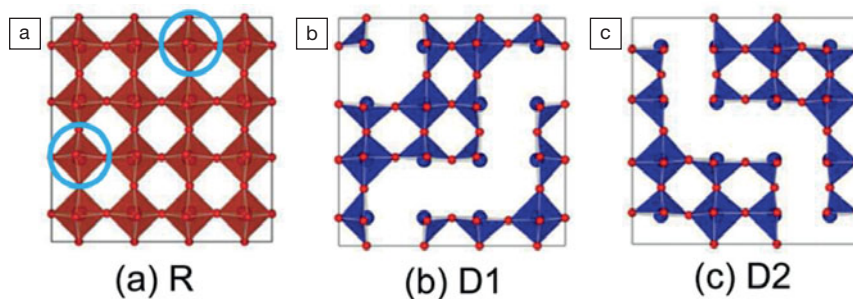




“Spin bag” model proposed for room-temperature ferromagnetism in $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$

Transition-metal perovskite oxides are used in many devices ranging from piezoelectric transducers to thermoelectric coolers and novel magnetic memories. Despite their abundance, many questions remain about fundamental magnetic ordering in these systems. Researchers Jerry Bettis Jr. and Myung-Hwan Whangbo at North Carolina State University, in collaboration with Hongjun Xiang at Fudan University in China, have now used density functional theory (DFT) to explore the origin of the room-temperature ferromagnetism in $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$ ($0.5 < \delta < 1.0$) (SYCO). They propose a novel kind of ferromagnetism in this oxygen-deficient perovskite, namely, the formation of ferromagnetic “spin bags.”

Reporting their results in the August 28 issue of *Chemistry of Materials* (DOI: 10.1021/cm302007q; p. 3117), the researchers explain the origin of ferromagnetism in SYCO, whose structure comprises two kinds of perovskite layers that alternate along the *c*-axis direction. Oxygen vacancies are absent in the oxygen-rich perovskite layers (R layers),



Schematic of the different perovskite layers present in the room-temperature ferromagnet $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$ ($0.5 < \delta < 1.0$). Panel (a) shows an oxygen-rich layer with no oxygen vacancies, while (b) and (c) demonstrate the oxygen-deficient layers with ordered oxygen vacancies. Each circled CoO_6 octahedron of the R layer contains a low-spin Co^{3+} ion, and forms a ferromagnetic spin bag with the surrounding four adjacent CoO_6 octahedra containing high-spin Co^{3+} ions. Reproduced with permission from *Chem. Mater.* **24** (2012), DOI: 10.1021/cm302007q; p. 3117. © 2012 American Chemical Society.

but ordered oxygen vacancies are present in the oxygen-deficient perovskite layers (D1 and D2 layers). The research group carried out DFT calculations using a supercell for three situations. A first case has both the crystal structure and the G-type antiferromagnetic structure kept frozen, while a second case has the crystal structure frozen but the magnetic structure relaxed. The third case has both the crystal and magnetic structures relaxed.

The researchers find that the last two cases give rise to ferromagnetism with a Co magnetic moment close to that

measured experimentally ($\sim 0.25 \mu_B/\text{Co}$). Moreover, they find that the Co^{3+} ions in the R layers form isolated ferromagnetic “spin bags,” with each bag consisting of a low-spin Co^{3+} ion surrounded by four high-spin Co^{3+} ions in every R layer. They hypothesize that the formation of ferromagnetic spin bags stabilizes the ferromagnetism of SYCO, and are currently investigating other possible conditions for spin bag formation. This curious and novel concept of spin bag formation provides a fresh way of thinking about ferromagnetism in transition-metal oxides.

Steven Spurgeon

Energy Focus

Photovoltaic device made only of nanocarbon

A major goal of the solar photovoltaic research community is to make solar cells entirely from nanocarbon materials, and therefore free from the polymer binders that currently limit long-term stability. Michael S. Strano and colleagues from the Massachusetts Institute of Technology have now achieved just this, fabricating a solar cell containing only single-walled carbon nanotubes (SWNTs) and C_{60} as the active photovoltaic material, as reported in the August 22 issue of *Advanced Materials* (DOI: 10.1002/adma.201202088; p. 4436).

“It wasn’t clear that you could get a

photocurrent from a photovoltaic cell that’s built like this—there’s no polymer, there’s no silicon—it’s all carbon,” Strano said. “The major advantages are that you do not have to rely on semiconducting polymers that are unstable, and that the materials are renewable and cheaper than silicon.”

The SWNT active material absorbs near-infrared radiation—a portion of the electromagnetic spectrum not normally absorbed by solar cells. By combining this carbon-based cell with the best available silicon-based cells, Strano envisions a hybrid photovoltaic device that harvests the 40% of the solar spectrum that lies in the near-infrared region. This new class of solar cells could potentially be coupled with silicon technology,

which currently dominates the market, to achieve a significant increase in the amount of radiation absorbed and converted to electricity.

