

NANOSCALE MAGNETOMETRY

Microscopy with single spins

Two teams of researchers have exploited defects in diamond to demonstrate a new approach to magnetic sensing and imaging at the nanoscale.

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Scientists have been searching for tools that are sensitive enough to measure the faint magnetic moment of a single electronic or nuclear spin for decades. Because many chemical elements carry a nuclear magnetic moment, a technique that could routinely image nuclear magnetism on the nanometre scale would allow researchers to extract useful information from materials, such as the chemical identity of atoms or their three-dimensional arrangement in molecules. Writing in *Nature*, two independent teams led by physicists from Harvard University and the University of Stuttgart now demonstrate a new method that may bring this goal closer than ever — the use of isolated single spins in diamond as atomic-scale magnetic field sensors^{1,2}.

The detection of weak magnetic fields at small length-scales is a long-standing challenge in physics, and several experimental techniques have been developed to tackle this problem. A good figure of merit for a nanoscale magnetic sensor is its magnetic moment sensitivity, which is basically the smallest number of spins it can detect. Because the magnetic field of a dipole, like an electron spin, drops off as roughly r^{-3} , where r is distance, a good sensor has to be small and must be brought very close to the sample (see Fig. 1). At present the best sensitivities are attained with nanomechanical force sensors, such as those used in magnetic resonance force microscopy: these sensors have been used to observe a single-electron spin³ and to perform nuclear magnetic resonance imaging on length-scales of a few nanometres⁴.

The alternative approach pursued by the Harvard and Stuttgart teams takes advantage of the exceptional properties of a defect in diamond called a nitrogen-vacancy centre — a lattice imperfection in which an extra nitrogen atom sits next to a vacant site from which a carbon atom has been removed. The spin of the nitrogen-vacancy centre is very sensitive to its magnetic environment, and even a slight variation

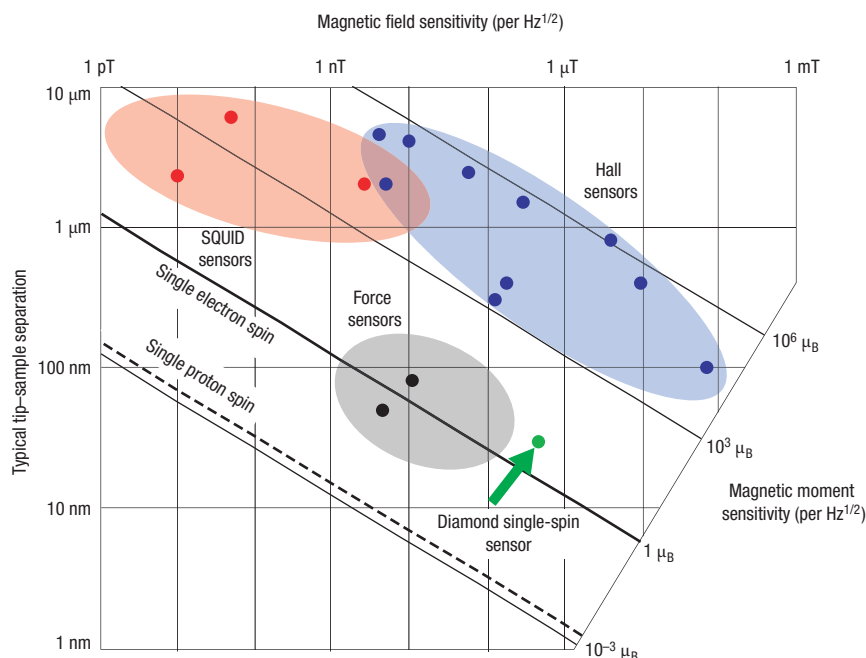


Figure 1 A variety of techniques have been developed to measure small magnetic moments. The dots in this graph are experimental values for nanomechanical force sensors^{3,4}, Hall sensors¹⁰, SQUID sensors^{11–13} and the diamond single-spin sensor of Lukin and co-workers¹. The key to nanoscale spin detection is to combine small tip-sample separations (vertical axis) with good magnetic field sensitivity (horizontal axis), with the best magnetic moment sensitivity being in the bottom left region of this graph. Detecting the spin of a single electron requires a magnetic moment sensitivity of 1 Bohr magneton (μ_B ; thick black diagonal line), whereas detecting the spin of a single proton requires an improvement of about 10^3 in sensitivity (dashed diagonal line). 1 Bohr magneton is roughly the magnetic dipole moment of an electron.

