chains, we model these moments as free-spins. This is reasonable given the temperature scale of the magnetization measurements. A conjecture of a free-spin contribution was also made in Ref. [30] to account for magnetization measurements. We therefore calculate \( M(H) \) as a composite model with half the moments included as free-spins. This accounts for the initial linear magnetization. As seen in figure 4(a), the composite AFM-FM HAC model calculation is a much better description of the the measurement than the composite AFM-AFM SL model. When \( M(H) \) is calculated using parameters derived from perturbation theory the situation is similar, but as expected the overall agreement with the data is not as good for either model.

The calculations illustrated in Fig. 4(a) are performed with no adjustable parameters. The AFM-FM HAC model accounts very well for both the low field and high field limits with deviations in the vicinity of 5 to 10 T. This may be a consequence of a field-induced collective ordered phase [22] that is not accounted for in the calculation. Willet et al. used finite chain calculations to obtain parameters that reproduce \( M(H) \) within a two chain model [23]. However, the exchange parameters they propose are incompatible with the INS data reported here, and can be ruled out by the observation of only a single excitation.

Figure 4(b) shows temperature dependent magnetic susceptibility, \( \chi(T) \). The solid line is a fit using the AFM-FM HAC:free spin composite model, with \( \chi(T) \) for the HAC calculated using a polynomial representation derived from finite-sized scaling [20]. The parameters \( J_1 = 0.973(4) \), \( J_2 = -1.235(5) \) meV and \( g = 2.096(1) \) are
reasonably consistent with INS results although clearly the latter provides a more direct measure of the exchange parameters. Figure 2(c) shows $\chi^{-1}(T)$. A linear fit for $120 < T < 270$ K leads to a value for the Curie-Weiss temperature, $\Theta = -0.9(1)K$. Linear fits to the composite model calculations of $\chi^{-1}(T)$ yield $\Theta = -0.4(3)K$ for the AFM-FM HAC, and $\Theta = -2.4(7)K$ for the AFM-AFM SL confirming the chain model is in better accord with the data.

Neutron scattering intensities for a straight HAC can be calculated using the coupled-cluster expansions [12]. Comparison to these using our HAC exchange parameters and noting the broad wave-vector dependence of the integrated intensity, cf. Fig. 3(a) and (b), the short bond in Fig. 3 is likely AFM. However, the bonding geometry in DMACuCl$_3$ is complicated by in-plane zig-zag and small out of plane components. We incorporate bond vectors within a single mode approximation (SMA) [2, 8] to calculate the dynamic spin correlation function. The SMA is justified by the observation that the INS data show a single peak with no appreciable additional intensity, and that the calculated spectral weight is dominated by single particle excitations for $\alpha \approx -1$ [12]. The SMA to the scattering intensity is

$$\tilde{I}_{m}(Q, h\omega) \propto \frac{|F(Q)|^2}{h\omega(Q)} \sum_d J_d \langle S_0 \cdot S_d \rangle [1 - \cos(Q \cdot d)] \delta(h\omega - h\omega(Q)).$$

(1)

$\langle S_0 \cdot S_d \rangle$ is the spin correlation function, $d$ is a bond vector, and the sum is over the AFM and FM bond, $d_1$ and $d_2$. We use 74 constant $Q$ scans ($h\omega \geq 0.5$ meV) in a global fit to Eq. (1) convolved with the instrumental resolution function and a dispersion based upon the AFM-FM HAC cluster-expansion using parameters in Tab. I. Parameters include an overall scaling factor and the ratio $A = \langle S_0 \cdot S_{d_1} \rangle / \langle S_0 \cdot S_{d_2} \rangle$. The results reproduce well the dispersion and intensity modulation and are shown as solid lines in Figs. 2 and 3(b,c) with $A = 0.26(4)$. Allowing exchange constants to be fit parameters results in $J_1 = 1.399(6)$ and $J_2 = -1.07(3)$ meV, and $A = 0.27(4)$.

The SMA has been applied to the AFM-AFM HAC, with the result that $\langle S_0 \cdot S_{d_1} \rangle$ is consistent with the isolated dimer expectation of $-3/4$, and the empirical value for $\langle S_0 \cdot S_{d_2} \rangle = \langle S_0 \cdot S_{d_2} \rangle = 0$ is. The significance of this is discussed by Brukner et al. [31], who shows that the intra-dimer correlation is a reflection of quantum entanglement in the bulk system. Entanglement is localized to within one dimer for the AFM-AFM HAC. In contrast for DMACuCl$_3$, the inter-dimer spin correlation is clearly non-zero. This is expected since as alpha tends to $-\infty$ the FM coupled spins can evolve towards a composite $S = 1$ entity, with a $T = 0$ spin-spin correlation in the Haldane chain extending over several lattice spacings [32]. Since the quantum correlation becomes spatially extended, adjacent dimers in the AFM-FM HAC can be thought of as more entangled than those in the AFM-AFM HAC. Notably, fitting the SMA for a purely AFM SL to the present data yields $A \approx 0$, indicating suppression of inter-dimer entanglement for purely AFM coupled dimers in that case as well.

