Intrinsic Ferromagnetism in Two-Dimensional Materials

Kenneth E. Madsen Literature Seminar November 1st, 2018

Magnetic materials hold extraordinary technological significance in a vast array of applications from power generation to data storage. While the behavior of these materials is largely well understood at the macroscopic scale, understanding how magnetism interacts at the quantum scale remains an active area of research.[1] Materials exhibiting intrinsic magnetism in one or two dimensions have long been sought after for the impact they may have on new technologies like spintronics and quantum computation.[2] While many reports have surfaced describing thin layer-magnetism, a material demonstrating ferromagnetic order as a single monolayer has, until very recently, remained elusive.[3]

The prospect of magnetic order at the monolayer limit was initially investigated theoretically by Mermin and Wagner.[4] Their predictions suggest that coherent magnetism in a monolayer is untenable at finite temperatures as thermal energy would rapidly disorder any long-range magnetic alignment. Experimental evidence from epitaxially grown metal films largely supports this conclusion.[5] In such films a rapid decay of the Curie temperature (the temperature below which ferromagnetic order exists) is observed as layer thickness decreases, converging to 0 K in monolayer films.

While the Mermin-Wagner theorem forbids intrinsic magnetic order in one or two dimensions, it is predicated on the assumption that magnetic moments within materials are entirely isotropic. Materials exhibiting inherently large magnetic anisotropy are not bound by this condition, and hold promise for lifting the constraints imposed by theory.[6] Magnetic van der Waals (vdW) materials offer such anisotropy; however, most vdW magnets possess insufficiently strong magnetic interactions to overcome thermal energy in the few layer regime.[3, 7]

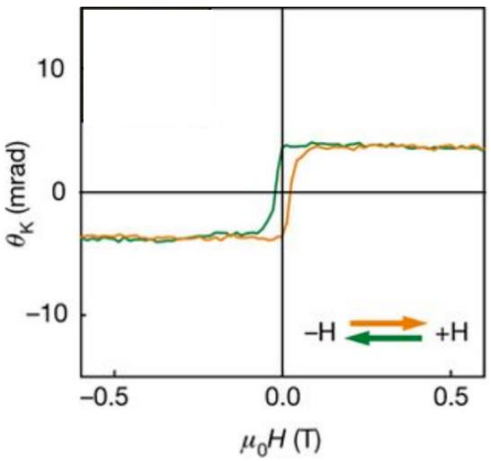

Figure 1. Ferromagnetic response of monolayer CrI_3 demonstrating clear hysteresis when probed with MOKE spectroscopy.

The first material to overcome this drawback and achieve monolayer ferromagnetism was demonstrated in 2017 by Xiadong Xu and coworkers at the University of Washington.[8] The bulk ferromagnet CrI_3 was investigated due to its ease of exfoliation and large out-of-plane magnetic anisotropy. Monolayers were exfoliated onto a SiO_2 substrate and interrogated with magneto-optical Kerr effect (MOKE) spectroscopy to probe their magnetic behaviors. Remarkably the authors demonstrate clear hysteretic behavior indicative of intrinsic ferromagnetism (Figure 1). What's more, only a mild reduction of the Curie temperature (T_C) is incurred transitioning from the bulk material (T_C = 61 K) to the monolayer (T_C = 45 K) suggesting weak magnetic coupling between layers, while maintaining strong intralayer magnetic coherence.

This result is significant in that it confirms the possibility of producing a ferromagnetic monolayer from bulk vdW materials. This has prompted a concerted research effort to discover other materials capable of the same effect and to understand the characteristics affording stable magnetic order. While it universally agreed upon that high anisotropy is critical in achieving two-dimensional magnetic order it is less clear how far magnetic structure can be modified while maintaining said order.

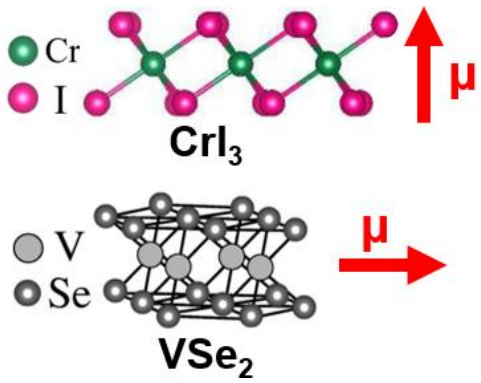

Figure 2. Crystal structures and magnetic orientations of CrI_3 and VSe_2. Red arrows indicate the direction of spontaneous magnetization in each material.

