

## Nanoscale phase competition accompanies colossal magnetoresistance

Charles Day

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excites the one-exciton coherence into a two-exciton coherence; if the two excitons are opposite in spin, they form a biexciton, and if they are parallel in spin, they form a so-called interaction-induced coherence with frequency equal to twice that of a single exciton. The third pulse takes the two-exciton coherence back down to a one-exciton coherence, which radiates a signal whose frequency is recorded on the  $\omega_3$  axis.

Figure 2a shows the spectrum as a function of  $E_2$  and  $E_3$ —one of the 2D measurements that first became possible with the MIT group's fully coherent spectrometer. On the  $E_3$  axis, pathways i, ii, and vi, which end up in a light-exciton coherence, are seen as peaks at the light-exciton energy of 1.5495 eV; the other three pathways have peaks at the heavy-exciton energy of 1.5416 eV. On the  $E_2$  axis, the peaks display the energies of the two-quantum coherences

formed during time  $t_2$ : Pathways i, ii, iii, and iv all have the energy of the mixed biexciton, which means that pathways i and ii are indistinguishable, as are pathways iii and iv.

Figure 2b shows a different projection of the same data along the  $E_2$  and  $E_1$  axes. Pathways i and ii are separated, but now they're superimposed on pathways iii and iv, respectively. Also, pathway v, the interaction-induced coherence with two heavy excitons—by far the most intense feature in the spectrum due to the large transition dipole moment of the heavy excitons—obscures the adjacent peak from pathways i and iii.

But 3D spectroscopy offers a way to get an unimpeded view of pathways i and ii, as shown in figure 2c. There,  $E_2$  is shown only over the range around the mixed-biexciton energy indicated by the shaded box in figure 2b, and more importantly,  $E_3$  is integrated only

over the range around the light-exciton energy shown by the box in figure 2a. Since the peaks from pathways iii, iv, and v fall outside that range, all that remain are the peaks from pathways i and ii, which are well separated on the  $E_1$  axis, so their intensities and linewidths can be measured directly.

Notes Nelson, "If you want to resolve the different contributions to the signal, it's essential to scan the additional dimension." Indeed, Nelson and company have been working on adding even more dimensions, using chains of five or seven pulses rather than three, in order to look at coherences of more than two excitons.

Johanna Miller

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# Nanoscale phase competition accompanies colossal magnetoresistance

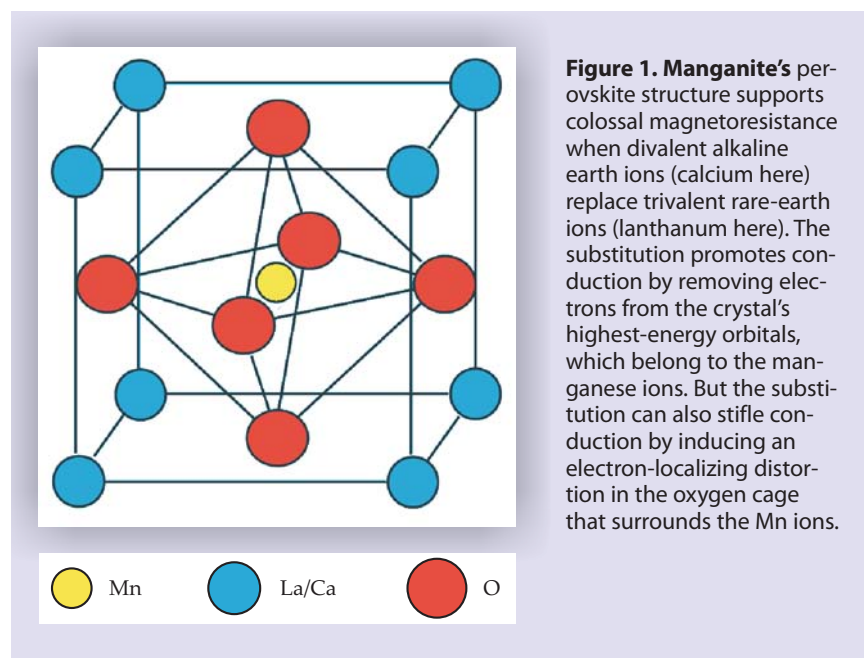
Doped manganites manifest competing phases of different electronic and magnetic order. Thanks to a new technique, the phases' nanoscale battleground can now be mapped.

