

Ferromagnetism found in two-dimensional materials

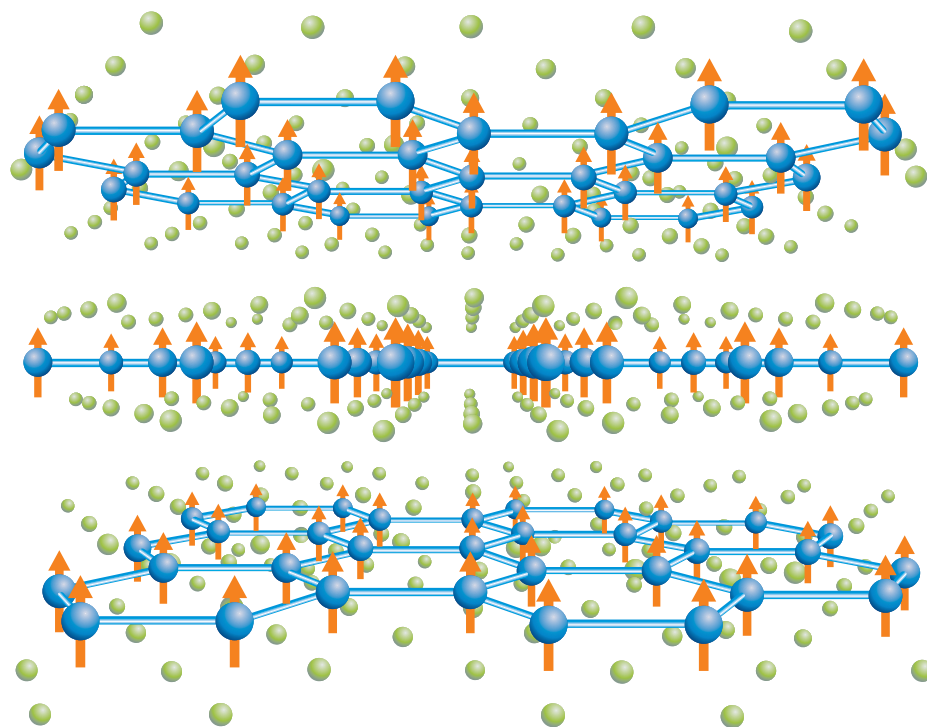
Whether long-range magnetic order could survive in the 2D limit was an open and fundamental question. The answer is that it can, but it has some surprises in store.

From graphene to black phosphorus and molybdenum disulfide, the past decade has seen fast progress in the field of two-dimensional materials. Made up of atomically thin layers with nothing but weak out-of-plane van der Waals forces to hold them together into a bulk solid, the materials are alluring from both basic and applied points of view. The physics of isolated 2D layers has proven rich and often surprising, in part because the reduced dimensionality changes the way quantum fluctuations compete with long-range order. Device engineers have already fashioned 2D transistors and dream of building all-2D circuitry. (See the article by Pulickel Ajayan, Philip Kim, and Kaustav Banerjee, *PHYSICS TODAY*, September 2016, page 38.)

Of all the types of condensed-matter behavior that have been observed and studied in 2D materials, ferromagnetism has been notably absent. But now two teams—one led by Xiang Zhang of the University of California, Berkeley, and the other by the University of Washington's Xiaodong Xu and MIT's Pablo Jarillo-Herrero—have observed clear signatures of ferromagnetism in the 2D materials CrGeTe_3 and CrI_3 . And they've both uncovered unexpected new effects that show just how puzzling 2D magnetism may turn out to be.^{1,2}

Flatland magnets

Theorists have long known that there's something different about magnetism in reduced dimensionality. The 2D Ising model—a planar lattice of interacting spins, each of which can point only up or down—undergoes a phase transition at



nonzero temperature to a state with long-range magnetic order. But the 2D Heisenberg model, in which the spins can point in any direction, does not.

