

of the properties of the GaSe/MoSe₂ misfit heterojunction showed efficient charge separation at the interface, which demonstrated strong coupling despite the 13% lattice mismatch, as revealed by photoluminescence quenching of the MoSe₂. The *p-n* junction also showed a gate-tunable photovoltaic response, with the photoresponsivity ranging from 5.5 mA/W to 25.3 mA/W with increasing gate voltage.

“This vdW epitaxial growth method opens up a whole new family of heterostructures because you no longer need

to worry about lattice matching at the unit cell,” comments Dave Johnson, an expert in misfit layer heterostructures at the University of Oregon. “The synthesis of heterostructures via vdW epitaxy, or other approaches, will change the way we think about materials optimization and enable the design of materials by actually modifying the identity, sequence, and nanoarchitecture of the heterostructured solid so that you can selectively tune device performance.”

This epitaxial growth protocol is not only limited to 2D semiconductors, but

is predicted to also be accessible to both 2D metals and insulators. Despite this promise, the challenge will lie in tuning the growth temperature and pressure for each individual material in order to address problems with interfacial contamination, diffusion, and evaporation. If these conditions can be met, the synthesis of vdW misfit heterostructures will unlock a realm of materials that have not yet been explored, and will allow the selective tuning of materials’ properties based on its epitaxial building blocks.

Tyler W. Farnsworth

Magnetic phenomena from the confines of a nonmagnetic material

There have been many recent advances in the synthesis, manipulation, and study of complex atomic-scale structures and interfaces. Among these, understanding the fundamental changes in physical properties in areas of reduced dimensionality has played an important role and has led to improvements in spintronics, digital memory, and transistor technologies. A study from the University of Geneva,

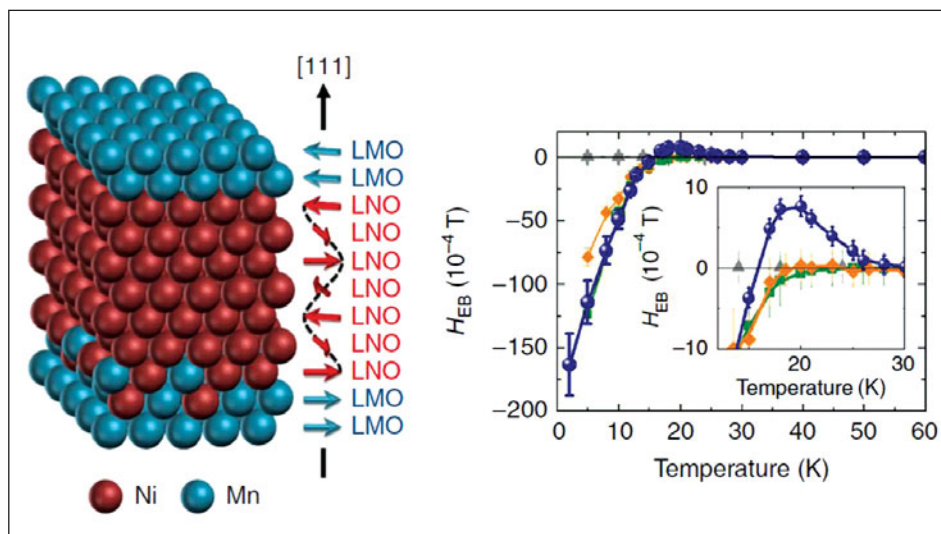
Switzerland, published in a recent issue of *Nature Communications* (doi: 10.1038/ncomms11227), demonstrates the complex evolution of magnetic phenomena occurring at the interfaces in multilayered perovskite oxides.

The researchers focused their efforts on [111]-oriented superlattices of LaNiO₃ (LNO)/LaMnO₃ (LMO). M. Gibert, the lead author, states “We focused on interface engineering, studying new properties that emerge at the interfaces of these oxide materials.”

At low temperatures, most materials in the LNO family of perovskite

nickelates are both electrically insulating and antiferromagnetic. However, LNO is known to be both metallic and nonmagnetic at all temperatures. Researchers have shown that growing thin epitaxial LNO films in the [111] direction in between layers of LMO can promote a dimensionality-induced insulating character as well as antiferromagnetic ordering of the magnetic moments. As Gibert describes it, “LNO in these specific conditions behaves more like all the other nickelates.” Furthermore, by restricting the LNO layer to only 7 monolayers (ML), they were able to promote a number of complex temperature-dependent exchange coupling phenomena.

In a layer this thin, the LNO monolayers were found to couple antiferromagnetically to each other creating a 4-unit-cell stack that equates to a net zero magnetic moment, just like the rest of the perovskite nickelates. However, if only 7 ML of LNO are sandwiched between the LMO layers, the 4-unit-cell sequence is unfinished and the magnetic moments at the ends of the LNO layer (at the interfaces) are pointing in opposite directions; see Figure. Since the LMO layer couples ferromagnetically (parallel) to the LNO layer by a charge-transfer mechanism, successive LMO layers are then



Model of the magnetic arrangement of 7-monolayer LaNiO₃ in the LaNiO₃/LaMnO₃ superlattice. The exchange bias sign reversal is exclusively observed for the superlattice with 7-monolayer LNO (blue), that is, not for 5-monolayer LNO or 8-monolayer LNO. Credit: *Nature Communications*.



antiferromagnetically coupled to one another through the LNO layer. This ferromagnetic coupling at the LNO/LMO interface in turn contributes to stabilizing the antiferromagnetism in the LNO layer.