**Colossal magnetoresistance** is aptly named. By subjecting a piece of appropriately doped manganite to a strong magnetic field and a moderately low temperature, one can raise its electrical conductivity by orders of magnitude.

Despite its prodigious magnitude, CMR has not led to any commercial devices since its discovery 15 years ago. Cooling a sample by the requisite few tens of kelvin isn't hard, but it is inconvenient for manufacturers. Worse, CMR shows up only at the mighty, tesla-scale magnetic fields used in magnetic resonance imaging scanners.

To physicists, however, CMR remains intriguing. Unlike its already commercialized cousins, giant magnetoresistance and tunneling magnetoresistance, CMR doesn't rely on the nanoscale layering of different materials. It's an intrinsic property of a single substance. Depending on the doping level and external conditions, a CMR material can be a ferromagnetic metal, a paramagnetic insulator, or an antiferromagnetic insulator in which the valence electrons arrange themselves in stripes and other kinds of charge order. (See *PHYSICS TODAY*, October 1996, page 19.)

Moreover, pairs of those other phases can coexist in CMR manganites whenever and wherever the tempera-



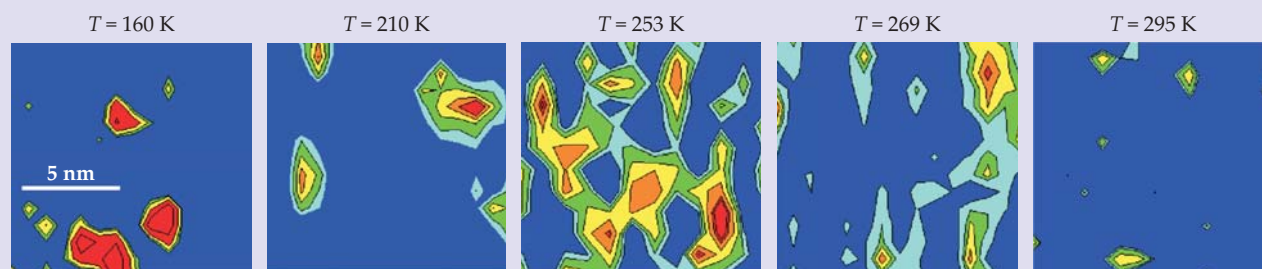
**Figure 1.** Manganite's perovskite structure supports colossal magnetoresistance when divalent alkaline earth ions (calcium here) replace trivalent rare-earth ions (lanthanum here). The substitution promotes conduction by removing electrons from the crystal's highest-energy orbitals, which belong to the manganese ions. But the substitution can also stifle conduction by inducing an electron-localizing distortion in the oxygen cage that surrounds the Mn ions.

ture, magnetic field, or mechanical strain reduces the energy differences between them. (See Neil Mathur and Peter Littlewood's article, *PHYSICS TODAY*, January 2003, page 25.)

The CMR effect itself arises when the paramagnetic insulating phase yields to the ferromagnetic metallic phase. Now, Jing Tao of Brookhaven National Labo-

ratory and her collaborators have found evidence that a charge-ordered, possibly antiferromagnetic phase plays a role too.<sup>1</sup> As her sample approached the CMR transition, patches of charge order appeared as if to forestall and thereby intensify the onset of metallic behavior.

Tao derived her results using a new technique, scanning electron nano-



**Figure 2. Regions of charge order** proliferate as the temperature  $T$  approaches 253 K, the value at which a 4-T magnetic field produces the biggest change in resistance. The appearance of charge order at the transition temperature is surprising, given that the transition itself occurs primarily between two phases, a paramagnetic insulator and a ferromagnetic metal, that lack charge order. The normalized intensity scale runs from the noise level of 1 (dark blue) through to the maximum value of 1.6 (red). (Adapted from ref. 1.)

diffraction (SEND). The technique combines electron diffraction's ability to reveal the presence of ordered structures with scanning microscopy's ability to reveal those structures' real-space distribution.

