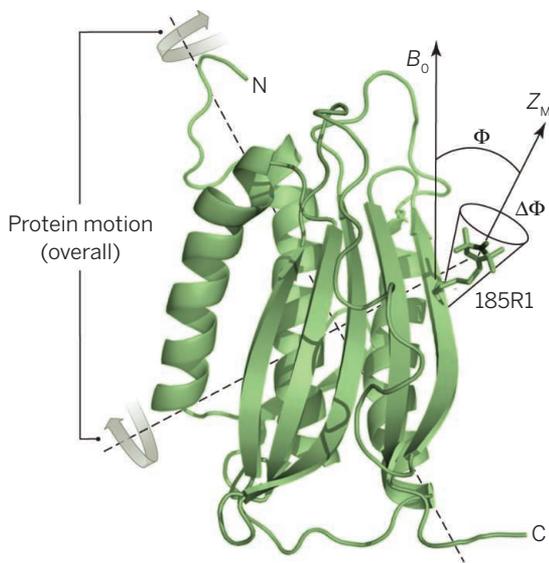


Once this had been accomplished, the race was on to image single proteins with the NV center. The first major milestone on this path was the detection of small volumes of nuclear spins, close to those volumes previously achieved by MRFM, except at room temperature. This was done by two groups simultaneously (7, 8). In the latter work, the technique was pushed a step farther by interrogating the nuclear spin ensemble to give information on their local environment. By applying these techniques to single proteins, low-resolution images should be possible. However, ultimately atomic-scale resolution image of proteins are needed, at least in the reaction centers. This requires the ability to locate individual nuclei.

In the past year, detection and imaging of near-single nuclear spins outside the diamond lattice was reported (9). Here, four



See it move. Dynamics of the spin label attached to the MAD2 protein. B_0 is the external magnetic field, Z_M is the spin label quantization axis, and $\Delta\Phi$ is the angular range of motion.

silicon nuclei were observed on a specially designed glass-like coating placed on the diamond surface. This work was important because it proved that the magnetic noise produced by unpaired electrons at or near the diamond surface could be overcome, at least in principle. Until then, this magnetic noise was a roadblock that made many question whether a single external nuclear spin could ever be detected by a NV center.

Although the earlier studies proved that it is possible to greatly reduce the numbers of troublesome diamond surface spins, it has so far not been possible to eliminate them completely. However, very recently it has been shown that these few remaining surface spins can often be stable enough to use as a resource—namely, making them into “reporter” spins to image single nu-

clei in their immediate environment (10); a single proton bound to the diamond surface was imaged.

However, what is ultimately needed is a way to deploy reporter spins that are not limited to the diamond surface but that can be detected at long range and selectively placed at critical locations in a protein where they can sense conformation changes. It is exactly this lofty goal that has now been accomplished by Shi *et al.* (see the figures). A nitroxide spin label is anchored to a region of interest on a single protein. Each nitroxide has a single unpaired electron spin that is capable of detecting nearby nuclei by a process known as the hyperfine interaction. The nitroxide reporter spin is ~10 nm from the NV and ~5 nm beyond the diamond surface, far enough to image remote parts of the protein. Not only were Shi *et al.* able to image the

location of the reporter electron spin, they could also detect a single nuclear spin nearby. Furthermore, by analyzing the hyperfine spectrum of this nuclear spin, the approximate angle of its preferred axis relative to an applied magnetic field could be deduced [see figure 3A in (2)]. From this orientation information, they were able to infer the approximate angular range of motion of that part of the protein, which is a measure of protein flexibility and/or conformation changes. More important, the average angular motions were found to occur on time scales relevant for biological interactions.

In the future, it will be necessary to monitor far more than one nuclear spin in the protein, and so better reporter spin labels are needed. Specifically, they must have longer spin coherence times to achieve longer-range nuclear spin imaging, and they must be photostable to the light used to interrogate the NV center. Finally, to image proteins in living cells, the bulk diamond used in these experiments must be replaced by a nanodiamond with similar NV magnetic sensitivity. ■

REFERENCES

1. J. S. Valastyan, S. Lindquist, *Dis. Model. Mech.* **7**, 9 (2014).
2. F. Shi *et al.*, *Science* **347**, 1135 (2015).
3. C. L. Degen, M. Poggio, H. J. Mamin, C. T. Rettner, D. Rugar, *Proc. Natl. Acad. Sci. U.S.A.* **106**, 1313 (2009).
4. G. Balasubramanian *et al.*, *Nature* **455**, 648 (2008).
5. J. R. Maze *et al.*, *Nature* **455**, 644 (2008).
6. B. Grotz *et al.*, *New J. Phys.* **13**, 055004 (2011).
7. T. Staudacher *et al.*, *Science* **339**, 561 (2013).
8. H. J. Mamin *et al.*, *Science* **339**, 557 (2013).
9. C. Müller *et al.*, *Nat. Commun.* **5**, 4703 (2014).
10. A. Ajoy *et al.*, *Phys. Rev. X* **5**, 011001 (2015).

