Half-magnetization plateau and the origin of threefold symmetry breaking in a triangular frustrated antiferromagnet

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(Dated: February 10, 2020)

We perform high-field magnetization measurements on the triangular lattice antiferromagnet Fe1/3NbS2. We observe a plateau in the magnetization centered at approximately half the saturation magnetization over a wide range of temperature and magnetic field. The existence of this plateau is direct evidence of a metamagnetic transition to a four-spin unit cell with an up-up-up-down configuration. We perform a spin-wave analysis to understand the shape of the magnetization plateau and determine that next nearest neighbour interactions are likely strong. This elucidates the origin of the Z3 symmetry breaking ground state, and illustrates the material is strongly frustrated. The strong frustration may be pertinent to the magneto-electric properties of Fe1/3NbS2, which allow electrical switching of anti-ferromagnetic textures at relatively low current densities.

The nearly degenerate landscape of ordered states available to frustrated magnets usually arises because of the presence of multiple channels of interaction. Diagnosing the relative magnitude of these interactions gives a direct insight into the physical origin of the frustration. The existence of magnetization plateaus at fractions of saturation, when a material is subjected to large external magnetic fields, is a powerful tool to this end. Such plateaus have primarily been studied in strongly insulating materials, where plateaus complement neutron scattering and other methods to understand the effective interactions between spins. Plateaus can also exist in materials with some degree of conduction, and in such systems they may provide insight into how magnetic order can control — and be controlled by — charge or spin currents.

When a layered transition metal dichalcogenide such as NbS2 is intercalated with magnetic species, a variety of magnetic states can form depending on the precise symmetry of the structure as well as the chemical nature and concentration of intercalants [1, 2]. The antiferromagnet Fe1/3NbS2 has recently been found to show stable, reversible switching between stable states by applied electrical current [3], via a similar mechanism to those proposed in other antiferromagnetic materials [4, 5]. However, determining the nature of the magnetic ground state has been challenging, as collinear and non-collinear order are energetically close and the true ground state depends strongly on the magneto-crystalline anisotropy [2]. The nature of the underlying ordering in Fe1/3NbS2 has been studied by both neutron scattering [6] of magnetic order and optical linear birefringence microscopy [7], which probes nematic structure in the electrical conductivity. Both measurements — electric and magnetic — find indications of threefold symmetry breaking in the ground state, whose origin is unclear.

We report here a hitherto unobserved plateau in the field-induced magnetization at half of the saturation value. Such a plateau, with an up-up-up-down structure (“UUUD”; three spins up and one down in a four-spin unit cell), has previously been argued to exist theoretically in both anisotropic classical [8] and isotropic quantum [9] models of triangular lattice antiferromagnets. In the isotropic case, the half-magnetization plateau exists whenever there is a significant next nearest neighbor magnetic coupling [10]. (We will discuss the magnetic Hamiltonian inferred from magnetization measurements and spin-wave analysis in more detail below.) However, experimental realizations of a half-magnetization plateau on a triangular lattice are relatively rare [11], and their observation is strong evidence for the presence of significant next nearest neighbor interactions.

The implication from theory is that the same interactions that generate the plateau are also responsible for a threefold symmetry breaking stripe phase in the ground state, for both quantum and classical models. The half-magnetization plateau found in Fe1/3NbS2 thus gives a strong clue to the physical mechanism of the threefold symmetry breaking in this material in zero applied field, and thereby provides a microscopic picture for the electrically switchable antiferromagnetic texture.