In their 1966 solution to the 2D Heisenberg model, David Mermin and Herbert Wagner clarified the situation. They showed that continuous symmetries, such as magnetism in the Heisenberg model, cannot be broken in 2D systems at temperatures above absolute zero because thermal fluctuations destroy any ordered state that tries to form.³ To exhibit ferromagnetism, they found, a 2D system must be magnetically anisotropic: Though not strictly limited to two states, as in the Ising model, the spins of a 2D ferromagnet must have a so-called easy axis along which they energetically prefer to lie. Real-world magnetic anisotropy, which usually arises from spin-orbit coupling, is not rare. But it's normally too small to make much difference.

Conventional bulk magnets, such as iron and nickel, show hints of having trouble retaining their magnetism in 2D: Crafting them into thinner and thinner films causes their magnetic transition temperature T_c to plummet. From an ap-

FIGURE 1. A FERROMAGNETIC VAN DER WAALS MATERIAL, such as CrI_3 shown here, is made up of a stack of 2D crystalline layers held together by strong in-plane covalent bonds but weak out-of-plane van der Waals forces. The magnetic chromium atoms, shown in blue, energetically favor an out-of-plane spin axis. Iodine atoms are shown in green. (Courtesy of Michael A. McGuire, Oak Ridge National Laboratory.)

plications point of view, that's not necessarily so bad. Each metal's bulk T_c is hundreds of degrees above room temperature, so it has plenty of room to fall. But ultra-thin films of bulk magnetic materials aren't suitable for what 2D device engineers have in mind. The films interact so strongly with their substrates that their magnetic properties are affected. And they're difficult and expensive to fashion into uniform layers of greater than nanoscale length and width.

To behave independently of its substrate and to form large-area, atomically sharp interfaces, a 2D ferromagnet must be a van der Waals material, like the one shown in figure 1. Its bulk form should be ferromagnetic—meaning that one of

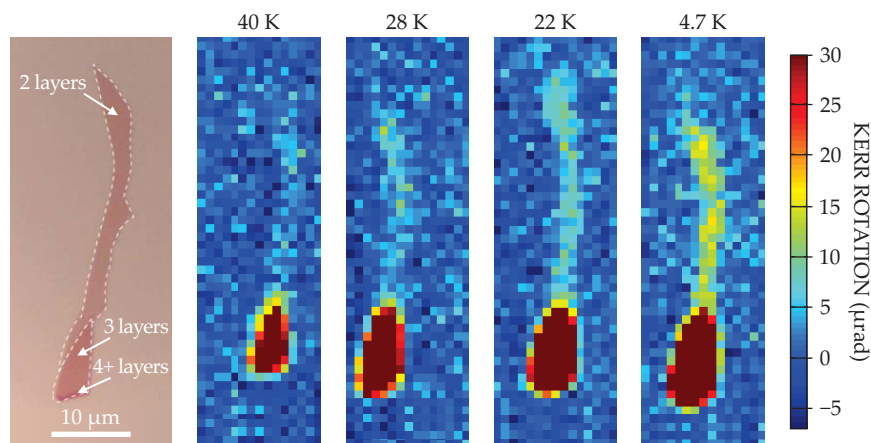


FIGURE 2. AS THE TEMPERATURE DROPS on a bilayer and trilayer sample of CrGeTe_3 , magnetic order appears and strengthens, as evidenced by magneto-optic Kerr effect measurements. The data, however, were collected with an applied magnetic field of 0.075 T; at zero field, the magnetic transition temperature is much lower. (Adapted from ref. 1.)

its component elements should be magnetic—and magnetically anisotropic. Several candidate materials have emerged, with the leading contenders all based on chromium. Although elemental Cr is antiferromagnetic at room temperature, plenty of Cr compounds are ferromagnetic, including CrO_2 and the van der Waals materials CrI_3 , CrSiTe_3 , and CrGeTe_3 .

Field effect

In the five years that Zhang has been working on 2D magnetism, he's considered several materials. He ultimately ruled out CrI_3 because it's unstable in air and CrSiTe_3 because its T_c of 33 K is too low. "We have an intuition that the transition temperature in 2D materials would be lower than it is in the bulk form," he says, "so we'd better consider those bulk crystals with higher transition temperatures." He concluded that the most suitable candidate was CrGeTe_3 —a structural cousin of CrSiTe_3 —with a T_c of around 70 K.

