Temperature-dependent magnetism in artificial honeycomb lattice of connected elements

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Artificial magnetic honeycomb lattices are expected to exhibit a broad and tunable range of novel magnetic phenomena that would be difficult to achieve in natural materials, such as long-range spin ice, entropy-driven magnetic charge-ordered states, and spin order due to the spin chirality. Eventually, the spin correlation is expected to develop into a unique spin-solid-state-density ground state, manifested by the distribution of the pairs of vortex states of opposite chirality. Here we report the creation of an artificial permalloy honeycomb lattice of ultrasmall connecting bonds, with a typical size of ≈12 nm. Detailed magnetic and neutron-scattering measurements on the newly fabricated honeycomb lattice demonstrate the evolution of magnetic correlation as a function of temperature. At low enough temperature, neutron-scattering measurements and micromagnetic simulation suggest the development of a loop state of vortex configuration in this system.

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I. INTRODUCTION

An artificial magnetic honeycomb lattice manifest a two-dimensional prototype of three-dimensional geometrically frustrated magnets where intriguing yet novel magnetism has been intensively explored in recent times [1,2]. It includes the ice analog of magnetism, spin ice, spin liquid, and exotic quantum-mechanical properties of the resonant valence bond state [3–5]. The concept of an artificial honeycomb lattice or a two-dimensional artificial structure was originally conceived to study the physics of spin-ice states [6–9]. Since then it has evolved into a general arena to not only explore the entire spectrum of novel magnetism in geometrically frustrated magnets but also a broad and tunable range of magnetic phenomena that would be difficult to achieve in natural materials [10,11].

It became possible due to a recent theoretical proposal, which suggests that a magnetic moment or spin can be considered a pair of magnetic charges of opposite polarities, as if it is a “dumbbell,” that interact via the Coulomb interaction [12,13]. The direction of magnetic moment or spin points from the negative to the positive charge.

The concept of magnetic charge can be utilized to describe the competing magnetic states in an artificial honeycomb lattice. Under this scheme, the moment along the honeycomb element can be represented as a dipole of ±1 unit charge. Since each vertex of the honeycomb lattice is joined by three moments, it can possess a net magnetic charge of ±3 or ±1 units depending on the direction of the moment along the honeycomb element [as described schematically in Figs. 1(a)–1(c)] [14]. Here, charges ±3 arise when all three magnetic moments along the honeycomb element point to or away from the vertex at the same time, respectively. Such an arrangement of moments is called an “all-in or all-out” configuration. On the other hand, if two of the moments point to the vertex and one points away from the vertex (or vice versa), then the vertex possesses a net magnetic charge of ±1 unit. This is often referred to as a “two-in and one-out” (or vice versa) configuration. At sufficiently high temperature, the lattice can be described as a paramagnetic gas and consists of the random distribution of ±3 and ±1 magnetic charges. Recent theoretical calculations have shown that an artificial magnetic honeycomb lattice can undergo a variety of novel ordered regimes of correlated spins and magnetic charges of both fundamental and practical importance as a function of temperature. It includes long-range spin ice, entropy-driven magnetic charge-ordered states, and spin order due to the spin chirality as a function of reducing temperature [15–18]. At low enough temperature, magnetic correlation is expected to develop into a spin-solid-state-density where the magnetization profile assumes a chiral vortex configuration involving six vertices of the honeycomb lattice [see Fig. 1(d)] [19]. The spin solid state, manifested by the distribution of the pairs of vortex states of opposite chiralities across the lattice, provides a unique opportunity to realize a magnetic material with net zero entropy and magnetization for an ordered ensemble of magnetic moments [10,19].