The researchers fabricated the layered cell starting with a glass-supporting substrate and a patterned indium-tin-oxide electrode. A 100-nm-thick film of SWNTs, all of the same (6,5) chirality, was deposited on the electrode, followed by a 70-nm-thick layer of C_{60} . The researchers topped the device with a silver film as the second electrode. The SWNT absorbs photons and creates a quasiparticle called an exciton—an electron-hole pair. The exciton moves to the C_{60} layer, which grabs the electron and sends the hole up to the cathode, thus producing a photocurrent.



A key to the group's success has been the ability to isolate large amounts of very pure (6,5) SWNTs, based on a process developed by Huaping Liu and colleagues at the National Institute of Advanced Industrial Science and Technology and the Japan Science and Technology Agency. "We've shown that if you put in an impurity of (6,4) SWNTs, there's something about the junction between two dissimilar nanotubes that

causes excitons to be irradiatively recombined, instead of separated and harvested for their current," said Strano. This happens even though (6,5) and (6,4) SWNTs have very similar bandgaps.

Strano acknowledges that this is a "humble advance" in photovoltaic research, because the efficiencies his group has measured to date for the nanocarbon devices are only about 0.1%. However, significant improvements can likely be

made by combining the two nanocarbon materials in ways that maximize the surface area and produce continuous phases.

"We see this as a starting point—it expands the tools and the available technologies for the energy engineer to build new kinds of photovoltaic cells," Strano said. "It carves out a new space in photovoltaic technology."

Tim Palucka

Nano Focus

Vanadium oxide bronze nanowires show unprecedented metal-insulator transition

Researchers are working to identify materials that could one day replace silicon to make computing faster. Sambandamurthy Ganapathy, Sarbajit Banerjee, and their colleagues at the University of Buffalo have found a vanadium oxide bronze whose unusual electrical properties in nanowire form, including unprecedented metal-insulator transitions, could increase the speed at which information is transferred and stored.

In the August 17 online edition of *Advanced Functional Materials* (DOI: 10.1002/adfm.201201513), the researchers report that they have synthesized single-crystalline $\beta\text{-Pb}_x\text{V}_2\text{O}_5$ nanowires from vanadium oxide and lead. When exposed to an applied voltage near room temperature, the nanowires transform

from insulators to metals that more readily conduct electricity. Each of these two states—insulator and metal—could stand for a 0 or 1 in the binary code that computers use to encode information, or for the "on" and "off" states that the machines use to make calculations.

"The ability to electrically switch these nanomaterials between the on and off state repeatedly and at faster speeds makes them useful for computing," said Ganapathy.

"Silicon computing technology is running up against some fundamental road blocks, including switching speeds," said Banerjee. "The voltage-induced phase transition in the material we created provides a way to make that switch at a higher speed."

As with other nanomaterials, the health and environmental impacts of the nanowires would have to be investigated before their widespread use, especially since they contain lead, Banerjee said.

One intriguing characteristic of the material they synthesized is that it only exhibits valuable electrical properties in nanoform. That is because nanomaterials often have fewer defects than their bulkier counterparts.

The distinctive structure in these nanowires is crucial to their ability to switch from an insulator to a metal. Specifically, in the insulator phase, the position of the lead in the nanowires' crystalline structure induces pools of electrons to gather at designated locations. Upon applying a voltage, these pools join together, allowing electricity to flow freely through them and transforming the material into a metal.

"When materials are grown in bulk, there's a lot of defects in the crystals, and you don't see these interesting properties," said Peter Marley who is lead author. "But when you grow them on a nanoscale, you're left with a more pristine material."

Cobalt-based nanomaterial catalyzes water splitting

Efficient storage technologies are required to exploit renewable energy sources such as wind and the sun. One strategy is the conversion of these energies into fuels such as hydrogen, which can be achieved by electrolysis of water—or water splitting—into H_2 and O_2 . A range of approaches have been investigated to achieve this goal. Devices based on proton-exchange membranes have

proven promising, but may ultimately not be viable because they rely on electrocatalysts made from scarce and expensive noble metals, such as Pt. Robust catalysts made from abundant elements such as Co, Ni, and Mn have also been developed for the evolution of oxygen gas from water (also called the oxygen evolution reaction, OER: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$), but few catalysts have been developed for the hydrogen evolution reaction (HER: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$).

Addressing this problem, V. Artero and co-researchers from the French com-

mission for Atomic Energy and Alternative Energies (CEA) centers in Grenoble and Saclay, and from the Free University Berlin, Germany, have recently developed a straightforward and practical approach to prepare a stable Co-based catalytic material for H_2 evolution.

As reported in the September issue of *Nature Materials* (DOI: 10.1038/NMAT3385; p. 802), Artero and co-researchers reduced $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from an aqueous phosphate buffer at a fluorine-doped tin oxide electrode. Electrolysis for 3 h at -1.0 V versus Ag/