Few-layer flakes of CrGeTe_3 can easily be peeled away from a bulk crystal by mechanical exfoliation, the same "sticky tape" method that spurred the study of graphene (see *PHYSICS TODAY*, December 2010, page 14). Monolayers of the material degrade quickly, but Zhang and colleagues got plenty of bilayers and trilayers—which are still perfectly respectable 2D materials. Different layer numbers are often present in the same sample, and they can be distinguished optically, as shown in the leftmost panel of figure 2.

The researchers monitored the material's magnetic properties using the mag-

neto-optic Kerr effect, or MOKE, the minute rotation in the polarization of a laser beam when it's reflected off a ferromagnetically ordered material. There are other ways to measure magnetism, such as with a superconducting quantum interference device, but they're less well suited for 2D samples, which by their nature involve a small amount of material. The MOKE signals from CrGeTe_3 are tiny—just tens of microradians—so the Berkeley researchers had to make their measurements with an ultrasensitive instrument in the lab of collaborator Jing Xia at the University of California, Irvine. (An earlier version of the Sagnac interferometer that enabled the sensitive measurements is described in *PHYSICS TODAY*, December 2006, page 23.)

As figure 2 shows, the magnetic behavior depends strongly on the number of layers. Although the MOKE signals can't be directly compared—a rotation of, say, 15 μrad doesn't mean the same thing in a bilayer as it does in a trilayer—it's evident that at 40 K the three-layer region is already significantly magnetized, but the two-layer region doesn't start to order until a much lower temperature.

The data shown in the figure were collected under a small perpendicular applied magnetic field of 0.075 T. That's a typical practice in studies of magnetic materials: The field helps to stabilize the magnetic moments and dissuade them from forming multiple magnetic domains pointing in all different directions. In bulk materials, the field doesn't make much difference to the properties of interest. But as Zhang and colleagues discovered, in 2D that's not the case.

phytron

Extreme. Precision. Positioning.

IN-VACUUM / CRYOGENIC STEPPER MOTORS and LINEAR ACTUATORS



- rotary or linear motion
- vacuum: 10^{-11} Torr
- cryogenic to 4.2 Kelvin
- radiation hardened to 10^8 rad
- integrated options:
gearheads, limit switches,
thermocouple,
superconducting wire

Reliability and Reputation
you can count on.
70 years in business,
35 years of vacuum experience.

info@phytron.com
tel. 802-872-1600

For example, the T_c of a bilayer is 44 K in a 0.3 T field and 28 K in a 0.065 T field. “We estimate that for the bilayer, the intrinsic T_c , under zero field, is probably below liquid-helium temperature, or about 4 K,” says Zhang, “but we did not observe it.” For a six-layer sample, the researchers measured a zero-field T_c of about 10 K, far below the 48 K transition temperature of 0.065 T.

The striking dependence of the transition temperature on the external field was unexpected and unprecedented. Zhang and colleagues interpret their observations as revealing a fundamental difference between 2D and 3D magnets. In bulk materials, the transition to a ferromagnetic state is governed by the exchange interaction between spins and their neighbors. “That’s usually equal to hundreds of tesla,” says Zhang, so it easily overwhelms an applied field of 0.3 T or less.

But in 2D, as Mermin and Wagner showed, the exchange interaction alone doesn’t produce magnetic order; the governing factor is magnetic anisotropy. And the magnetic anisotropy in CrGeTe_3 is modest: An off-axis applied field of less than 1 T is enough to orient spins away from their easy axis. A field of a similar order of magnitude, therefore, can have a dramatic effect on the magnetic transition.

