Direct visualization of surface spin-flip transition

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We report direct visualization of spin-flip transition of the surface layer in antiferromagnet MnBi$_2$Te$_7$, a natural superlattice of alternating MnBi$_2$Te$_4$ and Bi$_2$Te$_3$ layers, using cryogenic magnetic force microscopy (MFM). The observation of magnetic contrast across domain walls and step edges confirms that the antiferromagnetic order persists to the surface layers. The magnetic field dependence of the MFM images reveals that the surface magnetic layer undergoes a first-order spin-flip transition at a magnetic field that is lower than the bulk transition, in excellent agreement with a revised Mills' model. Our analysis indicates an enhancement of the order parameter in the surface magnetic layer, implying robust ferromagnetism in the single-layer limit. The direct visualization of surface spin-flip transition not only opens up exploration of surface metamagnetic transitions in layered antiferromagnets, but also provides experimental support for realizing quantized transport in ultra-thin films of MnBi$_4$Te$_7$ and other natural superlattice topological magnets.

Broken time reversal symmetry and topological band structure are the key ingredients for many interesting phenomena, such as the quantum anomalous Hall (QAH) effect and the topological magnetoelectric effect [1, 2]. Although the QAH effect has been demonstrated in ferromagnetic topological insulator (TI) thin films, the inherent disorder from doping results in inhomogeneity that limits the quantization to subkelvin temperatures [3, 4]. Intrinsic magnetic TIs provide an alternative approach to combine magnetism and topological band structure in stoichiometric compounds. For example, the Z$_2$ topological index in A-type antiferromagnets is protected by the symmetry of alternating ferromagnetic layers [6].

MnBi$_2$Te$_4$ is the first tangible candidate for an antiferromagnetic-TI (AFM-TI) [7, 9]. The observation of quantum transport in exfoliated flakes provides strong evidence of QAH and axion insulator states in zero magnetic field [10, 11], though it remains controversial [12]. Indeed, high-resolution angle-resolved photoemission spectroscopy (ARPES) reports gapless Dirac surface states, suggesting that the surface spin configuration is different from the out-of-plane A-type AFM order in bulk [13, 14]. Previous magnetic force microscopy (MFM) studies by some of us, however, confirmed that the A-type antiferromagnetic order persists to the surface layer of MnBi$_2$Te$_4$, in agreement with recent ARPES measurements [17, 18]. The robust A-type antiferromagnetic order is further corroborated by the observation of the long-sought surface spin-flip transition [17].

In spite of mounting evidence of the robust A-type AFM order, it is possible that surface relaxation is limited to the very top layer and strictly follows morphology of surface steps so that it escapes the MFM observation. This scenario, however, requires an abrupt transition from ordered to relaxed magnetic states within the septuple layer beneath each step edge. This is physically unlikely given the strong intralayer exchange coupling [19]. It is true, a further reduction of interlayer coupling by increasing the interlayer separation would favor a stronger surface relaxation effect, which can be visualized by magnetic imaging. The natural superlattice compounds MnBi$_2$Te$_4$−(Bi$_2$Te$_3$)$_n$ provide perfect system to test such a hypothesis. In these systems, n layers of Bi$_2$Te$_3$ are inserted between MnBi$_2$Te$_4$ layers, dramatically reducing the interlayer coupling without much impact on the uniaxial anisotropy [20, 22]. Thus, the metamagnetic transition becomes a spin-flip transition in MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ single crystals [20, 23]. ARPES measurements observed gapless Dirac surface states on the MnBi$_2$Te$_4$ termination, again suggesting strong surface relaxation of the A-type AFM order [20, 24]. Therefore, it is imperative to probe the surface magnetism of the MnBi$_2$Te$_4$ termination in MnBi$_4$Te$_7$. It is also interesting to find out whether there is a surface spin-flip transition proceeding the bulk one, which has been predicted theoretically but has evaded experimental observations [25].