### Competing phases

The broad labels ferromagnetic, paramagnetic, and antiferromagnetic don't fully describe the richness of manganite phases. Spin-up and spin-down electrons may arrange themselves in stripes or in a checkerboard pattern; the occupancy of atomic orbitals may alternate. Those and other arrangements arise when doping turns on the interplay between a manganite's crystal structure, shown in figure 1, and its spin, charge, and orbital degrees of freedom.

Like other undoped manganites,  $\text{LaMnO}_3$ , to pick an example, is an insulator at all temperatures and magnetic fields. Replacing some of the trivalent lanthanum ions with divalent calcium ions not only removes electrons, it also engenders lattice distortions because Ca ions are smaller than La ions.

The valence electrons whose mobility—or lack of it—manifests CMR come from the two most energetic of manganese's  $3d$  orbitals. Just below them in energy are three more  $3d$  orbitals, each degenerate and occupied by one electron. Those electrons are too tightly bound to take part in conduction; they behave together like a single spin- $3/2$  particle, a so-called core spin.

When the doping is moderate (that is, in  $\text{La}_{x-1}\text{Ca}_x\text{MnO}_3$  when  $0.15 < x < 0.5$ ), the core spins align ferromagnetically at a temperature that can be raised by applying a strong magnetic field. Thanks to that alignment, the valence electrons, whose spins are also polarized, can lower their energy by hopping between Mn atoms via intervening oxygen atoms. The process is known as

double exchange. Raising the temperature, lowering the magnetic field, or doing both reduces the core spins' ferromagnetic order and the valence electrons' hopping ability. The material becomes a paramagnetic insulator.

Double exchange can account for the existence of a magnetoresistive effect in  $\text{La}_{x-1}\text{Ca}_x\text{MnO}_3$  and other manganites, but not for the effect's magnitude. The Ca ions also influence the valence electrons' mobility through the Jahn–Teller effect: If the valence electrons confine themselves to their Mn atom, they can lower their energy by inducing a distortion in the oxygen cage that surrounds them.

The more Ca ions are present, the more room the cage has to flex and the stronger the Jahn–Teller effect is. When  $0.15 < x < 0.5$ , the Jahn–Teller effect is too weak to overcome double exchange and stifle conduction. The Jahn–Teller effect does, however, contribute significantly to the resistance in the paramagnetic state. Indeed, it's responsible for the “C” in CMR.

But when  $x > 0.5$ , the Jahn–Teller effect starts defeating double exchange. Conduction ceases, the core spins align antiferromagnetically, and the valence electrons arrange themselves in stripes or another charge- or orbital-ordered pattern.

That clear-cut picture of doping-determined behavior was established within a year of CMR's discovery, but it soon proved inadequate. Various experiments revealed that phases could coexist at values of  $x$  that favor one phase over its competitor. Even when the competition is balanced, odd behavior appears.

In 2002 James Loudon, Neil Mathur, and Paul Midgley of Cambridge University applied electron microscopy to a sample of  $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ . They found regions of ferromagnetic order and

charge order, as one might expect given the fine balance at  $x = 0.5$  between the two phases. But they also found a single region where the phases appeared to coincide to form a new phase, at least at the 20-nm resolution of their magnetic probe.<sup>2</sup>

The Cambridge result was consistent with earlier simulations by Elbio Dagotto of Oak Ridge National Laboratory and his collaborators.<sup>3</sup> At a few nanometers across, the regions of charge-ordered phase that form amid the ferromagnetic phase are indeed below the resolution limit. Moreover, those charge-ordered regions, argued Dagotto, Adriana Moreo, and Seiji Yunoki, are not inconsequential bystanders in the CMR transition but active participants.<sup>4</sup>

### Scanning diffraction

Four years ago, Tao set herself the goal of directly observing the phase coexistence and determining its role in CMR. The clearest signature of charge order comes from the diffraction spots caused by the Jahn–Teller distortion. Tao realized that if the beam of a transmission electron microscope could be made narrow enough and if it could be scanned across the sample, the charge order could be mapped on the nanoscale.

Standard TEMs have a beam size of about 4 nm. Tao shrank the beam on her microscope to 1.7 nm using optics developed at the University of Illinois at Urbana-Champaign, where she did her PhD work. She also took advantage of adaptations that her former group had made to scanning hardware and image reconstruction software.

