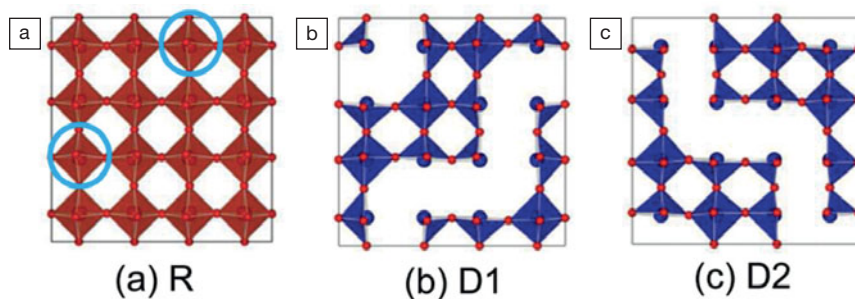




“Spin bag” model proposed for room-temperature ferromagnetism in $\text{Sr}_3\text{YCo}_4\text{O}_{10+\delta}$

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.