In this letter, we report that the A-type AFM order persists to the surface MnBi$_2$Te$_4$ termination, as illustrated by the termination dependence of the magnetic signal observed by MFM, excluding the previous proposed surface relaxation of the A-type AFM order [20, 24]. In addition, we discover a first-order spin-flip transition on the MnBi$_2$Te$_4$ exposed surface that precedes the bulk spin-flip transition, in excellent agreement with a revised Mills’ model [17, 26, 27]. A quantitative analysis further suggests enhanced surface magnetization on the MnBi$_2$Te$_3$ termination, indicating robust two-dimensional ferromagnetism could exist in the single-layer limit [28]. Therefore, MnBi$_4$Te$_7$ is promising material platform for achieving high temperature quantized transport in the thin film limit.

MnBi$_4$Te$_7$ single crystals are grown out of Bi$_2$Te$_3$ flux [29]. Samples are cleaved in ambient condition to expose fresh surfaces before being mounted to a cryogenic MFM [17, 30]. Because of the natural superlattice structure, the surface terminates at either MnBi$_2$Te$_4$ septuple layer (SL) or Bi$_2$Te$_3$ quintuple layer (QL). Figure 1 shows...
The typical topography of a cleaved surface of MnBi$_4$Te$_7$ single crystal [29]. A trench with step height $\sim$2.4 nm cut through the field of view. The step height is approximately the c-axis lattice constant, indicating that it consists of a MnBi$_2$Te$_3$ SL and a Bi$_2$Te$_3$ QL. There are also a few islands inside the trench. Along the red arrow in Fig. 1(a), there is an island with height of $\sim$1.1 nm, indicating it is a QL (Bi$_2$Te$_3$). Therefore, the majority of the surface is the MnBi$_2$Te$_4$ termination. Figure 1d shows the corresponding topographical line profile with a cartoon of the stacking order.

Figure 1(b) and (c) shows the MFM image measured with opposite tip moments at 5.5 K in zero external magnetic field. The tip moment is reversed by applying a 0.1 T external field, which is small enough without affecting the domain pattern but large enough to reverse the MFM tip moment. The bulk spin-flip transition is $\sim$0.13 T while the coercive field of MFM tip moment is $\sim$0.04 T [29]. The reversal of the MFM contrast with tip moment orientation confirms the magnetic signal is from the stray field of the sample. A curvilinear domain wall separating antiphase domains cuts across the trench. The MFM contrast reverses across the domain wall (blue arrow) or across the step on the same side of the domain wall (red arrow). The alternating MFM signal across both the domain wall and the step confirms that the out-of-plane A-type AFM order persists all the way to the surface MnBi$_2$Te$_4$ layer. The topographical and MFM line profiles with the corresponding magnetic structures are shown in Fig. 1(d) and (e). The absence of magnetic contrast on Bi$_2$Te$_3$ island suggests its magnetic signal is negligible at 5.5 K and higher temperatures even though Mn$_2$Bi defects in Bi$_2$Te$_3$ carry magnetic moments [31]. Thus, the Bi$_2$Te$_3$ layer behaves as a non-magnetic spacer in MnBi$_4$Te$_7$. Thus, the magnetic contrast observed in this work originate from the magnetic order in the MnBi$_2$Te$_4$ layers. At lower temperatures, the magnetism in Bi$_2$Te$_3$ layers could interact with the AFM order in MnBi$_2$Te$_4$ layers, which might be related to the substantial hysteresis loop of the bulk spin-flip transition [20][22][32].

The persistence of out-of-plane A-type AFM order suggests that MnBi$_4$Te$_7$ is a perfect system to explore the surface metamagnetic transition, similar to the surface spin-flop transition observed in MnBi$_2$Te$_4$ single crystals [17].