In summary, high resolution INS, combined with high field magnetization and susceptibility measurements show that DMACuCl$_3$ is a quasi-1d AFM-FM HAC with $\alpha \approx -1$, intermediate between weakly coupled dimer and Haldane regimes. The exchange parameters are determined from the dispersion using the results of coupled cluster series expansions. Applying the SMA to analyze the scattering intensity shows that the inter-dimer spin correlation is significant, indicating that the AFM-FM HAC may be a model system for studying the effect of spatially extended quantum entanglement on bulk properties.

We acknowledge discussions with M. Meisel, A. Zehludov, T. Barnes, R. R. P. Singh and W. Zheng. DM acknowledges B. Lake for drawing his attention to DMACuCl$_3$. Research sponsored by the Division of Materials Sciences and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. The NHMFL is supported by the DOE, NSF and Florida State University.

[1] D. Poilblanc et al., Phys. Rev. B 73, 100403(R) (2006).
[2] M. B. Stone et al., Phys Rev. B 64, 144405 (2001).
[3] T. Masuda et al., Phys. Rev. Lett. 96, 047210 (2006).
[4] M. M. Turnbull et al., Coord. Chem. Rev. 249, 2567 (2005).
[5] A. Brooks Harris, Phys. Rev. B 7, 3166 (1973).
[6] G. S. Uhrig and H. J. Schulz, Phys. Rev. B 54, R9624 (1996).
[7] T. Barnes et al., Phys. Rev. B 59, 11384 (1999).
[8] G. Xu et al., Phys. Rev. Lett. 84, 4465 (2000).
[9] B. Lake et al., J. Phys. Cond. Mat. 9, 10951 (1997) and A. W. Garrett et al., Phys. Rev. Lett. 79, 745 (1997).
[10] K. Hida, Phys. Rev. B 45, 2207 (1992) and K. Hida, J. Phys. Soc. Jpn. 63, 2514 (1994).
[11] S. Watanabe and H. Yokoyama, J. Phys. Soc. Jpn. 68, 2073 (1999).
[12] W. Zheng et al., Phys. Rev. B 74, 172407 (2006).
[13] K. Hida, J. Phys. Soc. Jpn. 67, 1416 (1998); M. Bocquet and Th. Jolicoeur, Eur. Phys. J. B 14, 47 (2000).
[14] Hamer et al, Phys. Rev. B 68, 214408 (2003) and Oitmaa et al.,Phys. Rev. B 54, 1009 (1996).
[15] R. Willet, J. Chem. Phys., 44, 39 (1966).
[16] B. C. Gerstein et al., J. Appl. Phys. 43, 1932 (1972).
[17] M. Hurley and B. C. Gerstein, J. Chem. Phys. 69, 6667 (1973).
[18] S. O’Brien et al., Inorg. Chim. Acta 141, 83 (1988).
[19] T. Nishikawa et al., J. Phys. Soc. Jpn. 67 1988 (1998); M. Hagiwara et al., J. Phys. Soc. Jpn. 66 1792 (1997); and I. Vasilevsky et al., Inorg. Chem. 30 4082 (1991).
[20] J. J. Borrás-Almenar et al., Inorg. Chem. 33 5171 (1994).
[21] Y. Ajiro et al., Physica B 329-333, 1008 (2003).
[22] M. B. Stone et al., AIP Conf. Proc. 850, 1015 (2006).
[23] M. B. Stone et al., Physica B 385-386, 438 (2006).
[24] Y. Inagaki et al., J. Phys. Soc. Jpn. 74, 2683 (2005).
[25] R.D. Willett et al., Inorg. Chem. 45, 7689 (2006).
[26] G. Huang, et al., Phys. Rev. B 43 11197 (1991).
[27] T. Barnes et al., Phys. Rev. B 47, 3196 (1993).
[28] R. Coldea et al., Phys. Rev. Lett. 88, 137203 (2002).
[29] http://alps.comp-phys.org/ and M. Troyer et al. Lec. Notes in Comp. Sci. 1505, 191 (1998).
[30] B. C. Watson, Ph. D. Thesis, Univ. of Florida (2000).
[31] C. Brukner et al., Phys. Rev. A 73, 12110 (2006).
[32] S. Ma et al., Phys. Rev. Lett. 69, 3571 (1992) and L. P. Regnault et al., Phys. Rev B 50, 9174 (1994).