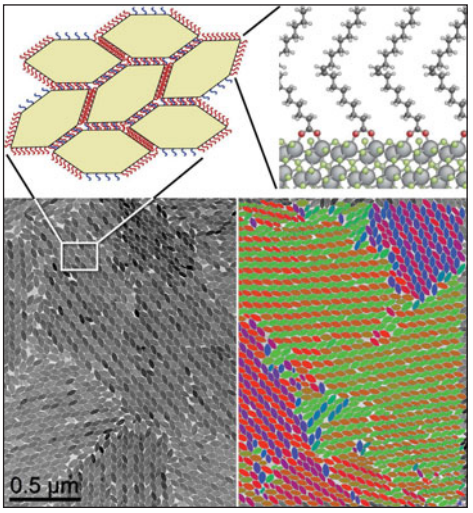
Nano Focus

"Interaction patchiness" leads to herringbone nanocrystal pattern

The programmed assembly of crystalline nanoparticles into large-scale superlattices promises the ability to construct materials with tailor-made properties. However, the ability to control the packing of nanocrystals with defined morphologies is only beginning to be realized. A mystery that has remained elusive is why some sets of nanocrystals arrange themselves in an alternating, herringbone style instead of the expected tiled patterns. Now a team of researchers from the University of Pennsylvania, the University of Michigan, the Massachusetts Institute of Technology, and Intelligent Material Solutions, Inc., in Princeton has found an answer, as reported in the online edition of *Nature Chemistry* (DOI: 10.1038/NCHEM.1651).



Rare-earth flouride nanoplates self-assemble at the liquid–air interface into the herringbone pattern.

By exploiting the differences in packing of oleic acid ligands around nanoparticles with well-defined facets, which leads to an "interaction patchiness," the researchers have succeeded in generating unique ordered assemblies of nanoparticles. Sharon Glotzer, the Stuart W. Churchill Collegiate Professor of Chemical Engineering at Michigan, introduced the concept of "patchiness" in 2004, and her group uses computer simulations to understand and design the patches.

Recently, her group was approached by Christopher Murray's group from the University of Pennsylvania. Murray's team made patterns with flat lanthanide fluoride nanocrystals, whose surfaces were functionalized with oleic acid. These particles have sizes of ~100 nm and by using lanthanides with different atomic radii, the researchers could control the morphologies of the nanoparticles to be anywhere between hexagonal and diamond-shaped.

The diamond shapes and the very long hexagons lined up as expected, the diamonds forming an Argyle-style grid and the hexagons matching up their longest edges like a foreshortened honeycomb. The hexagons whose sides were all nearly the same length should have formed a similar squashed honeycomb pattern, but instead, they lined up in a more complicated, alternating herringbone style.

"Whenever we see something that isn't taking the simplest pattern possible, we have to ask why," said Murray, the Richard Perry University Professor and professor of chemistry.

They posed the question to Glotzer's team.

Glotzer and her group built a computer model that could recreate the self-assembly of the same range of shapes that Murray had produced. They found that if the edges that formed the points were stickier than the other two sides, the hexagons would naturally arrange in the herringbone pattern. The teams suspected that the source of the stickiness was the carbon and hydrogen chains, which may attach to the point edges more easily.

Ju Li's group at the Massachusetts Institute of Technology calculated how the chains would attach to the edges at a quantum mechanical level. The team confirmed that because of the way that the different facets cut across the lattice of the metal and fluorine atoms, more hydrocarbon chains could stick to the four edges that led to points than the remaining two sides. As a result, the particles become patchy leading to the herringbone arrangement.

Glotzer said, "Our study shows a way forward making very subtle changes in building block architecture and getting a very profound change in the larger self-assembled pattern."

Bubbles in metallic glass facilitate fracture

Bubbles in champagne in a glass may add a festive fizz to the drink, but microscopic bubbles that form in metallic glass can signal serious trouble. In this normally high-strength material, bubbles may indicate that a brittle breakdown is in progress.

That's why researchers at Johns Hopkins University used computer simulations to study how these bubbles form and expand when a piece of metallic glass is pulled outward by negative pressure, such as the suction produced by a vacuum. Their findings were published in the May 3 issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.110.185502).

"A lot of people are interested in metallic glasses because of their strength and their potential use to make better cell phone cases, computer housings and other products," said Michael L. Falk, who supervised the research. "But what precisely causes these materials to break apart or 'fail' has remained a mystery. By studying the behavior of the bubbles that appear when these glasses crack, we were able to learn more about how that process occurs."

The nearly random arrangement of atoms gives metallic glasses distinctive mechanical and magnetic properties. Most metallic glasses are reasonably elastic and often spring back to their original shape after being bent. Still, when a powerful enough force is applied, they can break.