The experimental efforts to realize the temperature-dependent magnetic correlations in an artificial honeycomb lattice are limited due to the employment of the present nanofabrication method of electron-beam lithography (EBL) [1]. The EBL technique results in small sample size with large connecting element (or bond of the honeycomb lattice) of the order of 500 nm to a few micrometers. Such a large element size leads to an interelemental energy of $1 \times 10^4$–$1 \times 10^5$ K [1,20]. Recent explorations of large-element-size disconnected honeycomb lattices and other frustrated two-dimensional structures, e.g., square spin ice or tetris lattice, have revealed interesting thermal dependence of the magnetic properties [21–24]. An alternative approach to reduce the interelemental energy...
FIG. 1. Schematic description of spin configuration on a two-dimensional honeycomb lattice vertex and the atomic force micrograph. (a)–(c) Typical two-out, one-in and all-out spin arrangements on a vertex of a two-dimensional artificial magnetic honeycomb lattice resulting in net magnetic charges of $\pm Q$ and $\pm 3Q$, respectively. (d) Theoretical researches suggest that, at sufficiently low temperature, magnetic charges at the vertexes of an artificial honeycomb lattice can arrange themselves to create a spin solid state, manifested by the periodic arrangement of pairs of chiral vortex states. (e) A full-size atomic force micrograph of artificial honeycomb lattice, derived from a diblock porous template combined with reactive ion etching. The bond length, width, and lattice separation are approximately 12 nm, 5 nm, and 26 nm, respectively. (f) Atomic force micrograph of a typical metallic honeycomb lattice fabricated using the method described in the text and the Supplemental Material.

involves the idea of a disconnected honeycomb structure where magnetic elements are very thin and well separated. It has been shown that such a sample fabrication design significantly reduces the interelemental energy between the honeycomb bonds, thus making it possible to explore the predicted temperature-dependent phase diagram [25–28].

Here we propose a nanofabrication scheme that allows the creation of a macroscopic-size artificial honeycomb lattice with ultrasmall dimensions of the connecting elements: $\simeq 12$ nm $\times$ 5 nm $\times$ 5 nm. We report the temperature dependence of magnetization in the connected artificial honeycomb lattice, which exhibits a near-zero magnetization at low temperature. The ultrasmall connecting elements of the honeycomb lattice exhibit an estimated dipolar energy of the order of $\simeq 10$ K. Such a small interelemental energy makes the application of temperature a feasible tuning parameter to explore novel magnetic correlations in the artificial magnetic honeycomb lattice. Magnetic and neutron-scattering measurements on the newly fabricated system indeed reveal multiple magnetic regimes, suggestive of varying magnetic correlations, as a function of the reducing temperature. At low temperature, $T \lesssim 30$ K, neutron-scattering measurements suggest that the system tends to develop a loop state of the vortex configuration.

**II. SAMPLE FABRICATION AND MEASUREMENT METHODS**

The fabrication scheme of the artificial honeycomb lattice is described in detail in the Supplemental Material. Basically, it begins with the creation of a nanoporous polymer template, derived from a self-assembled diblock copolymer film, on top of a silicon substrate (see Fig. S1 in the Supplemental Material) [29,30]. The nanoporous template exhibits a typical pore diameter of $\simeq 12$ nm and the center-to-center lattice spacing of 26 nm. The silicon substrate, underneath the diblock template, is reactively etched using CF4 gas to transfer the hexagonal pattern to the substrate. In Fig. 1(e), we show the atomic force micrograph of the resulting hexagonal structure in the silicon substrate. The top layer of the hexagonal substrate depicts a honeycomb pattern. This property is exploited to create a two-dimensional metallic honeycomb lattice of the ultrasmall bond by depositing magnetic material in almost parallel orientation on top of the hexagonal silicon substrate only (see Fig. S2 in the Supplemental Material for a schematic description) [29]. The substrate is uniformly rotated about its axis during the deposition process. Figure 1(f) shows the atomic force microscopy image of a typical metallic honeycomb lattice. The new fabrication method, utilizing the diblock template technique, provides a large throughput sample of the artificial honeycomb lattice, which is quite suitable for the bulk properties investigation using various macroscopic probes. The honeycomb samples were preserved in a vacuum environment to reduce exposure to air. Magnetic measurements were performed using a Quantum Design magnetic property measurement system (MPMS) on a 5 mm $\times$ 5 mm sample. Polarized neutron-scattering experiments were performed on a 1 in.$^2$ sample at the magnetism reflectometer, beam line 4A, of the Spallation Neutron Source (SNS), at Oak Ridge National Laboratory. The instrument used the time-of-flight technique in a horizontal scattering geometry. The beam was collimated
FIG. 2. In-plane magnetic measurements and polarized off-specular neutron reflectometry data. (a) Here we show $M$ vs $T$ data in zero-field-cooled (ZFC) and field-cooled (FC) measurements at characteristic fields. $M$ vs $T$ measurements in different fields not only exhibit strong temperature dependence but also reveal multiple ordering regimes as functions of field and temperature (also see inset). (b) Spin-solid-state configuration, used to simulate the off-specular polarized reflectometry profile [(d), right]. (c) Off-specular neutron-reflectometry data recorded with spin-up incident polarization at $T=300$ and 5 K, respectively. Here, the $x$ axis indicates the in-plane correlation while the $y$ axis indicates the out-of-plane correlation. The specular reflection at room temperature, indicating a paramagnetic state, is replaced by a broad diffuse scattering extending along the $x$ axis, primarily due to the development of the spin solid phase. (d) Numerically simulated off-specular neutron-reflectometry profiles for paramagnetic [weakly ferromagnetic (FM)] honeycomb film (left) and the spin solid state (right) are consistent with the experimental data. Compared to the off-specular data where a very weak intensity is observed, specular reflection is strong in the FM case (left). Unlike the FM case, the simulated profile using the spin solid state [as shown in (b)] exhibits bands of broad scattering along the horizontal axis (right) with almost negligible specular intensity. The error bar represents one standard deviation in the experimental data.