Fe1/3NbS2 is a quasi-2D material with space group P6322 182 whose magnetism arises from the iron which sits between layers of NbS2 (Fig. 1 (a)). These magnetic atoms form triangular lattices in each layer, with adjacent layers staggered with respect to one another (Fig. 1 (b)). Charge from the iron atoms is transferred to the NbS2 conduction band, leaving them in a 2+ ionized state, with four unpaired localized electrons per atom [12, 13]. The macroscopic behavior of the material in low field is antiferromagnetic (AFM); microscopically,
FIG. 1. (a) The crystal structure of Fe$_{1/3}$NbS$_2$. Iron atoms sit between layers of NbS$_2$, aligned with the niobium atoms above and below. (b) Looking along the c-axis, the iron atoms in a given layer form a triangular lattice. These triangular lattices are shifted from layer to layer, with ferromagnetic interactions dominating between layers. Arrows with solid and dotted lines indicate one nearest neighbor (N.N.) and one next nearest neighbor (N.N.N.) pair, respectively.

the nearest neighbor and next nearest neighbor exchange interactions are both thought to be AFM, making this an interesting variety of frustrated AFM [2].

Heat capacity measurements show two clear transitions at zero field (Fig. 2 (b)). With the application of field, these transitions move apart from each other in temperature. The lower temperature transition has a further splitting at higher fields, indicating the presence of an additional intermediate phase.

Measurements of the magnetic susceptibility as a function of temperature in low applied fields show that there is an AFM regime below the transitions, and a paramagnetic regime above them (Fig. 2 (a)). Fitting to the paramagnetic regime, the Curie-Weiss Law yields an estimate of 4.5 $\mu_B$/Fe for the fully saturated moment of the material. This is in agreement with the values found in the literature, which predominantly range from 4.3 to 5 $\mu_B$/Fe [12,14–17], although there is one report as high as 6.3 $\mu_B$/Fe [1].

High field measurements further elucidate the nature of the phase transitions. Measurements at 0.6K and 20K of the magnetization as a function of applied field are shown in Fig. 3 (a). The full set of measurements, taken at temperatures ranging from 0.6K to 50K, is given in [18], and the phase boundaries determined from these measurements are shown in Fig. 4.

From these measurements it can be seen that there are three dominant phases at low temperature: (I) the zero field phase characterized by a small magnetic moment, (II) the ‘plateau’ phase characterized by a nearly constant magnetic moment centered around half the estimated saturation moment, and (III) a high field phase which approaches the fully saturated moment. The final phase gets pushed above 60T at the lowest temperatures. An intermediate phase bridging the zero field and plateau phase has only a weak feature in the magnetization (see Supplemental Material [18]).

The experimental phase diagram, Fig. 4, shows a non-monotonic dependence of the ordering temperature on applied field. This dependence can be explained by the double impact of an applied field on a quasi-2D system, as was argued by Sengupta et al. regarding the tetragonal AFM [Cu(HF$_2$)(pyz)$_2$]BF$_4$ [19]. Fluctuations of the mean field become significant in such systems. As the field increases, both the order parameter and these fluctuations are suppressed. The latter effect leads to an increase in the transition temperature in low field, and the former takes over and brings down the transition temperature at higher fields. In our case, there is the interesting addition of a second ordered phase, which is destroyed in that low field regime.

While the primary measurements were performed on a stack of co-aligned crystals in pulsed field, the nature of the plateau was confirmed both with a single crystal in pulsed field, and with a stack of crystals in a 30 T DC field. A comparison of these measurements to pulsed field is found in [18]. The DC measurement was additionally used to scale the pulsed field data, whose experimental apparatus measures magnetization up to a constant scal-
The plateaus are well explained by a 2D lattice model close to those of Refs. [8,9]. To justify this, we have performed ab-initio calculations using density functional theory (DFT). Details are given in [18]. DFT indicates that the coupling between adjacent layers is small, \( J_1 < 0.1 \text{ meV} \), and ferromagnetic, effectively decoupling adjacent iron layers. We can thus consider a 2D model using the spin degrees of freedom in a single Fe layer, which form a triangular lattice of quantum spin-2’s. We consider antiferromagnetic nearest neighbor (NN) and next nearest neighbor (NNN) couplings, as well as magneto-crystalline anisotropy:

\[
\hat{H} = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j - D \left(\mathbf{S}_i^z\right)^2. \tag{1}
\]

The presence of \( J_2 \gtrsim J_1/8 \) is required to have a four-spin 2D magnetic unit cell, which is necessary to capture the half-magnetization plateau [8,20]. We will see that this minimal model explains many key features of Fe\(_{1/3}\)NbS\(_2\).

