Weakly coupled alternating $S = \frac{1}{2}$ chains in the distorted honeycomb lattice compound Na$_2$Cu$_2$TeO$_6$

Shang Gao,$^{1,2}$ Ling-Fang Lin,$^3$ Andrew F. May,$^1$ Binod K. Rai,$^1$ Qiang Zhang,$^2$ Elbio Dagotto,$^{1,3}$ Andrew D. Christianson,$^4$ and Matthew B. Stone$^2$

$^1$Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
$^2$Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
$^3$Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA

(Received 3 October 2020; accepted 17 November 2020; published 2 December 2020)

Spin-$\frac{1}{2}$ chains with alternating antiferromagnetic (AF) and ferromagnetic (FM) couplings exhibit quantum entanglement as the integer-spin Haldane chains and might be similarly utilized for quantum computations. Such alternating AF-FM chains have been proposed to be realized in the distorted honeycomb lattice compound Na$_2$Cu$_2$TeO$_6$, but to confirm this picture a comprehensive understanding of the exchange interactions including terms outside of the idealized model is required. Here, we employ neutron scattering to study the spin dynamics in Na$_2$Cu$_2$TeO$_6$ and accurately determine the coupling strengths through the random phase approximation and density functional theory approaches. We find the AF and FM intrachain couplings are the dominant terms in the spin Hamiltonian, while the interchain couplings are AF but perturbative. This hierarchy in the coupling strengths and the alternating signs of the intrachain couplings can be understood through their different exchange paths. Our results establish Na$_2$Cu$_2$TeO$_6$ as a weakly coupled alternating AF-FM chain compound and reveal the robustness of the gapped ground state in alternating chains under weak interchain couplings.

DOI: 10.1103/PhysRevB.102.220402

Introduction. Spin-$\frac{1}{2}$ chains with alternating antiferromagnetic (AF) and ferromagnetic (FM) couplings are known to exhibit gapped excitations and exponentially decaying correlations [1,2], which are different from those of the spin-$\frac{1}{2}$ Bethe chains with uniform couplings [3] but more similar to the spectrum of integer-spin Haldane chains [4,5]. Assuming alternating couplings of $J_1$ (AF) and $J_2$ (AF ($\beta < 1$), the Hamiltonian of an alternating chain can be written as $H = \sum_j J_1 S_{j+1} \cdot S_j + \sum_j J_2 S_{j+1} \cdot S_j$. In the special case of $\beta = 0$, an alternating chain can be viewed as disconnected spin dimers, and the local singlet-triplet (triphon) excitations over the dimers account for the excitation gap in the spectrum. Nonzero $J_2$ couplings will introduce dispersion for the triplon excitations. At $\beta = 1$, one recovers the gapless character of a Bethe chain. In the whole range of $\sim \beta < 1$, theoretical calculations have revealed a hidden string order that is protected by the $Z_2 \times Z_2$ global rotation symmetry [6,7], showing that the gapped ground state of alternating chains is a symmetry-protected topological state of the same type as that of Haldane chains [8]. Considering the prospect of Haldane chains as the resource ground state for measurement-based quantum computation [9], the additional degrees of freedom in $S = \frac{1}{2}$ alternating chains may be important to explore further flexibility in qubit operations.

Experimental realizations of alternating AF-FM chains are limited to a few compounds, including CuNb$_2$O$_6$ [10], DMACuCl$_3$ [11], Na$_3$Cu$_2$SbO$_6$ [12], and BaCu$_2$V$_2$O$_8$ [13], where the exchange couplings have been accurately determined through neutron scattering. Recently, a new candidate compound, Na$_3$Cu$_2$TeO$_6$, was proposed [14–18]. Similar to Na$_3$Cu$_2$SbO$_6$, the Cu$^{2+}$ ions ($S = \frac{1}{2}$) in Na$_2$Cu$_2$TeO$_6$ form a distorted honeycomb lattice in the $ab$ plane, which are separated by the Na$^+$ layers along the $c$ axis (see Fig. 1). Magnetic susceptibility measurements on a powder sample of Na$_2$Cu$_2$TeO$_6$ revealed a spin gap $\Delta \sim 127$ K [14], which has been attributed to strong AF couplings $J_1$ in the density functional theory (DFT) calculations [14,16–18]. However, controversy remains as to the sign of the intrachain coupling $J_2$: Magnetic susceptibility data can be fitted equally well by the FM or AF $J_2$ model [15], and this ambiguity is not resolved by contradictory DFT results that support either AF [14,16] or FM [17,18] $J_2$ couplings. The magnitude of $J_2$ also remains