in the magnetic field will usually lead to a shift in the spin resonance frequency that can be detected by optical techniques. This sensitivity is due to the fact that the smallest measurable frequency shift is set by the inverse of the spin coherence time, which can be very long for spins in diamond and can exceed one millisecond in pure crystals at room temperature. This long coherence time is also an advantage in quantum information applications.

Diamond defects are also extremely stable from a chemical point of view, which allows them to survive just nanometres from the surface of the crystal. It has recently been

pointed out that such a near-surface spin, when combined with a scanning device, could be used as a nanoscale magnetic-field sensor^{5–7}.

The latest experiments show how sensitive a diamond magnetometer really is. Using a bulk single crystal of ultrapure diamond, which exhibits the longest spin lifetimes, Mikhail Lukin of Harvard and co-workers¹ demonstrate a magnetic-field sensitivity as small as 3 nT when allowing for 100 s of signal averaging, corresponding to roughly 30 nT per $\text{Hz}^{1/2}$. For smaller crystals (with a diameter of about 30 nm), which are harder to produce with the same degree of

purity, the Harvard team was able to achieve a sensitivity of $0.5 \mu\text{T}$ per $\text{Hz}^{1/2}$. If one assumes that such a nanodiamond (or rather the defect inside) can be brought to within 30 nm of a sample, this sensitivity is roughly equivalent to 7 Bohr magnetons per $\text{Hz}^{1/2}$, which is sufficient to detect the magnetic moment of about seven electron spins in 1 s (see Fig. 1). This level of sensitivity is almost within a factor of ten of the current capability of nanomechanical force sensors, the most sensitive general-purpose spin detection method available today⁴. Given the proof-of-principle character of the diamond magnetometry experiments, there is certainly considerable scope for future improvement. Indeed, pushing the sensitivity below the single-spin level could pave the way for the magnetometer to be used as a quantum read-out device, which would make possible a variety of quantum measurement experiments.

By attaching a tiny diamond to the tip of the cantilever in an atomic force microscope, Fedor Jelezko of the University of Stuttgart and co-workers² also demonstrate that it is possible to perform nanoscale magnetic imaging with a single spin. In their experiment, they map the magnetic field of a small ferromagnetic test structure, achieving a spatial resolution of about 20 nm. Significantly, the resolution in this approach is restricted only by the magnetic sensitivity of the spin and the field gradient of the ferromagnet, not the size of the atomic-scale diamond defect.

To image on the scale of individual atoms and molecules, it will be necessary to improve the sensitivity and resolution of diamond magnetometers by several

orders of magnitude. For this purpose, the separation between the diamond spin and the sample must be reduced and the spin lifetime must be increased — meaning smaller, purer nanocrystals. Ideally, only a single nitrogen-vacancy defect should be present in a perfect single crystal, so methods for the controlled implantation of single nitrogen impurities into ultrapure crystals are crucial. It is also an open question how much the size of nanodiamonds can be reduced, and how close to a surface the defects can be placed, without corrupting their magnetic sensing capability.

Finally, diamond sensors may end up being useful for an entirely different application. Given that the single spin can map unknown magnetic fields with nanometre spatial resolution, what about the opposite? Can one use a known magnetic field distribution to locate a diamond nanoparticle precisely? In a proof-of-principle experiment Jelezko and co-workers demonstrate the potential of this approach for high-resolution optical microscopy. By scanning a nanoscale magnetic tip over an immobilized nanodiamond, they are able to locate the position of the particle with nanometre precision. They also show that two diamond spins roughly 100 nm apart can be resolved with an accuracy of 20 nm — well below the diffraction limit of optical microscopy, which is at about 200 nm (see the Supplementary Information to ref. 2). When used as fluorescent biomarkers in cells, nanodiamonds could enable similar improvements to be made to the resolution of optical microscopy.