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QUANTUM MECHANICS

Look but don't touch the metals

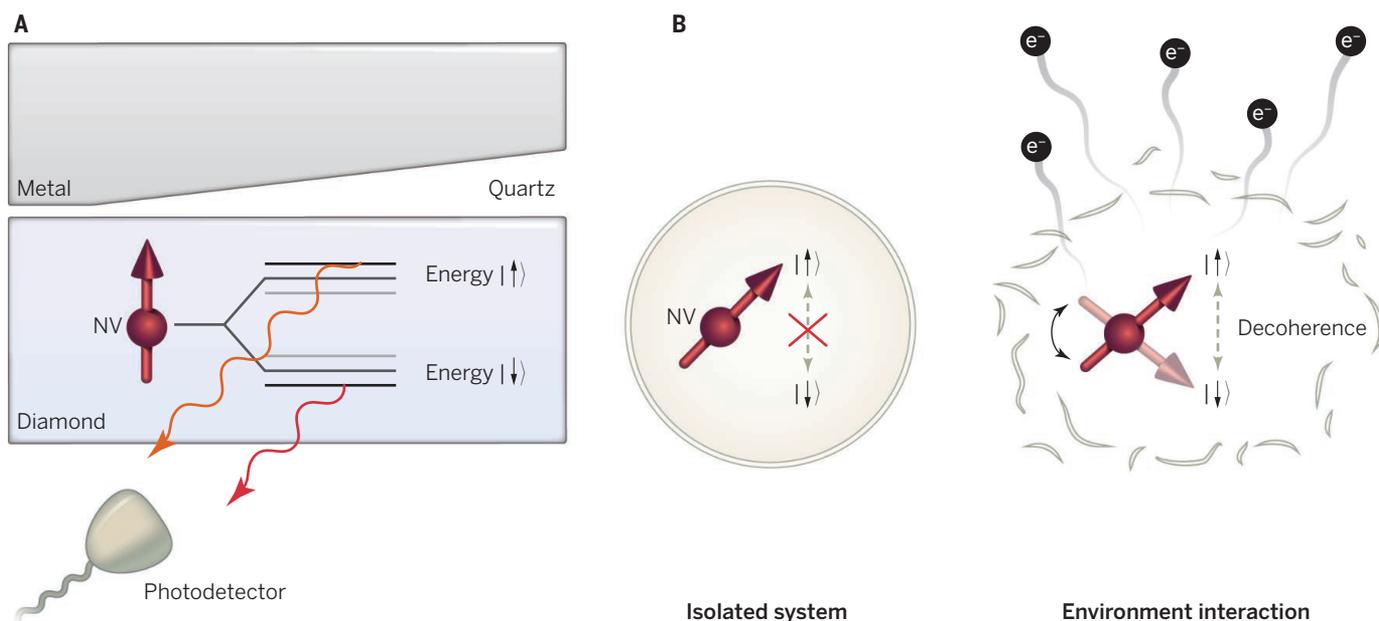
Nitrogen-vacancy defects in diamond can probe metallic conductivity at a distance

By Liam P. McGuinness^{1,2} and Fedor Jelezko^{1,3}

Metallic conductivity is a familiar phenomenon, but metals can display surprising and exotic behavior, such as superconductivity and the quantum Hall effect. Advances in nanotechnology have led to new questions about how metallic conductivity might change in structures with dimensions approaching a few atoms. On page 1129 of this issue, Kolkowitz *et al.* (1) provide us with another tool for answering these questions: a magnetic sensor based on atomic defects in diamond.

Conductivity measurements have historically used sensors similar to an electrical multimeter, in which electrical contacts are placed across a device to measure its properties. The approach is akin to many people's first exploratory investigations of a new toy—pick it up and touch it. However, like delicate toys that can be damaged by even the most careful handling, miniaturized electrical devices are now at the point where the measuring contacts disrupt the material characteristics. For this reason, “look but don't touch” methods such as superconducting quantum interference devices (SQUIDs) and cold atomic gases have been developed. Instead of measuring resistance and conductivity via electrical contact to the sample, the magnetic field produced by electron motion is observed from a distance.