"Our lab team is interested in learning just how susceptible metallic glasses are to fracturing and how much energy it takes to create a crack," said Falk, a professor in the Whiting School of Engineering's Department of Materials

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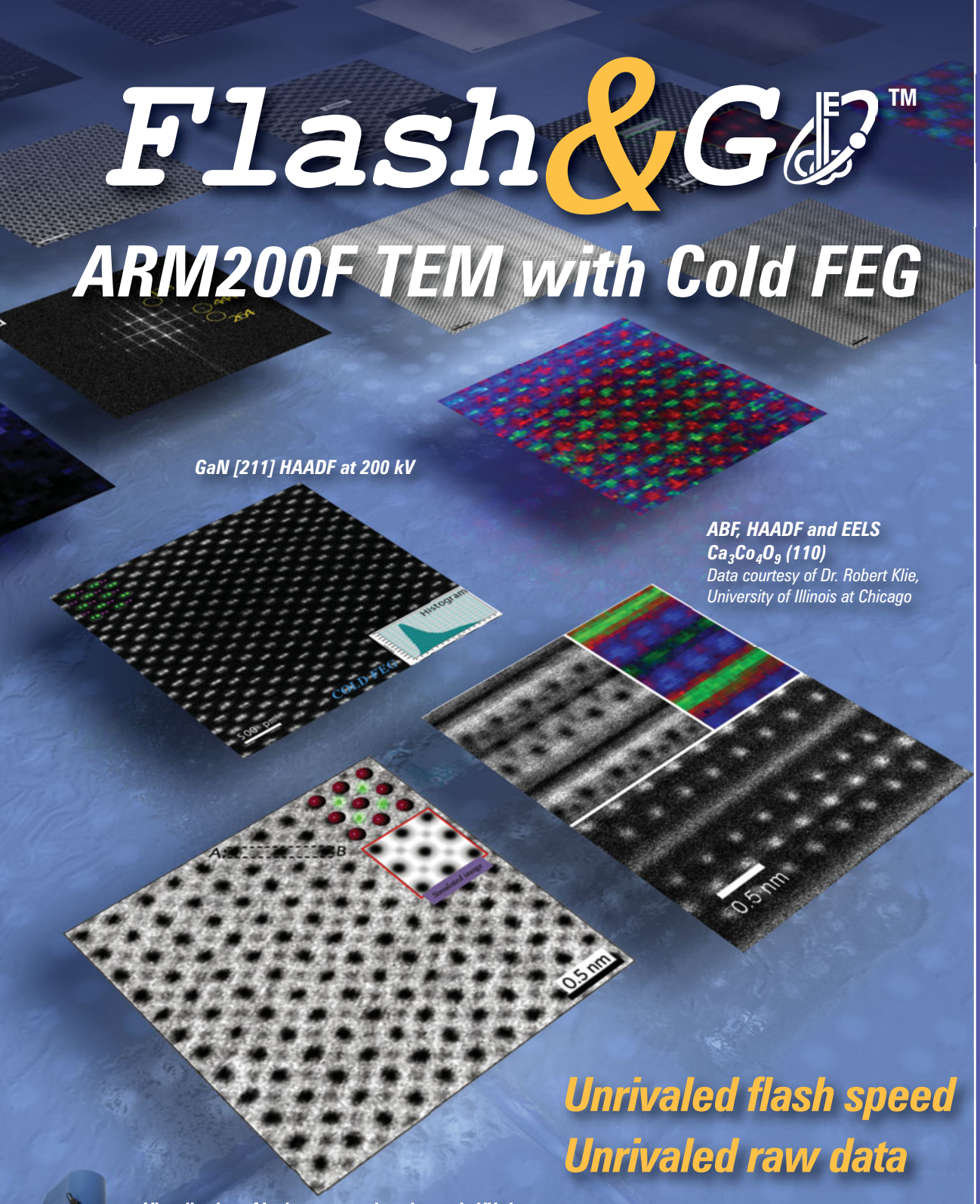

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Visualization of hydrogen atomic columns in YH_2 by ABF imaging (Y = red, H = green) *Data courtesy of Ryo Ishikawa and Dr. Eiji Abe (The University of Tokyo)*

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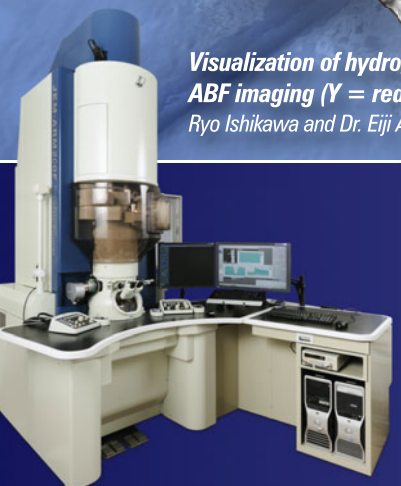

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Science and Engineering. "We wanted to study the material under conditions that prevail at the tip of the crack, the point at which the crack pulls open the glass. We wanted to see the steps that develop as the material splits at that location. That's where dramatic things happen: atoms are pulled apart, bonds are broken."