Half-magnetization plateaus are present in two close variants of Eq. (1) studied in the literature — with \( D = 0 \) in [8] and a 3D generalization in [8]. The physical origin of the magnetization is a succession of three phases that appear with increasing field (Fig 3(c)). (I) At zero field, the model favors a "stripy" AFM phase, with a magnetic unit cell of two atoms, one pinned up and the other pinned down. (II) Applying a sufficiently strong out-of-plane field causes a transition to the so-called UUUD phase, with three of the four spins in the magnetic cell aligned with the field and the last anti-aligned. This phase is stabilized both by quantum fluctuations for \( J_2/J_1 > 1/8 \) [8] and large magneto-crystalline anisotropy \( D/J_1 \) [18]. (III) Finally, for sufficiently high fields, the magnetization saturates and all spins are aligned with the field. These phases have net magnetization which is, respectively, almost exactly zero, one-half, and one times the saturation magnetization of iron, \( 2g_{\text{Fe}}\mu_B \approx 4.18\mu_B \). This is consistent with the measurements in Fig. 3(a).

To employ the model Eq. (1), we estimate the parameter values \((J_1, J_2, D)\). While we cannot uniquely determine these parameters, we can significantly constrain their values. Following Ref. [21], we relate the magneto-crystalline anisotropy to the in- and out-of-plane Curie-Weiss temperatures (found from our fits to be \(-110 \text{ K} \) and \(-26 \text{ K} \), respectively). This yields a magneto-crystalline anisotropy of approximately \( D \approx 1 \text{ meV} \). Our ab-initio DFT calculations give an anisotropy in the range of \( D = 0.3 - 0.7 \text{ meV} \) [18]. The DFT values for \( D \) are close to the experimental estimate, confirming our estimate of \( D \) as reasonable. The Curie-Weiss temperatures can similarly be related to the sum of all coupling constants, giving an estimate of \( \sum_j J_j = 6(J_1 + J_2 + \cdots) = 1.3 \text{ meV} \), where the factor of 6 arises because each atom has six nearest and next nearest neighbors. Given that this value of 1.3 meV is for all couplings for a single spin (including ferromagnetic interlayer interactions which do not enter our 2D model), together with the reasonable assumption that the intralayer interactions dominate, we can surmise that \( J_1, J_2 < 1 \text{ meV} \). The presence of a plateau at high fields furthermore suggests that \( J_2/J_1 > 1/8 \) and that \( D/J_1 > 1/8 \). Almost all parameters that are consistent with the above constraints give comparable results.

In the following, we choose representative parameters \((J_1, J_2, D) = (0.4, 0.1, 1.0) \text{ meV} \) that satisfy the above conditions to directly compare Eq. (1) to experiment, by calculating the magnetization as a function of applied magnetic field. We consider a magnetic unit cell of four atoms — necessary to capture the UUUD phase — and use linear spin-wave theory (LSWT). We introduce four species of magnons, one for each site in the unit cell, via a Holstein-Primakoff transform on Eq. (1). We can rewrite
where $\hat{H}_{\text{class}}$ is the classical Hamiltonian and $\hat{H}_{\text{magnon}}$ is a quadratic Hamiltonian in the four species of magnons (details of this derivation are given in [13]). We then find the classical ground state — and hence the phase — by minimizing the classical spin configuration $\hat{S}_i$. With the classical ground state in hand, we can compute the magnetization along the $c$-axis as $\sum_i S_i^c + \Delta S_i^c$, where the spin reduction $\Delta S_i^c$ is the expectation of $\hat{S}_i^c$ calculated in the thermal state of $\hat{H}_{\text{magnon}}$ at finite field and temperature. The result is shown in Fig. 3 (b).