Tao used  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  as her sample. At that doping, applying a 4-T magnetic field at 253 K causes the material's resistivity to drop by 50%. (Other manganites show a bigger CMR

effect.) By scanning the SEND beam across the sample, Tao obtained a sequence of diffraction patterns. The brightest spots in each pattern corresponded to the undistorted lattice. Whenever the beam passed over a region of charge-ordered phase, additional faint spots appeared.

Figure 2 shows the maps Tao constructed from the intensity distribu-

tions of the charge-ordered spots. The regions of charge-ordered phase are indeed nanoscale. And they proliferate and spread as the CMR transition temperature of 253 K is approached from either direction. At their greatest extent, the charge-ordered phase occupies 22% of the sample volume.

Doping is inherently inhomogeneous: An  $x$  value of 0.5 doesn't imply

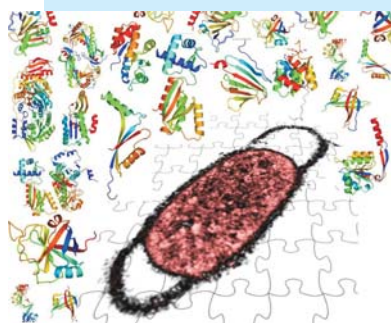
that every Mn ion is surrounded by exactly four Ca ions and four La ions. Given that Ca ions promote the charge-ordered phase, could local overdoping account for the maps in figure 2? Tao repeated the scans over her sample. Each run yielded the same overall behavior but with a different distribution of regions. Immobile dopants would have yielded the same distribution.

## physics update

These items, with supplementary material, first appeared at <http://www.physicstoday.org>.

**Element 114 verified.** In the 10 years since researchers at the Joint Institute for Nuclear Research in Dubna, Russia, first reported producing the superheavy element 114 (see *PHYSICS TODAY*, April 1999, page 21), some tens of other sightings of the element (as well as elements 115, 116, and 118) have been documented—but all by the same group. Now a team at Lawrence Berkeley National Laboratory, led by Heino Nitsche and Ken Gregorich, has confirmed the results. Such independent verification is important, particularly given evidence of fabricated results for other superheavy elements (see *PHYSICS TODAY*, September 2002, page 15), but it is complicated by experimental challenges, including picobarn ( $10^{-40}$  m<sup>2</sup>) reaction cross sections and radioactive targets. Working with the lab's 88-inch cyclotron, the Berkeley team followed a process similar to that used at Dubna: They aimed an accelerated beam of calcium-48 ions at a target containing plutonium-242. The reaction products passed through a gas-filled mass spectrometer, which separated out the nuclei of interest, to a detector that yielded energy and timing information not only for the products but also for any alpha particles or fission fragments they emitted. Amid the data the researchers collected over their eight days of running the experiment, they found two correlated chains of decays that they identified as starting with <sup>286</sup>114 and <sup>287</sup>114. Although the lifetimes (tenths of seconds), decay modes, and decay energies agree with the Dubna results, the cross sections measured by the Berkeley team are lower. That discrepancy, say the researchers, could be due to statistical fluctuations or to some of the element-114 nuclei overshooting the detector. (L. Stavsetra et al., *Phys. Rev. Lett.* **103**, 132502, 2009.) —RJF

**Shaping a cell's metabolic network.** In a single cell, thousands of simultaneously occurring biochemical reactions carry out such functions as converting and storing energy and regulating



nutrient levels; together, those processes make up the cell's metabolic network. Computational biology involves, among other things, the linking of metabolic pathways to form a metabolic network model, a promising tool for pre-clinical drug studies and other medical research. However, such computational models do not traditionally include the function-determining structural details of a network's macromolecules;

for example, an enzyme's ability to catalyze reactions and regulate the cell's response to external stimuli is determined by its three-dimensional configuration. Now, an international team led by Adam Godzik at the Burnham Institute for Medical Research in California has taken a rare step and introduced atomic-level protein structural data to the metabolic network model of an ancient thermophilic bacterium, *Thermotoga maritima*, shown in the optical microscope image. The image also shows schematics of proteins in their 3D configurations, which, when they were expressed in the reconstructed metabolic network, helped the research team solve the puzzle of how proteins evolve when their cell networks grow larger. It turns out that only 37% of *T. maritima*'s proteins are essential to the formation of its metabolic network; those "core-essential" proteins adopt the bulk—61%—of the bacterium's relatively few unique 3D configurations. The finding suggests that the core-essential proteins evolved their structure to perform additional functions in distinct pathways. (Y. Zhang et al., *Science* **325**, 1544, 2009.) —JNAM

