Opportunities and challenges of 2D magnetic van der Waals materials: magnetic graphene?

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A new material matters in condensed matter physics, so much so that if one looks at the history of the condensed matter physics over the last half century one immediately realizes that there have been star materials almost every decade. These new classes of materials shaped, and have been continuously shaping, the big questions of the time. For example, there were spin glasses, heavy fermions, high-temperature superconductors, manganites and multiferroic materials, to name only a few.

The recent entry of graphene is no different from its predecessors, if not more revolutionary [1, 2]. One particularly amazing aspect of the graphene physics is how so much of the new physics was, at least initially, observed in graphene produced by such a simple mechanical exfoliation method using Scotch tape. The simple elegance of doing physics with Scotch tape on graphene impressed the community so much that it has remained the first method of choice when it comes to producing monolayer van der Waals (vdW) materials. Recent developments have led to several new vdW materials being discovered, or rather rediscovered, and the list of the vdW materials continues to grow very fast [3].

However, there is one particular class of systems: magnetic vdW materials, conspicuously missing in the current list. In figure 1, we show, for the past 15 years, the number of annual publications on the subject ‘van der Waals’ compared with those on ‘magnetic exfoliation’. Looking at the statistics, it is striking that although there were over 600 papers published in 2015 alone under the keyword van der Waals materials, there are less than 10 publications under the name of magnetic exfoliation. These statistics amply illustrate how much the field of the magnetic van der Waals materials has been underexplored. As we argue in the remainder of this paper, we are in a very sorry state given the potential made possible by this new class of materials. This paper, we hope, will serve as a timely wake-up call for this situation.

Traditionally, vdW or layered magnetic materials have been considered as useful candidates for the study of low-dimensional magnetic systems [4]. Transition metal phosphorus trisulfide (or thiophosphate), TMPS₃, is one such example, and its bulk properties have been extensively studied using various techniques [5–11]. It is a very attractive aspect from a materials point of view that TMPS₃ can host several transition metal elements at the TM sites with correspondingly diverse physical properties: TM = Mn, Fe, Co, Ni, Zn and Cd. One can also replace S by Se while keeping the same crystal structure, adding more flexibility to the choice of materials. This diversity of different physical properties in these materials will turn out to be a huge advantage when it comes to actual applications.

Interestingly enough, all three principal spin Hamiltonians are reported in these materials: two-dimensional (2D) Ising system (FePS₃), 2D Heisenberg system (MnP₃S₃) and 2D XY system (NiPS₃, CoP₃S₃) [8, 9]. From a study of the critical behavior, however, MnPS₃ was claimed to be closer to an XY-like system [10]. More recently, it was theoretically proposed that a rare spin-valley coupling might be realized in one of these materials, MnPS₃ [12]. Another interesting theoretical finding is that upon carrier doping in the range of 10¹⁴ cm⁻² the magnetic ground state can be tuned from the antiferromagnetic to ferromagnetic ground states [13]. Then MnPS₃ was reported to have a linear magnetoelectric (ME) coupling induced by the magnetic ordering and claimed to be a pure ferrotoroidic compound [14]. Adding further motivation to this class of materials, TMPS₃ has a band gap of 1.5–3.5 eV [15], nicely matching the energy range of visible light.

TMPS₃ has a weak van der Waals interaction between the layers and so it can be easily cleavable. With hindsight, it is rather surprising that it has taken so long to produce a monolayer
of these compounds. At least there are now two independent reports with the realization of monolayer and multilayers of these systems [16–18]. It is interesting to note that the magnetic elements form a honeycomb lattice just like graphene, so one can call it ‘magnetic graphene’.

Both groups have used the Scotch-tape method to achieve their goals and characterized their samples using the AFM and Raman techniques. As in graphene, Raman spectroscopy is found to be a very useful tool in determining the thickness of TMPS$_3$: both $E_g$ and $A_{1g}$ Raman peaks show a clear thickness dependence [16]. The other noticeable exfoliated magnetic material is Bi-based high-temperature superconductor [3, 19]. With this successful mechanical exfoliation of TMPS$_3$, the door is now wide open for exploring the physical properties on the scale of a few atomic layers and, more importantly, to exploiting its potentials for novel devices. We note that with these huge opportunities, it is a welcome sign to see other magnetic vdW materials joining this rare group: for example, there have been reports on CrSiTe$_3$ [20].

One can think of several applications for a successfully exfoliated magnetic TMPS$_3$ monolayer. One of the most obvious cases is to use it for the study of fundamental 2D magnetism with reducing thickness, as illustrated in figure 2. It sounds very strange, but, to the best of our knowledge, no experimental test has been done using a real magnetic material of the Onsager solution for 2D Ising magnets [21]. The only experimental test which we are aware of was carried out using sub-monolayer CH$_4$ absorbed on graphite, which is an odd coincidence [22]. It is not that we have any doubt about the answer that Onsager came up with some 70 years ago, but it would be fantastic to see the results obtained from a real magnetic material confirming this historic achievement.

Moreover, with the variation of the magnetic atoms of TMPS$_3$ it will also be possible to extend this test of fundamental magnetism to other spin Hamiltonians and to demonstrate the Merin–Wagner–Hohenberg theorem [23, 24]. Another advantage of having the magnetic vdW monolayer of TMPS$_3$ is that Mott physics with strong correlations might be naturally realized in the 2D materials. If found to be correct, it will then open another window of fascinating opportunities to explore correlated physics on naturally occurring 2D systems. Furthermore, it will be of general interest to know how control parameters only available with these 2D magnetic systems such as the substrate and the width of the monolayer affect the transition temperature. More specific to TMPS$_3$, it will also be intriguing to examine the strain effects on the magnetism as a recent theory suggested [25]. At the same time, with the band gap of TMPS$_3$ nicely overlapping with the energy range of visible light, it will be interesting to investigate how the band gap varies as one reduces the thickness and/or the samples are put under external strain. Other potentially more far-reaching applications will be found with its use as a component of heterostructures with other vdW materials such as graphene. Over the past few years, we have witnessed an explosive growth of this field of vdW materials-based heterostructures with numerous novel discoveries ensuing therefrom.
One is left only to guess how the already fast-growing field will change with the introduction of this new functionality of magnetism to the arsenal of vdW materials.

Despite the high notes, we have to admit that challenges lie ahead, in particular how to prepare the sample in a controlled manner, e.g. with an accurate thickness control. The other problem that might hinder the progress is a lack of handy characterization tools. As most conventional techniques used for bulk magnetic materials have only limited usage for atomically thin magnetic vdW materials, we are in desperate need of new techniques. However, with our own experience we can be sure that the following techniques will be found helpful for the field in future: Raman, AFM (atomic force microscopy), PEEM (photoemission electron microscopy), MFM (magnetic force microscope) and MOKE (magneto-optic Kerr effect).

All in all, we have no illusion as to how difficult and challenging the road ahead will be even to achieve only part of these goals. However, failure or success will be another instance of true science-in-making. Given the opportunities, these roads will certainly be worth taking.

Acknowledgments

We acknowledge Cheol-Hwan Park and Jon Leiner for their critical reading of the manuscript. The work at the IBS CCES was supported by the research program of Institute for Basic Science (IBS-R009-G1).

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Figure 2. Schematic of how one can study the thickness dependence of the fundamental magnetic properties using the magnetic vdW materials such as the transition temperatures and the ground states. [26, 27].