The good agreement between measurement and theory in Fig. 3 is a result of several factors that compound to make LSWT particularly accurate in this situation. Previous work needed to carefully determine the ground state out of many candidates of nearly equivalent energy $\approx 10^{-4}$ [8, 9, 20]. However, we find that when $D \geq J_1 + J_2$, the phases are clarified at the classical level [18] and only the stripy, UUUD, and saturation phases are present with first-order transitions between them. This is because $D$ increases the band gap of the magnon band. For example, in the stripy phase in zero field, the gaps at the band bottoms at zero temperature are

$$\Delta E(\Gamma) = 2SD, \quad \Delta E(K) = 2SD + 3SJ_1$$  \hspace{1cm} (3)$$

at the $\Gamma$ and $K$ points, respectively, if $J_2 \geq J_1/2$ [22]. This large gap makes LSWT more reliable at low temperature because the number of magnons will be small; $\Delta S_i^c/S$, the expansion parameter for LSWT, decreases with increasing $D$. (The fact that $\hat{S}_i$ is spin-2 rather than 1/2 further increases the accuracy.) Conceptually, a large anisotropy $D$ vastly narrows down the possibilities for the ground state to the phases where the spins are almost aligned with the out of plane axis — and there are only a few such possibilities.

The UUUD phase responsible for the half-magnetization plateau is stable at the classical level over a wide range of applied fields. The model Eq. (1) qualitatively reproduces the critical field strengths and quantitatively captures the magnitude of the magnetization. However, it fails to describe some of the fine features of the measurements, such as the variation of critical field strength with temperature, and the small, positive slope of the magnetization within plateaus. In addition, the intermediate phase detected by measurements between the plateau and stripy order, is also not captured by the model. On the other hand, as a minimal model that only includes a subset of the degrees of freedom and must be solved approximately, the model is highly consistent with measurements. We may conclude that Eq. (1) is a good minimal model that captures the main experimental features of the magnetization response of Fe$_{1/3}$NbS$_2$. 

The applicability of the lattice model suggests that Fe$_{1/3}$NbS$_2$ is proximate to many other phases, some of which are possibly similar to supersolid phases discussed by Seabra and Shannon [8]. One of these may describe the boundary phase dividing stripy and plateau orders in Fig. 3. As described in Supplemental Materials [18], this intermediate phase has a kink in the magnetization at approximately $\sim 1.6\mu_B$, or around a third of the saturation magnetization. This may associate the intermediate phase with an UUD transition which appears naturally in the same lattice models [8], but our data is inconclusive on this matter.

The agreement of the experimentally observed magnetization with a 2D spin wave model suggests that the magnetic behavior, while largely two-dimensional, involves conventional magnetic phases. This model could be further confirmed by inelastic neutron scattering, which should be able to detect the relatively large gap in the magnon spectrum in Eq. (3). The existence of a half-magnetization plateau is a strong indication that next nearest neighbor interactions are significant in these materials, which both ensures the system is highly frustrated and has a large impact on the zero-field ground state. The three-fold anisotropy seen in optical measurements [7], for example, originates from a magnetic order driven by a large ratio of $J_2/J_1$, likely stripy in
The recent demonstration of electrical switching at relatively low current densities may involve the coupling of spin polarized currents to this correlated landscape of magnetic states, suggesting a promising arena in the search for antiferromagnetic spintronic materials in frustrated magnets.

ACKNOWLEDGMENTS

This work was supported as part of the Center for Novel Pathways to Quantum Coherence in Materials, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Basic Energy Sciences. Work by J.G.A. and S.C.H. was funded in part by the Gordon and Betty Moore Foundations EPiQS Initiative, Grant GBMF9067 to J.G.A. Work by T.C. and D.E.P. was supported by NSF Graduate Research Fellowship Program, NSF DGE 1752814. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and DMR-1644779 and the State of Florida.

