IMAGING

Peering at protons

Unusual properties of a diamond defect are exploited to achieve progress toward nanometer-scale magnetic resonance imaging (MRI).

MRI can be used to nondestructively generate remarkably detailed images of the body and its tissues by detecting electromagnetic signals generated by hydrogen nuclei. Unfortunately, attempts to shrink this approach down for subcellular-scale imaging have yielded diminishing returns. This is largely due to the extremely weak signals generated by individual protons and the need for tiny detectors sensitive enough to cull those faint signals from background noise.

Detection schemes based on atomic-scale diamond defects with unusual magnetic field–sensing properties could offer a practical way forward. Physicists are enthusiastic about so-called 'nitrogen-vacancy' centers as a promising tool for applications ranging from imaging to quantum computing. Now, two research teams have used these structures to sensitively detect faint magnetic signatures generated by mere handfuls of protons, a potential step toward three-dimensional imaging at the molecular scale.

Diamonds with nitrogen-vacancy center are missing two adjacent carbon atoms from their crystalline scaffold; one of these is replaced by a nitrogen atom, and the other slot remains empty. "This leaves some unpaired electrons in the bond because of the vacancy," explains Dan Rugar, of the IBM Almaden Research Center, "and unpaired electrons have a quantum mechanical property called spin that renders them magnetic." When this nitrogen-vacancy center is positioned very close to the surface of the diamond, it can react to magnetic fields generated by molecules on that surface. The nitrogen-vacancy center offers a clear optical readout, producing a change in its fluorescence when illuminated with green laser light that correlates with externally induced magnetic field fluctuations. "It's the smallest magnetic sensor we know of today," says Friedemann Reinhard, a researcher working with Jörg Wrachtrup at the University of Stuttgart. "It's essentially a single atom that we can 'read' and use to sense a magnetic field on a nanometer or Angstrom scale."

Rugar's team devised an 'active' strategy (Mamin *et al.*, 2013) similar to conventional MRI, in which the nuclear spins in a sample are placed in an external magnetic field and then manipulated via radiofrequency pulses. To maximize the strength of their signal, they collaborated with David Awschalom's team at the University of California at Santa Barbara, who devised diamond substrates where the nitrogen-vacancy center resides in a special layer that greatly reduces background noise when magnetized. This allowed them to detect protons in a small volume of polymer layered above the nitrogen-vacancy center. "We calculated the volume we're detecting from, and it's on the order of 20 nanometers cubed," says Rugar.

In contrast, the approach devised in the Wrachtrup laboratory (Staudacher *et al.*, 2013) uses no radiofrequency pulse manipulation and relies purely on 'passive' nitrogen-vacancy center monitoring. The underlying principle is based on the statistical behavior of small numbers of protons in a magnetic field. "Although the protons are randomly oriented—let's say half of them are pointing 'up' and half are pointing 'down'—it's never exactly 50:50," says Reinhard. His team attempted magnetic resonance spectroscopy of mere tens of thousands of protons in their various liquid samples, and thus even a seemingly modest skewing of proton spins from an equal distribution could generate a polarized magnetic field that detectably modulates the optical signal produced by a nearby nitrogen-vacancy center. "For us, a bath of protons is just a radio station generating a signal that we can detect," says Reinhard.

The German team's technique is fast and more resistant to background noise, making it promising for scanning-style applications. Conversely, the IBM team's method is currently less sensitive but provides greater control over how the sample is manipulated and could potentially generate much more detailed three-dimensional information, although considerable work remains to be done. "We're focused primarily on whether we can extend it to do nanometer-scale imaging," says Rugar. "This is just a first 'baby step' towards something more ambitious."

Michael Eisenstein

RESEARCH PAPERS

Mamin, H.J. *et al.* Nanoscale nuclear magnetic resonance with a nitrogen-vacancy spin sensor. *Science* **339**, 557–560 (2013).

Staudacher, T. *et al.* Nuclear magnetic resonance spectroscopy on a (5-nanometer)^3 sample volume. *Science* **339**, 561–563 (2013).