Correlated Materials Get in Sync

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Materials that can be reversibly switched from insulators to metals could enable a variety of new applications.

In 2006, Shriram Ramanathan had just entered the academic world when he learned about a material that would set the trajectory for his career. Then a new professor in applied physics at Harvard University, Ramanathan stumbled upon a study about vanadium dioxide (VO₂) exhibiting an unusual property: a thin film of VO₂ on glass, when stimulated with a laser, transformed from a transparent electrical insulator to a reflective metal in just hundreds of femtoseconds.

Trained as an electrical engineer and fresh out of a 3.5-year stint with Intel, Ramanathan immediately wondered how fast the transition could be done with electricity. That could have huge implications for making ultrafast electronics.

Since then, Ramanathan, now a materials scientist at Purdue University, has devoted most of his time and attention to VO₂ and just one other material, samarium nickel oxide (SmNiO₃), which caught his attention around 2010.

VO₂ and SmNiO₃ both belong to a family of materials known as strongly correlated materials. “Our entire electronic universe is made by three things”: metals, insulators, and semiconductors, Ramanathan says. To him, VO₂, SmNiO₃, and a subset of other strongly correlated materials occupy a unique fourth position because they can embody the other three. “They have this fantastic property of being able to go from insulating to semiconducting to metallic,” he says. “That is the most remarkable thing.”

That insulator-to-metal transition can be triggered by a number of stimuli, such as a change in temperature, exposure to light or electric fields, mechanical strain, or absorption of chemical species. Depending on the stimulus, the transition could occur as fast as femtoseconds, or as slow as minutes or hours.

The transition produces a dramatic change in several material properties at once, says Junqiao Wu, a materials scientist at the University of California, Berkeley. Not only do electrical properties like resistivity change, he says, but also optical properties like refractive index. Often, these properties change by multiple orders of magnitude. In the case of VO₂, the insulator-to-metal transition completely transforms its crystal structure. SmNiO₃ undergoes more subtle distortions in the nickel–oxygen bonding, but those distortions still produce large changes in properties.

This dramatic yet highly controllable behavior means that correlated materials could not only turbocharge existing computing applications but also enable new ones in disparate fields. “Sensing, switching, modulating signals—those are all fair game,” says Richard Haglund, a physicist at Vanderbilt University.

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Building upon decades of research on the materials’ properties and preparation, scientists are now exploring how correlated materials can be used practically in the real world. They could help give silicon devices a much-needed boost by enabling neuromorphic computing architectures, which mimic how the brain processes information. Or they could open up new applications in infrared camouflage or thermal management in space. “The key here is to be creative,” Ramanathan says.

Crystal chemistry
In 1959, physicist Frank Morin of Bell Labs discovered that the electrical conductivities of a variety of vanadium oxides and titanium(III) oxide plummeted rapidly within a narrow temperature window as he cooled the oxides. With this study, Morin provided the first experimental evidence of the metal-to-insulator transition. The transitions were attributed to the materials’ electronic structure. Their electrons repel each other so strongly that the electrons’ movement and freedom are very much influenced by their neighbors, Wu explains. He likens the electrons in strongly correlated materials to children sitting in a classroom with fixed seats, where any child can switch seats only if another child agrees to vacate theirs. In a classical insulator, the children would be not be able to move from their seats. In a classical metal, the children would be running amok. But for correlated materials, with the right stimuli, the children can begin moving from seat to seat in a coordinated way, and thus transition from an insulator to a metal.

A layer of samarium nickel oxide on sapphire (bottom row) appears to stay between 100 and 105.8 °C to an infrared camera even as the actual temperature is raised to 140 °C. Credit: Alireza Shahsa/University of Wisconsin–Madison.

Although several strongly correlated materials can change from insulators to metals, including various transition metal oxides, only a few have a shot at breaking free from the laboratory and making a difference in the world, Ramanathan says. First, the transition needs to be reversible—that is, the materials’ transitions must “cycle back and forth very, very reproducibly,” he says. Second, the material’s transition needs to occur above room temperature to be practical for real-world devices. VO₂ stood out early on because it transitions around 68 °C. SmNiO₃ transitions at 130 °C. That higher transition temperature makes SmNiO₃ more suitable for electronics, which often operate at temperatures up to 100 °C.

Achieving these stable, reversible transitions took a long time, though. Bulk crystals of VO₂ would crack after just one insulator-to-metal transition. After Morin’s 1959 discovery, it took researchers until the 2000s to observe reversible transitions in high-quality, crystalline thin films of VO₂, Ramanathan says.