FIG. 1. (a), (b) Crystal structure of Na$_2$Cu$_2$TeO$_6$ viewed along the (a) $b$ and (b) $c^*$ axes with the Cu$^{2+}$ ions forming chains along the $b$ axis. The size of the unit cell is indicated by black lines. The Cu$^{2+}$ spins are coupled through alternating $J_1$ (red) and $J_2$ (blue) interactions along the chain and $J_3$ interactions (gray) between the chains. Cu-O bonds of different lengths are indicated in the CuO$_6$ octahedron at the left bottom corner of (b), with $b_1 = 1.978(1) \, \text{Å}$, $b_2 = 1.999(1) \, \text{Å}$, and $b_3 = 2.533(1) \, \text{Å}$.
to be determined, as comparable $J_2$ and $J_3$ couplings might invalidate a spin chain scenario.

To establish whether Na$_2$Cu$_2$TeO$_6$ represents a rare realization of the alternating AF-FM spin chains, here we perform inelastic neutron scattering (INS) experiments on a single-crystal sample of Na$_2$Cu$_2$TeO$_6$ to determine the exchange coupling strengths. We confirm the spin gap originates from the dominant AF coupling $J_1$ (22.8 meV), and the interchain coupling $J_3$ is found to be much weaker (1.3 meV). Most importantly, we reveal the intrachain coupling $J_2$ to be FM with a strength (−8.7 meV) that is much higher than $J_3$, thus establishing Na$_2$Cu$_2$TeO$_6$ as a weakly coupled alternating AF-FM chain compound. Through the DFT calculations, the alternating signs of the interchain couplings can be attributed to their different exchange paths.

Experimental details. Polycrystalline Na$_2$Cu$_2$TeO$_6$ was utilized as a source material for crystal growth in a flux based on TeO$_2$ and Na$_2$CO$_3$. Details for the polycrystal synthesis and characterization can be found in the Supplemental Material [19]. Powders of these materials in a ratio of 2(Na$_2$Cu$_2$TeO$_6$):1(Na$_2$CO$_3$):4(TeO$_2$) were mixed and loaded into a Pt crucible that was covered with a Pt lid. The crucible was heated rapidly to 900 °C at which point it was turned off to cool. The translucent green crystals were recovered by boiling the product-filled crucible in a hot aqueous solution of potassium hydroxide, followed by additional rinsing in de-ionized water.

INS experiments on Na$_2$Cu$_2$TeO$_6$ were performed on the fine-resolution Fermi chopper spectrometer SEQUOIA at the Spallation Neutron Source (SNS) of the ORNL. A single crystal (mass ∼140 mg) was aligned with the (001) vector vertical. A closed cycle refrigerator (CCR) was employed to reach temperatures $T$ down to 5 K. The incident neutron energy was $E_i = 60$ meV, and Fermi chopper frequencies of 180 and 420 Hz were selected in the high-intensity and high-resolution modes, respectively. Data were acquired by rotating the sample in 1° steps, covering a total range of 200° at 5 K and 100° at higher temperatures. Data reductions and projections were performed using MANTID [20] and HORACE software [21].

First-principles calculations using the projector augmented-wave (PAW) method were performed based on the DFT as implemented in the Vienna ab initio simulation package (VASP) code [22–24]. The generalized gradient approximation (GGA) and the revised Perdew-Burke-Ernzerhof (PBEsol) function were used to treat the electron density of states with orbital $d_{x^2−y^2}$ were constructed using the WANNIER90 code [27,28].

Results. As shown in Fig. 1(a), the large separation of $c = 5.92$ Å between the honeycomb layers indicates likely negligible interlayer couplings. This is immediately confirmed in our single-crystal INS experiment. Figure 2(a) plots a representative slice of the measured spectrum along the $Q_1$ direction that is perpendicular to the ab plane. A single excitation mode is observed at $\sim 18$ meV, which is flat within the instrument resolution (1.6 meV at the elastic line). In contrast, strong dispersions in the energy range of $E = [17, 28]$ meV are observed in the ab plane as summarized in Figs. 3(a)–3(d), thus confirming all the related couplings to be within the honeycomb layers.