One criticism of these techniques has been their inability to measure nanometer-sized devices, because most are limited to the micrometer or millimeter scale. Recently, single dopants in diamond were proposed for experiments in nanoscale magnetic sensing (2, 3). Optically active dopants often carry ground-state spin, and for the nitrogen-vacancy (NV) color center in particular, the spin state can be coupled to photons and achieve ultrasensitive optical readout of the spin levels (4, 5). As spin en-



A light touch. (A) Single defects in diamond known as NV centers are placed at the surface and separated from the metal layer with a gradient quartz spacer, tens of nanometers in thickness. The spin energy levels of the NV center can be monitored optically, and their response to magnetic fields (which can increase the energy gap) used as a sensitive magnetometer. (B) Rather than measuring the energy levels directly, the relaxation rate between sublevels provides information about the external environment. Well-isolated quantum systems have low relaxation rates because the environment does not provide enough energy to flip the NV spin. Bringing a noisy environment (such as moving electrons) near the NV center induces quantum decoherence and can be used to monitor dynamics in order to differentiate diffusive electron motion from ballistic motion.

ergy levels depend on the external magnetic field (known as the Zeeman effect), this technique provides a precise magnetic sensor with little more experimental setup than an optical microscope and a piece of diamond (see the figure, panel A). In (1), single NV centers were implanted in diamond with an ion beam with a well-defined energy. Careful control of the distance to the metal layer is a key point in the experiment. Kolkowitz *et al.* controlled distance by introducing a wedged quartz spacer between the diamond and metal, and boosted magnetic sensitivity by using a decoherence microscopy technique (6). Instead of measuring the energy of the spin levels directly, they monitored the relaxation rate between levels.

This approach takes advantage of the exquisite sensitivity of quantum systems to their environment. Quantum decoherence, resulting from interaction with the external environment, is the bane of many physicists' existence, and is generally avoided at all costs. Indeed, this pernicious interaction is one reason quantum computers are so difficult to build, and is also why quantum effects are not seen in everyday life. However, Kolkowitz *et al.* turn the paradigm on its head to use quantum decoherence for their benefit: Because decoherence

is caused by the environment, it can be used to provide information about the local surroundings (see the figure, panel B). Careful monitoring of the relaxation rates unraveled details of electron transport in a nearby metal layer. Clear differences for the cases of diffusive motion of electrons in polycrystalline silver (ohmic behavior) and ballistic motion of electrons in single-crystal films were demonstrated.

So how little "touch" is imparted onto the investigated metal by the team's noncontact method? Electrical isolation is ensured by the quartz layer separating the silver from the sensor, whereas physical contact can be avoided completely by fixing the diamond to a scanning tip (7). More concerning might be the unavoidable "back-action" that measurements produce in quantum physics. Kolkowitz *et al.* address this issue by measuring what is an essentially classical system, where the quantum back-action is negligible. The field produced by their single-spin sensor is completely swamped by the many thousands of electrons in the metal. However, at low temperatures, where quantum effects become relevant, quantum interaction between NV ensembles and superconducting resonators has indeed been demonstrated (8, 9).

The readout laser is perhaps the most invasive part of the measurement protocol. Illumination of metals with light can produce substantial changes in conductivity and can even lead to ejection of electrons

(the photoelectric effect). However, all of the information was gathered in the dark, when the laser was turned off and stored in the NV state. A short laser pulse was applied only at the end of the measurement to read out the sensor. Laser illumination can actually be used as a resource, in concert with diamond-based readout, to manipulate magnetic properties at the nanoscale, as shown recently (10).

The work of Kolkowitz *et al.* provides researchers with another tool for probing the importance of dimensionality, geometry, and topology on conductivity at the nanoscale. It is an important complement to well-established electrical readout techniques (11) and joins a growing repertoire of diamond sensors being applied to a diverse range of materials. As far as metals and conductivity are concerned, diamonds are nearly untouchable. ■

REFERENCES

1. S. Kolkowitz *et al.*, *Science* **347**, 1129 (2015).
2. A. Gruber *et al.*, *Science* **276**, 2012 (1997).
3. B. M. Chernobrod, G. P. Berman, *J. Appl. Phys.* **97**, 014903 (2005).
4. G. Balasubramanian *et al.*, *Nature* **455**, 648 (2008).
5. J. R. Maze *et al.*, *Nature* **455**, 644 (2008).
6. J. H. Cole, L. C. L. Hollenberg, *Nanotechnology* **20**, 495401 (2009).
7. P. Maletinsky *et al.*, *Nat. Nanotechnol.* **7**, 320 (2012).
8. Y. Kubo *et al.*, *Phys. Rev. Lett.* **105**, 140502 (2010).
9. X. Zhu *et al.*, *Nature* **478**, 221 (2011).
10. J.-P. Tetienne *et al.*, *Science* **344**, 1366 (2014).
11. A. Brenneis *et al.*, *Nat. Nanotechnol.* **10**, 135 (2015).

¹Institute of Quantum Optics, Ulm University, Ulm, D-89069 Germany. ²School of Physics, University of Melbourne, Melbourne, 3010 Australia. ³Center for Integrated Quantum Science and Technology (IQST), Ulm University, Ulm, D-89069 Germany. E-mail: fedor.jelezko@uni-ulm.de