**An exoplanet as dense as Earth.** Of the more than 350 planets that have been observed to date orbiting alien suns, only a handful have known densities. (For more on exoplanets, see *PHYSICS TODAY*, May 2009, page 46.) Now an international team led by Didier Queloz (Geneva Observatory, Switzerland) has introduced the newest member of that club, Corot-7b, the only exoplanet to have a measured density comparable to that of Earth. The result suggests that Corot-7b, like Earth, has a rocky composition. The planet and its host star Corot-7 were named after the *Convection, Rotation, and Planetary Transits* satellite, which in 2008 observed a star whose intensity periodically dimmed once every 20.4 hours—the result of a planet partially eclipsing the star. The small degree of dimming and the known size of the star established that Corot-7b has a radius about twice that of Earth's. To obtain the mass of the planet, Queloz and colleagues turned to the High Accuracy Radial Velocity Planet Searcher, a spectrograph that could precisely measure the sinusoidally modulating Doppler shifts in the light emitted by Corot-7 as it is gravitationally tugged to and fro by the small planet orbiting it. The greater the amplitude of oscillation, the greater the planet's mass. Obtaining the result required the Queloz team to filter out obscuring noise due to sunspot-like activity on the star. As a bonus, the residual signal included a component with a 3.69-day period. Queloz and colleagues attribute that to a previously unknown second planet, about eight times as massive as Earth. (D. Queloz et al., *Astron. Astrophys.*, in press, doi:10.1051/0004-6361/200913096.) —SKB

**Earth's energy balance since 1950.** Combining the powerful notion that energy is conserved with observational data on surface temperature, ocean heat content, and radiative fluxes, researchers have determined our planet's energy budget for the past half century—without recourse to any climate models. En-

That the charge-ordered phase appears to be intimately associated with the CMR transition is consistent with Dagotto's most recent simulations.<sup>5</sup> Weak, charge-ordered correlations are present in the insulating paramagnetic state. As the temperature is reduced toward the transition temperature, the correlations strengthen, creating regions of charge order. "Then, at the

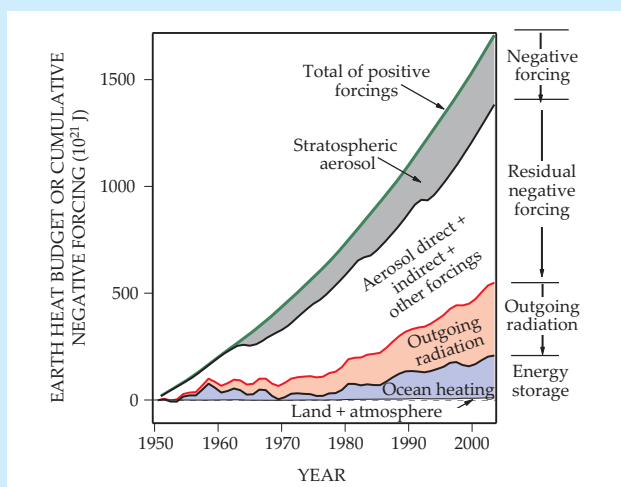
transition itself," Dagotto says, "the ferromagnetic state abruptly emerges, as if its lower energy defeats the charge-ordered state's higher entropy."

Support for that picture, which is based on simulating clusters of up to 256 Mn atoms, may come when Tao extends her investigation to other doping values.