Layer effect

Xu and Jarillo-Herrero have each been working on 2D magnetism since 2014, encouraged by work from Oak Ridge National Laboratory’s Michael McGuire that identified the layered ferromagnet CrI_3 as a promising candidate material.⁴ At a conference in the summer of 2016, they realized their common interest and complementary expertise: Xu’s is making magnetic measurements and Jarillo-Herrero’s is sample preparation and characterization. “So we joined forces,”

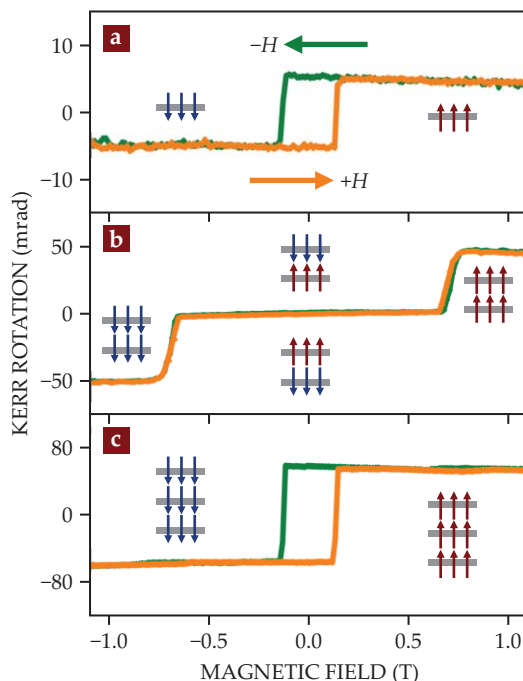


FIGURE 3. HYSTERESIS LOOPS, which form when a magnetic field H is swept from positive to negative and back again, are a signature of ferromagnetism. In samples of CrI_3 , (a) the monolayer exhibits hysteresis, (b) the bilayer does not, and (c) the trilayer does. Though not yet fully understood, the results indicate that bilayers tend toward antiferromagnetic order, with one layer spin up and the other spin down. The data shown here were collected at a constant temperature of 15 K. (Adapted from ref. 2.)

says Jarillo-Herrero, “and after that, progress was quite fast.”

Bulk CrI_3 has a similar T_c to CrGeTe_3 , 61 K, and stronger magnetic anisotropy—a field of 3 T is required to reorient the spins. It’s also well suited to mechanical exfoliation. But it has the considerable disadvantage of being unstable: If not protected from oxygen and moisture, 2D flakes degrade in a matter of seconds.

The flakes can be exfoliated and manipulated in an inert atmosphere with the help of a glove box, cumbersome as that may be. But Xu’s apparatus for making MOKE measurements doesn’t fit inside the glove box—and furthermore,

Xu’s lab is 3000 miles away from Jarillo-Herrero’s lab where the samples are prepared. “It took a long time, but we developed a packaging technique,” says Jarillo-Herrero. “The CrI_3 flakes were sealed in a chip carrier with a transparent cover. Even monolayer samples would survive this way for many weeks.”

Optical measurements, including MOKE, could be performed through the transparent lid while the sample sat safe in its oxygen- and water-free atmosphere. Because the MOKE signal from CrI_3 is orders of magnitude larger than the signal from CrGeTe_3 —milliradians instead of microradians—ultrasensitive measurements were not needed.

The researchers sought a telltale signature of ferromagnetism: a hysteresis loop. As an applied magnetic field parallel to the magnetization is swept downward, a ferromagnetic state should remain intact as the field reaches zero and even after it goes slightly negative. Likewise, when the field is swept from negative to positive, an opposite-pointing magnetic state should persist.

Indeed, as shown in figure 3, that’s what they found—for monolayers. For bilayer samples, the situation was both different and baffling. Not only was there no hysteresis, but there was no net magnetization for fields weaker than 0.65 T. With a trilayer, the familiar hysteresis loop returned.

Xu and Jarillo-Herrero concluded that the bilayer orders antiferromagnetically, with the top layer spin up and the bottom one spin down or vice versa. But why it does that—and why the ferromagnetic order returns in the trilayer—remains unexplained. “Lots of theorists are working now to understand this,” says Xu, “and the possible consequences for novel devices.”