Several avenues for extending fluorescence microscopy to the nanoscale are currently being pursued but they will require substantial innovation to reach the molecular level^{8,9}. For nanodiamonds the resolution is set by the magnetic field sensitivity, not by the optical properties of marker molecules. As the Stuttgart team points out, nanometre resolution can be achieved without any probes located closer than typical cell dimensions. Critically, diamond nanoparticles are also very well suited for *in vivo* experiments — they are non-toxic and it is easy to modify their surface chemistry for targeted applications in biology.

Defects in diamond have attracted interest from a variety of disparate fields, such as spintronics, materials science and bioimaging, and it is exciting to see how diamond magnetometry brings all these efforts together to create a novel field of research that will, in turn, open up new possibilities for all of them.

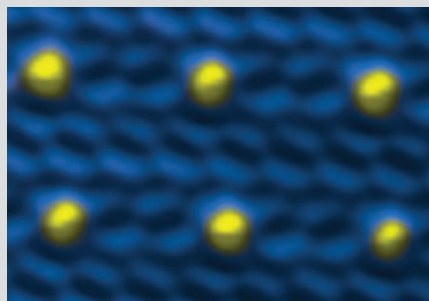
References

1. Maze, J. R. *et al.* *Nature* **455**, 644–647 (2008).
2. Balasubramanian, G. *et al.* *Nature* **455**, 648–651 (2008).
3. Rugar, D., Budakian, R., Mamin, H. J. & Chui, B. W. *Nature* **430**, 329–332 (2004).
4. Degen, C. L. *et al.* Presented at 49th Experimental NMR Conference, Asilomar, California, 9–14 March 2008; <<http://enc-conference.org/longabs/E081130.0000VER.1.pdf>>.
5. Chernobrod, B. M. & Berman, G. P. *J. Appl. Phys.* **97**, 014903 (2005).
6. Degen, C. L. *Appl. Phys. Lett.* **92**, 243111 (2008).
7. Taylor, J. M. *et al.* *Nature Phys.* **4**, 810–816 (2008).
8. Willig, K. I., Rizzoli, S. O., Westphal, V., Jahn, R. & Hell, S. W. *Nature* **440**, 935–938 (2006).
9. Betzig, E. *et al.* *Science* **313**, 1642–1645 (2006).
10. Boero, G., Demierre, M., Besse, P. A. & Popovic, R. S. *Sens. Actuat. A* **106**, 314–320 (2003).
11. Kirtley, J. R. *et al.* *Appl. Phys. Lett.* **66**, 1138–1140 (1995).
12. Gardner, B. W. *et al.* *Rev. Sci. Instrum.* **72**, 2361–2364 (2001).
13. Huber, M. E. *et al.* *Rev. Sci. Instrum.* **79**, 053704 (2008).

MOLECULAR SWITCHES

Order and control

Molecules that can reversibly switch between at least two states in response to an external trigger are essential for the development of molecular electronics. Azobenzene — a molecule composed of two phenyl rings linked by a nitrogen–nitrogen double bond — has been of particular interest in this regard because it can reversibly isomerize between *trans* and *cis* forms under the influence of light, an electric field or tunnelling electrons. However, future devices will require functional molecules, integrated into larger architectures that can be addressed selectively. Now Stefan Hecht of Humboldt University in Berlin, Leonhard Grill of the Free University



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of Berlin and colleagues have shown that molecules can be collectively switched with spatial selectivity (page 649).

The researchers used an asymmetric azobenzene derivative containing a

single methoxy group ($-\text{OCH}_3$), which was adsorbed on a gold surface and examined with a scanning tunnelling microscope (STM). Voltage pulses from the STM tip were used to transform the molecules from the relatively flat *trans* configuration to the three-dimensional *cis* configuration. The team found that the probability of switching was significantly influenced by the surrounding molecules and supporting surface. As a result, they were able to create the same lattices of *cis* isomers in repeated switching cycles. The image here shows a STM image of such a lattice, with the *cis* isomers in yellow surrounded by the *trans* isomers in blue.

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