Charles Day

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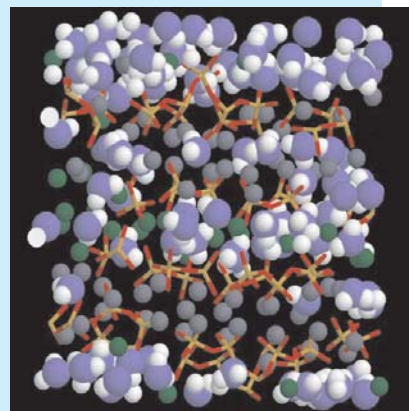


ergy in the form of heat is added to Earth by the Sun's direct radiation and by the well-characterized radiative contributions from greenhouse gases. Those positive contributions (so-called forcings) are balanced, as shown in the figure, by stratospheric aerosols of volcanic origins that reflect incoming sunlight, increased outgoing IR radiation from a warming Earth, long-term heating of Earth—almost entirely of its oceans, which have far higher heat capacities than the atmosphere, land, or ice—and a residual term that mainly represents direct and indirect cooling effects of anthropogenic aerosols throughout the atmosphere. The analysis shows that the anthropogenic aerosols contribute a net cooling of  $1.1 \text{ Wm}^{-2}$ , in agreement with the 2007 assessment by the Intergovernmental Panel on Climate Change but with tighter error bars. The researchers, led by Daniel Murphy of the National Oceanic and Atmospheric Administration in Boulder, Colorado, say that the agreement gives confidence both in their technique and in the global circulation models used by the IPCC. They also found that the aerosols' effects over time reflected the stabilized amount of atmospheric sulfates that resulted from the adoption of emission controls in North America in the 1970s. (D. M. Murphy et al., *J. Geophys. Res.* **114**, D17107, 2009.) —SGB

**Modeling cement hydrates.** Concrete is the most prevalent synthetic material on Earth, yet the detailed nature of its primary binding constituent, hydrated cement, is only poorly understood. When cement, a dry powder that consists mostly of calcium oxide and silicate, is mixed with water, the material hardens through the formation of a complex hydrated oxide called calcium-silicate-hydrate. But the microscopic structure of C-S-H is largely unknown—even its stoichiometry, as suggested by convention with hyphens. C-S-H's structure had been thought to be related to that of two naturally occurring calcium silicate minerals, but those minerals can't explain C-S-H's observed properties. Armed with recent measurements of C-S-H's density and its

ratio of calcium to silicon atoms, a team of researchers at MIT has proposed a new molecular model for C-S-H based on atom-scale simulations: Layers of calcium ions (gray in the figure) are surrounded by silicon (yellow) and oxygen (red) arranged as short silica chains one, two, and five units long;

between those layers are water (oxygen in purple, hydrogen in white) and interlayer calcium ions (green) that ensure overall neutrality. The model's chemical composition,  $(\text{CaO})_{1.65}(\text{SiO}_2)(\text{H}_2\text{O})_{1.75}$ , agrees well with results from neutron scattering experiments. In addition to reproducing the known structural properties of the material, the model also suggests that at short length scales C-S-H should be viewed as a glassy phase. With an atom-level model of the C-S-H structure now in hand, the researchers hope to be able to manipulate the macroscopic properties of concrete, such as its strength and temperature resistance. (R. J.-M. Pellenq et al., *Proc. Natl. Acad. Sci. USA* **106**, 16102, 2009.) —RJF



**Earth's core catches a wave.** A journey to Earth's center would take us through the crust, the mantle, and then two regions of the core. Innermost of those is an iron crystalline solid; surrounding that is a freely flowing, conducting fluid, capped by a thin boundary layer that abuts the rocky mantle. The presence of the fluid core is deduced from seismic studies, and its dynamics can be extracted—with a few assumptions—from time-dependent observations of Earth's surface magnetic field (see *PHYSICS TODAY*, February 2008, page 31). A new study does just that, by using nearly 150 years' worth of surface magnetic measurements to determine the magnetic flux in the liquid core. Motions there are modeled with a set of 20 nested cylinders coaxial with Earth's rotation axis and the key assumption that fluid waves in the core must balance Lorentz, Coriolis, buoyancy, and pressure forces. Jean Dickey (NASA's Jet Propulsion Laboratory) and Olivier de Viron (Institute of Earth Physics, Paris, and University Paris Diderot) found four robust modes of angular-momentum oscillations corresponding to waves—with periods of 85, 50, 35, and 28 years and diminishing amplitudes—that propagate inward from the core-mantle boundary. There was some previous observational evidence for two of the modes, and theorists had predicted all four modes having similar periods. Now, the strong concurrence of all the results lends credibility to the new modes' existence. (J. O. Dickey, O. de Viron, *Geophys. Res. Lett.* **36**, L15302, 2009.) —SGB ■