At the site where this breakup begins, a vacant space—a bubble—is left behind. Falk's research group discovered that cavitation—spontaneous formation of tiny bubbles under high negative pressures—plays a key role in the failure, or breakdown, of metallic glasses.

Falk said, "Once it appears, it releases energy as it grows bigger, and it may eventually become big enough for us to see it under a microscope. But by the time we could see them, the process through which they had formed would be long over."

Therefore, to study the bubble's nucleation, Falk's team used a computer model of a cube of a metallic glass made of copper and zirconium, measuring only about 30 atoms on each side. By definition, a bubble appears as a cavity in the digital block of metallic glass, with no atoms present within that open space.

The simulations revealed that these bubbles emerge in a way that is well-predicted by classical theories, but that the bubble formation also competes with attempts by the glass to reshuffle its atoms to release the stress applied to a particular location. That second process is known as shear transformation. As the glass responds to pressure, the researchers found which of the two processes has the upper hand—bubble formation or shear transformation—varies. They determined that bubbles dominate in the presence of high tensile loads. But when the pulling forces were small, the atom reshuffling process prevailed.

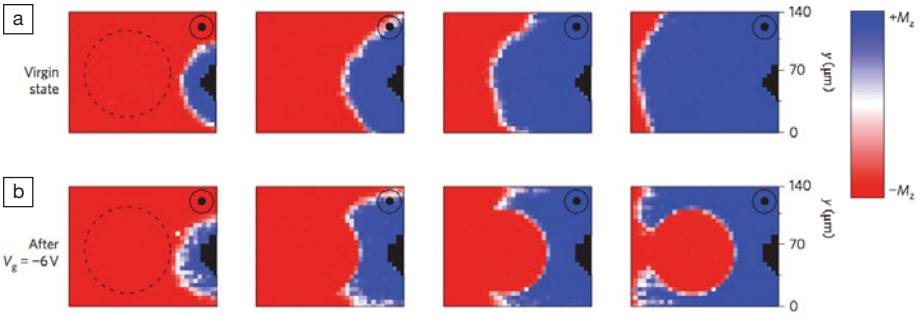
Falk and his colleagues hope their findings can help scientists developing new metallic glass alloys for products that can take advantage of the material's high strength and elasticity, along with its tendency not to shrink when it is molded to a particular shape. These characteristics are important for applications, for example, in cell phones and computers.

"Our aim is to incorporate our findings into predictive models of failure for these materials," Falk said, "so that they can be optimized and used in applications that require materials that are both strong and fracture-resistant."

Electric field utilized to locally pin magnetic domain walls

Advances in thin-film synthesis and characterization have enabled the development of electrically switched magnetic materials for novel memory applications. These devices are typically switched by substrate-strain transfer or electrostatic field effects, but such mechanisms are slow and of limited utility. Writing in the June issue of *Nature Nanotechnology* (DOI: 10.1038/NNANO.2013.96; p. 411), researchers Uwe Bauer, Satoru Emori, and Geoffrey Beach at the Massachusetts Institute of Technology (MIT) now report an electric and magnetic field coupling mediated by magnetic domain wall pinning. The researchers describe new insight into fundamental defect-domain wall interactions and believe that such a mechanism may form the basis for faster, more efficient memories.

The researchers first deposited thin-film heterostructures of Ta(4 nm)/ Pt(3 nm)/ Co(0.9 nm)/GdOx (3 nm) using dc magnetron sputtering and capped them with an array of Ta/Au gate electrodes. They chose this particular compound because the perpendicular magnetic anisotropy (PMA) of Co is sensitive to interfacial O^{2-} ions; by applying an electric field it is possible to displace the ions at the interface and reversibly switch the PMA of Co. To visualize domains, the researchers used a technique called magneto-optical Kerr effect (MOKE) microscopy, which relies on the change in polarization and phase of a laser reflected from the film. The researchers first nucleated a magnetic domain on the surface of the film using an external tungsten microprobe and then mapped the expansion of the domain. Their results directly reveal magnetic domain wall growth under the application of an external magnetic field.



A series of polar magneto-optical Kerr effect microscopy maps showing expansion of a magnetic domain (blue) under an applied magnetic field of 170 Oe with increasing time (from left to right). Row (a) shows the material in its virgin state, without electric-field poling. In this case the domain propagates unperturbed. Row (b) shows the material after poling the dashed region, which then acts to pin the propagating domain. Reproduced with permission from *Nature Nanotech*. (2013), DOI: 10.1038/NNANO.2013.96. © 2013 Macmillan Publishers Ltd.

The researchers find that by poling the Ta/Au contact, it is possible to locally change the interface anisotropy and pin magnetic domain walls around the contact. In a series of elegant measurements, the group finds that it is possible to create a nonvolatile memory cell based on a series of domain wall traps with increasing pinning strength. These results may lead to magnetic memories based on electric-field pinning of magnetic domain walls, while the techniques developed for this study may be extended to other studies of domain wall kinetics.

Steven Spurgeon

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