The lack of dispersion out of the ab plane allows us to integrate data along $Q_z$ for better statistics. Figure 2(b) plots the scattering intensity integrated in the range of $Q_z$ in $[-2, 2]$ (r.l.u.) and $E$ in $[17, 28]$ meV. Along the $Q_z$ direction, intensity is strongly modulated with a periodicity of $\sim 1.5$ (r.l.u.). For dimer systems, it is established that intensity of the triplon excitations is modulated by the dimer structure factor $S(Q) \propto [1 − \cos \left(\mathbf{Q} \cdot \mathbf{r}\right)]$, where $\mathbf{r}$ is the vector that connects the two spin sites within the dimer [29–31]. Therefore, the modulation along $Q_z$ indicates that dimers in Na$_2$Cu$_2$TeO$_6$ are forming along the b axis, and its periodicity tells the bond distance $r$ within the dimers. As shown in Fig. 2(c), the model that assumes dimers forming over the $J_1$ bonds with a distance of $r_1 = 2b/3$ accurately describes the intensity modulation,
The dispersion relation can be expressed as:

$$J = \frac{1}{\Delta_0} \exp\left(-\frac{\Delta_0}{T}\right),$$

where $\alpha, \gamma, \text{ and } \Gamma_0$ are fitting parameters, and $\Delta_0$ is the gap size at 0 K and is fixed at 18.0 meV. The validity of the activated behavior further confirms the similarity between the $S = \frac{1}{2}$ alternating AF-FM chains and the integer-spin Haldane chains, thus revealing the robustness of the topological ground state against weak interchain couplings.

**Discussion.** The emergence of spin chains in Na$_2$Cu$_2$TeO$_6$ can be ascribed to the distortion of the honeycomb lattice. As shown in Fig. 1(b), the exchange paths of $J_1$ involve the longest Cu-O bonds $b$ of the distorted octahedra. Therefore,
the $J_3$ couplings are expected to be weak as the unoccupied Cu $3d_{x^2-y^2}$ orbitals disfavor the elongated bond direction, which reduces the electron hopping between the chains.

The sign of the interchain couplings $J_2$ is more subtle, and different scenarios exist in the previous DFT calculations [14,16–18]. As summarized in the Supplemental Material, our DFT calculations confirm the alternating FM and AF intrachain couplings, in agreement with the experiment. The contrasting $J_1$ and $J_2$ couplings can be understood through the Wannier functions (WFs) as plotted in Fig. 5(a). Due to the contributions from the O 2$p$ states, the WFs overlap directly over the $J_1$ paths but are almost orthogonal over the $J_2$ path. Therefore, the $J_1$ path, in spite of its longer distance, develops a stronger coupling than that over the $J_2$ path. Based on the WFs, the signs of the couplings can be understood through the Goodenough-Kanamori-Anderson rules [42–45] as shown in Fig. 5(b). For the $J_1$ couplings, the Cu-O⋯O-Cu supersuperexchange leads to an AF interaction between the Cu$^{2+}$ spins, while for the $J_2$ couplings, the interaction becomes FM as the angle of $\angle$ Cu-O-Cu is close to $\sim90^\circ$, which means a pair of orthogonal O 2$p$ orbitals with parallel spins are involved in the virtual electron hopping.

**Conclusions.** Neutron scattering experiments have been performed on the honeycomb lattice compound Na$_2$Cu$_2$TeO$_6$ to study its spin correlations. A triplon excitation mode was observed, which exhibits strong dispersion along the chain but weak dispersion perpendicular to the chain. Under the random phase approximation, the intrachain couplings were found to be alternating AF and FM, and a weak interchain coupling was also established. The emergence of spin chains in Na$_2$Cu$_2$TeO$_6$ was ascribed to the distortion of the honeycomb lattice, and the alternating intrachain couplings were understood through the DFT calculations. Our works establish the existence of weakly coupled alternating AF-FM spin-$1/2$ chains in Na$_2$Cu$_2$TeO$_6$ and reveal a robust gapped ground state that is similar to that of the integer-spin Haldane chains.

**Acknowledgments.** We acknowledge helpful discussions with Jyong-Hao Chen, Tong Chen, and Tao Hong. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. This research used resources at the Spallation Neutron Source (SNS), a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory (ORNL). ORNL is managed by UT-Battelle, LLC, under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The U.S. Government retains, and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this manuscript, or allow others to do so, for U.S. Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan [51].