The researchers also demonstrated the exchange bias effect in the LNO/LMO heterostructures, a phenomenon that finds tremendous use in applications such as magnetic recording media. This unique effect, which originates from a balance between anisotropy energy (keeping magnetic moments aligned in a preferred direction) and exchange energies (coupling magnetic moments to

one another) at an interface, produces a shift along the field axis of the magnetic hysteresis measurement. At low temperature ($T < 15$ K), a negative shift occurs in the LNO/LMO superlattice. However, at slightly higher temperatures (15 K $< T < 30$ K), there is a sign reversal of the exchange bias field that shifts the magnetic hysteresis measurement toward the positive field axis. Finally, at $T > 30$ K, this effect makes way for the antiferromagnetically coupled state described earlier.

This complex magnetic behavior is explained through an asymmetry in the

interfacial energy terms at the top and bottom LNO/LMO interfaces that arises from the intermixing of Ni and Mn atoms. The competition between the anisotropy energy of the LNO layer and the interfacial energies at each of the LNO/LMO interfaces, all of which vary with temperature, leads to the complex evolution of the exchange bias phenomena.

These results demonstrate that the restriction of dimensionality that occurs at oxide interfaces can promote unique magnetic phenomena in a material that is typically nonmagnetic.

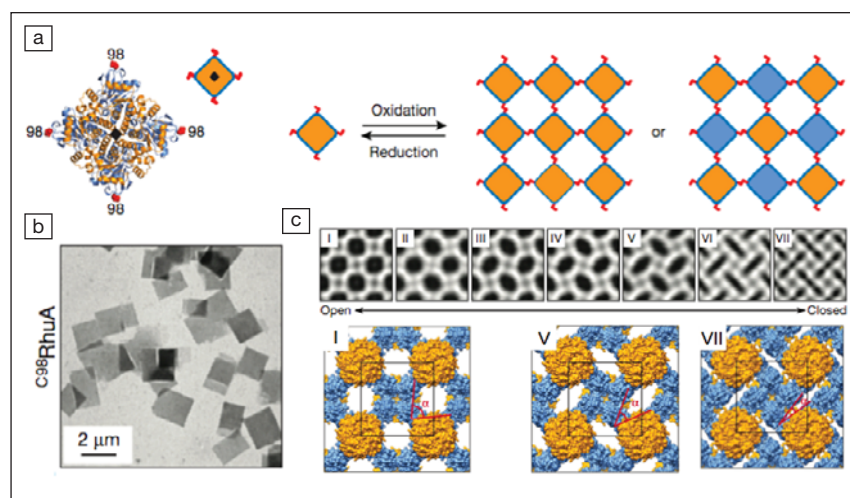
Ian McDonald

Proteins link up to form dynamic 2D materials

Two-dimensional (2D) materials like graphene are highly attractive due to their unique electronic and mechanical properties. However, flexible methods for bottom-up assembly of such planar structures remain to be developed. The ability to customize the chemistry or structure of 2D crystals through assembly would be very valuable, expanding the potential of these materials for practical applications. Recent work by investigators at the University of California, San Diego and Purdue University suggest that a biological approach to 2D crystal synthesis, using engineered proteins as lattice elements, offers unprecedented flexibility for tuning self-assembly. This study is described in a recent publication of *Nature* (doi:10.1038/nature17633).

The researchers worked with the protein L-rhamnulose-1-phosphate aldolase, or “RhuA,” a model system which has previously been used as a building block for protein crystal self-assembly. In contrast to previous efforts to engineer protein crystal formation by merging multiple protein units or utilizing computational design strategies, the approach utilized in the current work is remarkable in its simplicity.

RhuA is a homotetramer, that is, a protein complex, with C₄ symmetry. This provides the tetramer with



(a) Schematic of RhuA tetramer structure and possible modes of two-dimensional assembly; (b) transmission electron microscope image of C⁹⁸RhuA crystals; and (c) seven conformations assumed by the coherently dynamic C⁹⁸RhuA crystals, with three structural schematics further illustrating the structural changes. Credit: *Nature*.

a square-like geometry suitable for checkerboard-like lattice assemblies; see part (a) in the Figure. To achieve 2D structures, the researchers inserted either single or double amino acid mutations at the tetramer corners that could serve as linkage sites that drive assembly. Three variants were created, including either single or double cysteine mutations, or double histidine mutations at tetramer corners.

Once obtained, the purified RhuA variants were induced to assemble by adding a reducing reagent (such as β-mercaptoethanol) to drive disulfide

bridge formation or a soluble metal (e.g., Zn²⁺) to initiate metal bridge linkages.

Initial evidence of protein assembly could be easily observed by the eye as a cloudy precipitate, allowing a wide variety of potential assembly buffer chemistries to be rapidly explored. Once initial conditions were identified, transmission electron microscopy analysis was used to further characterize potential crystalline materials.

All three RhuA variants yielded crystalline assemblies. Products from the single cysteine variant, C⁹⁸RhuA, were most interesting, forming near defect-free single crystals up to several micrometers in