In MnBi$_4$Te$_7$, the insertion of Bi$_2$Te$_3$ layer dramatically reduces the interlayer exchange interaction without affecting the uniaxial magnetic anisotropy. Therefore, the metamagnetic transition becomes a spin-flip transition [20][22]. The bulk spin-flip (BSF) transition field is $\mu_0 H_{BSF} \approx 0.13$ T at 5.5 K, in good agreement with recent MFM studies [28][32]. Thus, the surface MnBi$_2$Te$_4$ layer with antiparallel moment is expected to undergo a surface spin-flip transition before the bulk transition because of reduction of Weiss field due to the missing of half nearest neighbors [25]. Figure 2(a-f) show selected MFM images measured at various out-of-plane magnetic field after 0.01 T field cooling through the Néel temperature ($T_N \approx 13$ K) [22]. Positive field value indicates the direction of field is up. Curvilinear domain walls separating $\alpha$ ($\uparrow\downarrow\uparrow\downarrow$) and $\beta$ ($\downarrow\uparrow\downarrow\uparrow$) antiphase domains are highlighted in Fig. 2(a). The spin configurations of two types of antiphase domains are illustrated in Fig. 2(g). As magnetic field is increased to 0.03 T, a few bubble-like features with dark contrast appear only on antiparallel surfaces ($\beta$ domains above the trench) as shown in Fig. 2(b), indicating a metamagnetic transition that proceeds the bulk spin-flip transition. More dark features nucleate and expand with further increasing magnetic field. The dark contrast take over the whole antiparallel
FIG. 2. (Color Online) (a-f) Selected MFM images taken at 5.5 K with increasing magnetic fields, which are labeled on the corner of each image. The color scales from (a) to (f) are 0.06, 0.11, 0.12, 0.12, 0.26 and 3 Hz, respectively. The AFM domain walls are traced out with dashed lines in (a). The boxed areas α and β in (a) corresponds to parallel and antiparallel surface, respectively. (g)/(h) Magnetic structures of areas α and β before/after the surface spin-flip transition, respectively. (i) H-dependence of MFM contrast between areas α and β, and that of forced ferromagnetic (FM) domain population during the bulk spin-flip (BSF) transition (between 0.1 and 0.17 T). The colored arrows indicate the field sweeping direction. Above 0.17 T, the system is in the FM state.

The observed surface spin-flip transition field \( (\mu_0 H_{BSF}) \) is approximately 1/4 of that of the bulk one. We observed similar ratio in different samples with slightly different transition temperature and fields \[29\]. Furthermore, the ratio doesn’t vary much for \( T < 10 \) K \((-80\% of T_N)\), suggesting that the SSF transition follows the BSF one. To understand the mechanism of SSF transition, we performed analysis using a revised Mills’ model in the high anisotropy limit \((K/J \gg 1)\). Here \( K \) is the uniaxial anisotropy energy, and \( J \) is the exchange energy \[6, 34, 35\]. In comparison, the previous modeling of the surface spin-flip transition in MnBi\(_2\)Te\(_4\) is in the low anisotropy limit \((K/J \ll 1)\) \[17\]. Therefore, in contrast to the claim of recent MFM studies \[33\], there is no surface spin-flip transition in MnBi\(_2\)Te\(_4\).

FIG. 3. (Color Online) (a) Total energy as a function of exchange field, for the four magnetic phases with twelve spin-lattice sites \((N = 12)\) and reduced surface exchange coupling \((\lambda J = 0.5)\). First order phase transitions are expected at the crossing points \( h_1, h_2 \) and \( h_3 \), which are surface spin-flip (SSF), second-layer spin-flip (SLSF), and bulk spin-flip transitions, respectively. (b) The crossing points with respect to the surface exchange coupling \( \lambda J \) and the surface spin moment \( \lambda S \). The SLSF phase can appear only when the surface parameters are reduced as \( \lambda J \cdot \lambda S < 1 \). (c) Schematics illustration of the surface spin-flip states where red and blue represent antiphase domains. Assuming the external field points up, SSF (SLSF) occurs at the first (second) layer of antiparallel (parallel) surface as highlighted by orange filling.