In a 2D device, a ferromagnetic material could be used in components such as

Insaco machines to tolerances 100 times smaller than the diameter of a human hair.

We machine sapphire, ceramics and quartz

www.insaco.com | 215.536.3500

Earning your trust since 1947



sensors and memory modules. Unfortunately, the newly discovered ferromagnets' low transition temperatures—and CrI_3 's instability—make them unsuitable for most practical applications. But the very observation that 2D ferromagnetism is possible suggests that it could also be seen in other, as-yet-undiscovered van der Waals materials. Perhaps one of them will have the right combination of high T_c , chemical stability, and mechanical flexibility.

The search for better 2D ferromagnets will likely proceed in parallel with the exploration of 2D magnetism itself. In addition to clarifying the details of the effects they've already observed, Zhang, Xu, and Jarillo-Herrero also hope to work on include how 2D magnets behave when layered with other 2D materials, such as semiconductors,⁵ superconductors, and other magnets; whether magnetic properties can be controlled electrically, optically, and mechanically; and the

2D versions of novel spin textures, such as skyrmions.

Johanna Miller

References

1. C. Gong et al., *Nature* **546**, 265 (2017).
2. B. Huang et al., *Nature* **546**, 270 (2017).
3. N. D. Mermin, H. Wagner, *Phys. Rev. Lett.* **17**, 1133 (1966).
4. M. A. McGuire et al., *Chem. Mater.* **27**, 612 (2015).
5. D. Zhong et al., *Sci. Adv.* **3**, e1603113 (2017).

Coral isotopes track the rise of anthropogenic nitrogen

THOMAS DECARLO

Coal use in China has jumped sharply over the past 15 years. The concomitant nitrogen oxide emissions have left their subtle mark on a remote island.

Nitrogen is critical to life on Earth: Every amino acid of every protein molecule in every living thing contains at least one N atom. The N_2 molecules that make up most of the atmosphere, however, are nearly inert, and the element must be converted into some other chemical form before organisms can use it. That conversion can be accomplished in a few ways: lightning; N fixation by various species of bacteria and algae; and, more recently, industrial synthesis of ammonia for fertilizer. Fossil-fuel combustion, too, adds to the supply of chemically available N by releasing organic material from long-dead organisms previously trapped underground.

Human activities are known to have a sizeable and deleterious effect on the global N cycle. (See the article by Ann Kinzig and Robert Socolow, *PHYSICS TODAY*, November 1994, page 24.) In many cases N availability is the limiting factor that determines how fast a population of organisms can grow. Nitrogen pollution, such as fertilizer runoff, can stimulate overgrowth, including algae blooms, that then upsets the balance of the local ecosystem.

But the geographic extent of the disruption is poorly understood because data on the N cycle from before the rise of pollution are sparse, particularly from



remote areas. Now National Taiwan University's Haojia Ren and her colleagues have used isotope measurements to derive a 45-year N record from the coral reefs of Dongsha Atoll, an uninhabited group of islands in the South China Sea, 340 km from land.¹ Not only did the researchers detect a clear increase in anthropogenic N taken up by the coral, but they were also able to pinpoint the increase precisely enough in time to correlate it with the recent changes in Chinese pollution levels.

Heavy nitrogen

Corals, such as the one in figure 1, are colonies of countless tiny animals called polyps. (See *PHYSICS TODAY*, September 2016, page 15.) Like many other inverte-

FIGURE 1. TO COLLECT A CYLINDRICAL CORAL SAMPLE, 3 cm across and tens of centimeters long, Kan-Min of the Dongsha Atoll Research Station drills into a large coral colony. The pneumatic drill is powered by a spare scuba tank.

brates, the polyps in reef-building corals form rigid exoskeletons for protection. Over time, new generations of polyps grow on the exoskeletal remains of their ancestors, and the corals get steadily larger—by as much as a centimeter or two per year.

Because the old exoskeletons in the interior of a coral colony are devoid of living tissue, they remain largely unchanged from the time when their long-dead polyps were alive. Like tree rings and