To investigate possible variations of the 2D magnetic structure Matthias Batzill and coworkers looked at VSe_2 for its peculiar magnetic properties.[9] While most vdW magnets, CrI_3 included, show out-of-plane magnetic order VSe_2 exhibits an in-plane magnetic moment (Figure 2). Further VSe_2 is paramagnetic in the bulk, only demonstrating ferromagnetism in few layer samples.[10] Through molecular beam epitaxy, VSe_2 islands were grown on graphite and capped with a thin (10 nm) protective coating of Se. With MOKE spectroscopy it is confirmed that ferromagnetic ordering resides in VSe_2 at temperatures exceeding 330 K. It was also shown that the in-plane magnetic orientation is preserved at the monolayer level. Such a high Curie temperature suggests highly stable magnetic coherence within the monolayer, however, it remains unclear if this stability is in any way correlated to the change from out-of-plane to in-plane magnetism.

Despite the uncertainty of its origin, the extraordinarily high Curie temperature in monolayer VSe_2 holds promise for the application of 2D magnets to room temperature applications. To further broaden the potential applications of these materials an understanding of their electronic structures is critical. While most vdW magnets are insulators, with the electrons contributing to magnetism isolated to transition metal sites, there are a few examples of metallic vdW magnets exhibiting itinerant magnetism.

Itinerant magnetism describes a condition whereby magnetism originates from electrons in the conduction band rather than the valence band. Since these electrons can transmit through the solid, magnetism is no longer isolated to individual transition metal sites. To affirm the existence of itinerance at the monolayer limit the Xu group investigated a known itinerant material Fe_3GeTe_2 (FGT) which, in its bulk form, is a metallic ferromagnet (T_C = 210 K).[11, 12] Bulk single crystals of FGT were exfoliated onto a gold substrate and subjected to magnetic characterization again using MOKE spectroscopy.

Hysteretic behavior reveals that monolayer FGT displays ferromagnetic ordering below 130 K. The authors then monitored the spontaneous magnetization of FGT samples with decreasing temperature. They observe a large decrease in Curie temperature with layer thickness, strikingly similar to thin films of metallic magnets. Further, the rapid saturation of magnetization with decreasing temperature (Figure 3) suggests that magnetic itinerance is maintained in monolayer FGT samples. Fitting this saturation to theory bolsters this argument as the saturation behavior matches well with previous literature examples of itinerant magnetism. This also

suggests that modifications to the electronic properties of vdW materials, from insulating to conducting, does not preclude monolayer magnetism.

Overall, these investigations demonstrate that magnetic order is certainly accessible in the monolayer regime with a variety of vdW materials. Further, modification to the magnetic and electronic structure is feasible without destroying the ferromagnetic properties of the monolayer. While these results are exciting, more research is necessary to develop a complete understanding of the factors contributing to two-dimensional magnetism. Additionally, the role substrate interactions and defect formation play on the magnetic properties of monolayer samples should be investigated more completely. Current research directions in this area are largely focused on the discovery of new materials that exhibit 2D magnetism among other interesting properties. Other directions include the investigation of heterostructured materials and the development of devices using mono or bilayer vdW magnets[13]. While the current state of this research is currently in its infancy, the outlook is bright for these materials in both fundamental studies of magnetic interactions and in new applications.

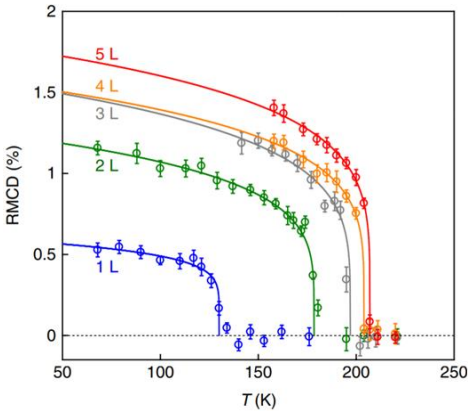

Figure 3. Spontaneous magnetization of FGT samples with decreasing temperature. Solid lines represent mathematical fitting to theory

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