The Mills’ model is effectively a one-dimensional spin
chain model where each spin represents the magnetic moment of each layer in A-type AFMs [20]. The strong uniaxial anisotropy ($K/J \gg 1$) forces all spins to align on the vertical easy axis. In this limit, the anisotropy term can be omitted from the original model, the total energy is simplified to $E = J \sum_{i=1}^{N-1} S_i \cdot S_{i+1} - \sum_{i=1}^{N} S_i \cdot h$. Thus, the total energy of AFM ground state is, $E_{AFM} = -(N-3+2\lambda_J \lambda S)J$, where $\lambda_J$ is the ratio of the revised surface exchange coupling to the bulk one, and $\lambda S$ is the ratio of the revised surface spin moment to that in bulk [0]. Here, $\lambda_J$ and $\lambda S$ are phenomenological parameters that characterize the effect of surface relaxation. The $E_{AFM}$ is independent of external field because of compensated magnetic moments. If the surface layer or the second layer moment reverses, the Zeeman energy gain of the uncompensated moments would result in first-order transitions. Figure 3(a) shows the total energies of four spin states for $\lambda_J \lambda S < 1$. The schematics are shown in Fig. 3(c). First-order phase transitions occur at threshold fields of $h_1 = \lambda_J J$, $h_2 = (1 + \lambda_J \lambda S)J$, and $h_3 = 2J$, where the lowest total energy evolves from AFM state to the force ferromagnetic state via the SSF and second-layer spin-flip (SLSF) states. Note that the $h_1$ only depends on $\lambda_J$. As discussed earlier, the ratio $H_{SSF}/H_{BSF}$ is approximately 1/4, which is $h_1/h_3$ in our model. Thus, the ratio of revised surface exchange can be estimated as $\lambda_J = 2h_1/h_3 \approx 0.5$. In other words, the exchange coupling is approximately half of the value in bulk of MnBi$_2$Te$_4$, probably due to surface relaxation effect. Interestingly, the revised Mills’ model also predicts a second-layer spin-flip transition ($h_2$) between the SSF transition ($h_1$) and the bulk transition ($h_3$) for $\lambda_J \lambda S < 1$. Otherwise, the total energy of the SLSF phase is always above the lowest energy states [29] so that the system undergoes a phase transition from SSF to FM states above a threshold field of $h_{SSF-FM} = 2[(N-3+\lambda_J \lambda S)/(N-2)]J$, which approaches $h_3$ in the bulk limit ($N \rightarrow \infty$). Experimentally, no signature of the SLSF transition is observed before the bulk spin-flip transition begins ($\sim 0.1$ T), indicating $\lambda_J \lambda S \geq 1$. However, the SLSF transition might be hidden by the relatively broad ($\sim 0.07$ T) BSF transition.

To explore whether the SLSF transition is overshadowed by the BSF transition, we performed field “annealing” experiments by carefully increasing magnetic field to induce partial but reversible BSF transition ($\mu_0 H \leq 0.14$ T) [29]. For negative field, the surface of $\alpha$ domains undergo SSF transition at $-0.03$ T [29]. Figure 3(a) shows the MFM image taken at $-0.09$ T after sweeping magnetic field to $-0.1$ T. Interestingly, numerous small patches with dark contrast appear on the parallel surface indicating a partial SLSF transition. As shown in Fig. 3(b) and (c), more fraction of $\beta$ domains undergo partial SLSF transition with increasing fraction of dark patches after $-0.12$ and $-0.14$ T field “annealing”. So the SLSF transition field is very close to that of BSF transition, i.e., $h_2 \approx h_3$, indicating $\lambda_S \approx 2$. Therefore, these results suggest that the moment of the surface MnBi$_2$Te$_4$ layer is larger than the bulk value. The enhanced surface moment indicates that a robust 2D ferromagnetism could persist in the single layer MnBi$_2$Te$_4$ limit, which is favorable for exploring the quantum transport in thin films or flakes of MnBi$_4$Te$_7$ and related superlattice compounds.

In summary, we discover the SSF transition in AFM-TI MnBi$_4$Te$_7$, in good agreement with a revised Mills’ model. Furthermore, we observed a partial SLSF transition, suggesting enhanced magnetic moment in the surface MnBi$_2$Te$_4$ layer. The alternating domain contrast across the domain wall or step edge observed in MnBi$_4$Te$_7$ unambiguously confirms the persistence of A-type AFM order to the surface MnBi$_2$Te$_4$ layer. The discovery and direct visualizing of SSF transition paves the way for exploring surface or 2-dimensional magnetic states of functional AFMs for spintronic applications [36]. Moreover, the robust ferromagnetism in the single-layer limit opens door to realize QAH or axion insulator states in the ultra-thin films of the natural superlattice MnBi$_4$Te$_7$ and related compounds [20, 21, 37].

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