with a set of slits before the sample and measured with a two-dimensional (2D) position-sensitive $^3$He detector. Polarization and analysis used reflective supermirror technology.

III. MAGNETIC AND NEUTRON-SCATTERING MEASUREMENTS

Magnetometry is a key macroscopic probe to obtain information about the static and dynamic magnetic properties of a system as functions of temperature and field. The macroscopic size of the newly designed artificial honeycomb lattice is well suited for investigation using this measurement technique. We have performed detailed magnetic measurements on the recently fabricated artificial honeycomb lattice of connecting permalloy (Ni$_{90}$Fe$_{20}$) bonds. A magnetic field was applied along an in-plane direction to the sample. As shown in Fig. 2(a), the zero-field-cooled (ZFC) and field-cooled (FC) curves of $M$ vs $T$ measurements depict the temperature dependence with multiple magnetic regimes in the honeycomb lattice. At $T \geq 300$ K, the system is a paramagnetic gas (spin gas). As temperature is reduced, the system crosses over into a weak magnetic ordered state at $T \approx 250$ K, indicated by small downward cusp in the low field data [also see the inset in Fig. 2(a)]. For further decrease in temperature below $T = 100$ K, another small downward cusp—indicating a new magnetic regime—is detected. As the applied field increases, the irreversibility between the FC and ZFC curves gradually shifts to lower temperature, before disappearing at $H \geq 500$ Oe. The strong sensitivity of various magnetic correlation regimes to the applied field is also consistent with previous observations of the field-induced avalanche effect in the large-element-size artificial honeycomb lattice, where the field application tends...
to destroy the delicate short-range spin-ice order due to two-in and one-out (or vice versa) magnetic configuration [1,8,14].

The temperature-dependent magnetization curves exhibit a tendency toward the zero magnetization state (see ZFC curves) at temperatures below \( T = 30 \text{ K} \). This behavior becomes more apparent at higher magnetic field. For instance, at \( H = 500 \text{ Oe} \), the net magnetization of the honeycomb lattice reduces rapidly towards zero value at \( T \leq 30 \text{ K} \) from the large saturation value. This behavior is only observed in the zero-field-cooled measurement, i.e., when the sample is cooled to the base temperature in zero magnetic field. Thus, the system develops the near-zero magnetization state in the “absence” of a magnetic field. As soon as a magnetic field is applied, the correlated moments tend to abandon that delicate zero-magnetization state. When cooled back in an applied field (as small as \( H = 25 \text{ Oe} \)), the moments remain locked into the field-aligned value. The lock-in temperature reduces with increasing magnetic field. Our efforts of accessing the net-zero-magnetization state in the newly fabricated permalloy honeycomb lattice was hampered by the technical limitation of the present superconducting quantum interference device (SQUID) magnetometer, which could not be cooled below \( T = 5 \text{ K} \). Nonetheless, the trend towards zero moment as \( T \to 0 \text{ K} \) is apparent in the ZFC curve of the magnetization data. Magnetic measurements were also performed for the perpendicular field application to the sample plane. As shown in Fig. S3 in the Supplemental Material [29], no appreciable change in the magnetization pattern of ZFC and FC curves was detected for the perpendicular field application. This behavior is not surprising for such a thin (\( \approx 5 \text{ nm} \)) honeycomb film [31]. The perpendicular direction acts as the hard axis for the magnetization reversal to take place.