[1] R. H. Friend, A. R. Beal, and A. D. Yoffe, The Philosophical Magazine: A Journal of Theoretical Experimental and Applied Physics 35, 1269 (1977).
[2] S. Mankovsky, S. Polesya, H. Ebert, and W. Bensch, Physical Review B 94, 184430 (2016).
[3] N. L. Nair, E. Maniv, C. John, S. Doyle, J. Orenstein, and J. G. Analytis, Nature Materials 1 (2019).
[4] J. Zelezny, H. Gao, K. Vyborny, J. Zemen, J. Masek, A. Manchon, J. Wunderlich, J. Sinova, and T. Jungwirth, Physical Review Letters 113, 157201 (2014).
[5] P. Wadley, B. Howells, J. Zelezny, C. Andrews, V. Hills, R. P. Campion, V. Novak, K. Olejnik, F. Maccherozzi, S. S. Dhesi, S. Y. Martin, T. Wagner, J. Wunderlich, F. Freimuth, Y. Mokrousov, J. Kunes, J. S. Chauhan, M. J. Grzybowski, and T. Jungwirth, Science 351, 587 (2016).
[6] B. Van Laar, H. M. Rietveld, and D. J. W. Ijdo, Journal of Solid State Chemistry 3, 154 (1971).
[7] A. Little, C. Lee, C. John, S. Doyle, E. Maniv, N. L. Nair, W. Chen, D. Rees, J. W. F. Venderbos, R. Fernandez, J. G. Analytis, and J. Orenstein, arXiv:1908.00657 [cond-mat] (2019).
[8] L. Seabra and N. Shannon, Physical Review B 83, 134412 (2011).
[9] M. Ye and A. V. Chubukov, Physical Review B 96, 140406 (2017).
[10] M. Ye and A. V. Chubukov, Phys. Rev. B 95, 014425 (2017).
[11] A. I. Coldea, L. Seabra, A. McCollam, A. Carrington, L. Malone, A. F. Bangura, D. Vignolles, P. G. van Rhee, R. D. McDonald, T. Srgel, M. Jansen, N. Shannon, and R. Colden, Physical Review B 90, 020401 (2014).
[12] O. Gorochov, A. L. Blanc-soreau, J. Rouxel, P. Imbert, and G. Jehanno, Philosophical Magazine B 45, 621 (1981).
[13] M. Sundararajan, A. Narayanasamy, T. Nagsaran, C. Sunandana, G. S. Rao, D. Niarchos, and G. Shenoy, Journal of Physics and Chemistry of Solids 44, 773 (1983).
[14] F. Hulliger and E. Pobitschka, Journal of Solid State Chemistry 1, 117 (1970).
[15] B. V. Laar, H. Rietveld, and D. Ijdo, Journal of Solid State Chemistry 3, 154 (1971).
[16] K. Arzenhofer, J. Van Den Berg, P. Cossee, and J. Helle, Journal of Physics and Chemistry of Solids 31, 1057 (1970).
[17] N. Doi and Y. Tazuke, Journal of the Physical Society of Japan 60, 3980 (1991).
[18] See Supplemental Material for (A) details of the spin-wave calculation and (B) unabridged magnetization measurements and other experimental details.
[19] P. Sengupta, C. D. Batista, R. D. McDonald, S. Cox, J. Singleton, L. Huang, T. P. Papageorgiou, O. Ignatchik, T. Hermannsdorfer, J. L. Manson, J. A. Schlueter, K. A. Funk, and J. Wosnitza, Physical Review B 79, 060409 (2009).
[20] M. Ye and A. V. Chubukov, Phys. Rev. B 95, 014425 (2017).
[21] D. C. Johnston, Phys. Rev. B 95, 094421 (2017).
[22] If $J_2 \leq J_1/2$, the gap at $K$ is given by $S[4D(D+J_1+4J_2)+3J_1(8J_2-J_1)]^{1/2}$, which becomes classically unstable for $D = 0$ and $J_2/J_1 < 1/8$.