[1] K. Hida, Ground-state phase diagram of the spin-1/2 ferromagnetic-antiferromagnetic alternating heisenberg chain with anisotropy, Phys. Rev. B 46, 8268 (1992).
[2] K. Hida, Excitation spectrum of the spin-1/2 ferromagnetic-antiferromagnetic alternating Heisenberg chain, J. Phys. Soc. Jpn. 63, 2514 (1994).
[3] H. Bethe, Zur Theorie der Metalle. I. Eigenwerte und Eigenfunktionen der linearen Atomkette, Z. Phys. 71, 205 (1931).
[4] F. D. M. Haldane, Nonlinear Field Theory of Large-Spin Heisenberg Antiferromagnets: Semiclassically Quantized Solitons of the One-Dimensional Easy-Axis Néel State, Phys. Rev. Lett. 50, 1153 (1983).
WEAKLY COUPLED ALTERNATING $S = \frac{1}{2}$ ...

PHYSICAL REVIEW B 102, 220402(R) (2020)
layers and Unconventional Criticality without Frustration in BaCuSi$_2$O$_6$, Phys. Rev. Lett. 124, 177205 (2020).

[37] K. Wierschem and P. Sengupta, Characterizing the Haldane phase in quasi-one-dimensional spin-1 Heisenberg antiferromagnets, Mod. Phys. Lett. B 28, 1430017 (2014).

[38] T. Jolicœur and O. Golinelli, $\sigma$ model study of Haldane-gap antiferromagnets, Phys. Rev. B 50, 9265 (1994).

[39] M. P. Nightingale and H. W. J. Blöte, Gap of the linear spin-1 Heisenberg antiferromagnet: A Monte Carlo calculation, Phys. Rev. B 33, 659 (1986).

[40] A. Zheludev, S. E. Nagler, S. M. Shapiro, L. K. Chou, D. R. Talham, and M. W. Meisel, Spin dynamics in the linear-chain $S = 1$ antiferromagnet Ni(C$_3$H$_{10}$N$_2$)$_2$N$_3$(ClO$_4$)$_2$, Phys. Rev. B 53, 15004 (1996).

[41] A. K. Bera, B. Lake, A. T. M. N. Islam, and A. Schneidewind, Critical properties of coupled anisotropic Haldane spin chains in a magnetic field, Phys. Rev. B 92, 060412(R) (2015).

[42] P. W. Anderson, Antiferromagnetism. Theory of superexchange interaction, Phys. Rev. 79, 350 (1950).

[43] J. B. Goodenough, Theory of the role of covalence in the perovskite-type manganites [La,M(II)]MnO$_3$, Phys. Rev. 100, 564 (1955).

[44] J. B. Goodenough, An interpretation of the magnetic properties of the perovskite-type mixed crystals La$_{1-x}$Sr$_x$CoO$_{3-x}$, J. Phys. Chem. Solids 6, 287 (1958).

[45] A. S. Moskvin, N. S. Ovanesyan, and V. A. Trukhtanov, Angular dependence of the superexchange interaction Fe$^{3+}$-O$^2-$-Cr$^{3+}$, Hyperfine Interact. 1, 265 (1975).

[46] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Physica B: Condens. Matter 192, 55 (1993).

[47] Z. Wang, N. Qureshi, S. Yasin, A. Mukhin, E. Ressouche, S. Zherlitsyn, Y. Skourski, J. Geshev, V. Ivanov, M. Gospodinov, and V. Skurnyev, Magnetoelectric effect and phase transitions in CuO in external magnetic fields, Nat. Commun. 7, 10295 (2016).

[48] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study, Phys. Rev. B 57, 1505 (1998).

[49] H. Jeschke, I. Opahle, H. Kandpal, R. Valentí, H. Das, T. Saha-Dasgupta, O. Janson, H. Rosner, A. Brühl, B. Wolf, M. Lang, J. Richter, S. Hu, X. Wang, R. Peters, T. Pruschke, and A. Honecker, Multistep Approach to Microscopic Models for Frustrated Quantum Magnets: The Case of the Natural Mineral Azurite, Phys. Rev. Lett. 106, 217201 (2011).

[50] O. Janson, I. Rousochatzakis, A. A. Tsirlin, M. Belesi, A. A. Leonov, U. K. Rößler, J. van den Brink, and H. Rosner, The quantum nature of skyrmions and half-skyrmions in Cu$_2$OSeO$_3$, Nat. Commun. 5, 5376 (2014).

[51] http://energy.gov/downloads/doe-public-access-plan.