In order to gain more insight into the low-temperature magnetic properties in artificial permalloy honeycomb lattices of ultrasmall elements, we have also performed polarized neutron experiments, namely, polarized neutron reflectometry (PNR) and off-specular scattering. The off-specular measurements allow us to understand the development of the in-plane magnetic structure as a function of temperature in the system. In Fig. 2(c), we plot the off-specular data in the spin-up polarization channel at \( T = 300 \text{ and } 5 \text{ K} \), where the vertical direction corresponds to the out-of-plane correlation and the horizontal direction corresponds to the in-plane correlation. The vertical line across the origin represents the specular reflectivity. The measurement at \( T = 300 \text{ K} \) already exhibits significant intensity in the specular data, as is typical for most samples and can be expected due to the saturated honeycomb structure with no in-plane magnetic contrast. Upon cooling to \( T = 5 \text{ K} \), the off-specular signal increases significantly (notice the logarithmic color scale). Also, no specular beam can be distinguished from the off-specular background and the difference between the spin-up and spin-down components vanishes. Because the nuclear structure will not change significantly upon cooling, this can only be explained by a significant change in the magnetic order. The signal itself is very flat along the \( x \) direction, suggesting the development of an in-plane magnetic correlation. A numerical simulation of the scattering profile [see Fig. 2(d)], using a vortex magnetic configuration of the spin solid state, as shown in Fig. 2(b), reproduces essential features of the experimental data, such as the band of broad scattering along the horizontal direction and an almost negligible specular reflection. It suggests that the system tends to develop a spin solid state at low temperature.

The underlying magnetism at low temperature is further investigated using magnetic hysteresis measurements. In Fig. 3(a), we plot \( M \) vs \( H \) at two characteristic temperatures of \( T = 5 \text{ and } 250 \text{ K} \). Measurement at \( T = 5 \text{ K} \) reveals a sharp transition to a near-zero-magnetization state near the zero field value, which is completely absent at \( T = 250 \text{ K} \). To understand this, we have performed micromagnetic simulations on an artificial permalloy honeycomb lattice of similar element size and thickness by utilizing the Landau-Lifshitz-Gilbert equation of magnetization relaxation in a damped medium [32]. The artificial honeycomb lattice was simulated using \( 0.2 \times 0.2 \text{ nm}^2 \) mesh size on the OOMMF platform, with magnetic field applied in plane to the lattice [33]. The simulated magnetic hysteresis curve is shown in Fig. 3(b), which depicts a striking similarity with the experimental data. The magnetic correlation near zero field is found to be dominated by the distribution of the chiral vortex configurations. At moderate
field value, the finite magnetization in the artificial honeycomb lattice is described by the short-range spin-ice correlation of two-in and one-out states (and vice versa). At sufficiently high field, the moments tend to align with the applied field direction, thus maximizing the overall magnetization of the system. The micromagnetic simulations were also performed for the honeycomb lattice with distorted bond dimensions, varying between 10 and 15 nm in length, 4 and 7 nm in width, and 4 and 7 nm in thickness, to understand the role of the quenched disorder in the system. As shown in Fig. S5 in the Supplemental Material, no significant change in the magnetic hysteresis profile was detected in this case [29].

IV. DISCUSSION

In summary, we have presented a fabrication scheme to create a macroscopic-size artificial honeycomb lattice of ultrasmall elements. Detailed measurements on the newly fabricated permalloy honeycomb lattice reveal the temperature-dependent evolution of magnetic correlation in this two-dimensional geometry. While the analysis of neutron data suggests the development of a loop state of the spin solid phase at low temperature, there are several questions that remain unanswered. For instance, the mechanism behind the zero-magnetization state in ZFC/FC measurement is not understood. Although the system is expected to develop a zero-magnetization state in the spin solid state as $T \to 0$ K, it can also arise due to other mechanisms, such as the random distribution of moments. Therefore, further research is needed to understand the origin of the zero-magnetization state. The proposed sample design can also be helpful in exploring the temperature-dependent development of a Dirac string due to the effective monopoles [1]. Previously, such a state was demonstrated to exist in an applied magnetic field in a large-element-size magnetic honeycomb lattice using x-ray dichroism measurements [8].

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