Correlated materials can be made with typical crystal growing techniques used in electronics manufacturing, such as physical or chemical vapor deposition, but they have challenging new requirements. For example, getting the stoichiometry exactly right for VO₂ is crucial, Wu says. There are many oxides of vanadium—VO₂, V₂O₅, V₂O₃—that could form instead and contaminate the crystal. “If you grow VO₁.₅ or VO₂.₅, then your phase transition will not be as good,” he says. Controlling the partial pressure, or flow of oxygen, and temperature during crystal growth is thus key.

For SmNiO₃ and other related rare-earth nickelates, getting the right crystal structure is critical, Ramanathan says. In this case, the material must take on a perovskite crystal structure—which the researchers discovered could only be achieved at high pressures.

The researchers also found that they could change the insulator-to-metal transition temperature by introducing other elements. Doping with tungsten, for example, lowers the transition temperature of VO₂, while doping with gallium increases it. In another example, Ramanathan found that allowing hydrogen ions to diffuse into the SmNiO₃ crystal structure alters the insulator-to-metal transition, offering a new way of controlling material properties that could be exploited for certain applications.

Enabling new applications
Physicists are still working hard to understand these insulator-to-metal transitions, Haglund says, but in the meantime, researchers have been pushing correlated materials into applications.

Conventional transistors switch between an on and off state that correspond to low and high resistance levels to perform functions like memory storage. For more complex architectures like those in neuromorphic computing, “it’s no longer good enough to have just an on-off switch,” Ramanathan says. “You need to be able to create many levels between on and off.” In 2018, Ramanathan reported using hydrogen-doped SmNiO₃ and neodymium nickel...
oxide to make memory devices that can take on multiple states as hydrogen ions from a reservoir slowly migrate in or out of the oxides, varying the resistance along a continuum. The memory devices can switch between states in as little as 30 ns.

Haglund hopes to boost the optical switching performance of silicon photonic devices to raise data movement speeds to terabits per second. “The issue of data communication is now at least as challenging as computing itself,” he says. By adding a thin coating of VO₂ to a traditional silicon component called a ring resonator used for modulating optical data signals, Haglund hopes to achieve switching at sub-picosecond levels. That would be several hundred times as fast as the switching speeds possible with silicon-only components.

Haglund is also developing a VO₂ coating for NASA that can help spacecraft cope with heat when they face the sun and with cold when they are in the dark. Today’s spacecraft must carry large mechanical shutters or reflective shields to manage temperature differences. “It turns out, vanadium dioxide is almost an ideal solution to this problem,” Haglund says, because it turns metallic and reflects light when it is warm but reverts to insulating and transmissive when it is cold. The trick is to lower the transition temperature to NASA’s requirement of between 0 and 10 °C, he says. To do this, Haglund is experimenting with doping VO₂ with tungsten and forming the material into nanoparticles.

In December, Ramanathan and collaborator Mikhail Kats of the University of Wisconsin–Madison showed that SmNiO₃’s insulator-to-metal transition could enable an infrared camouflage coating. A thin film of SmNiO₃ on a sapphire substrate masked the thermal image of the substrate by giving off a constant amount of IR light within a temperature window. As the researchers raised the temperature from 100 to 130 °C, any increase in IR light from SmNiO₃ due to temperature was precisely canceled out by the material’s decreasing ability to emit IR light as it went from an insulator to a metal, Kats explains. Wu has also managed to achieve a similar camouflage effect with VO₂ but at room temperature.

Ramanathan has also found a novel application of SmNiO₃ as an electric field sensor. Because the material is sensitive to hydrogen ions, it can detect electric fields in saltwater when protons migrate inside its crystal lattice. The researchers believe such electrochemical sensors could be useful for detecting electric potentials generated by marine animals such as sharks, rays, and skates, or from maritime vessels.

Other than insulator-to-metal transitions, strongly correlated materials are coveted for unusual features in magnetic or superconducting properties. Even more could be in store if additional materials with practical properties could be found. Researchers at the Los Alamos National Laboratory and Northeastern University recently built a materials discovery tool that could help predict the properties of new strongly correlated materials.

“There are plenty to begin with, but I’m sure there are many, many more,” Ramanathan says. “They’re just waiting to be discovered.”

XiaoZhi Lim is a contributor to Chemical & Engineering News, the weekly newsmagazine of the American Chemical Society.