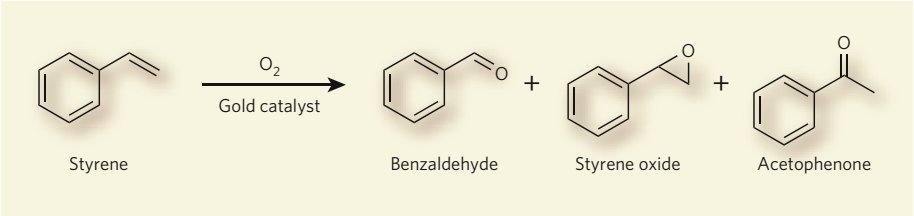

Figure 1 | Fruits of gold. Gold is generally considered to be an inert metal but when present as nanoparticles the situation is very different. Turner *et al.*[1] have used particles of gold less than 2 nanometres in diameter, derived from highly stable 55-atom clusters, to catalyse the selective oxidation of the aromatic alkene styrene. The reaction chiefly yielded benzaldehyde, with smaller amounts of styrene oxide and acetophenone.

studies. However, the study by Turner *et al.*[1] seems to be the first to use Au_{55} in the synthesis of supported gold catalysts. The Au_{55} clusters have a diameter of about 1.4 nanometres, essentially the size of the catalysts used in their work. The use of cluster chemistry would therefore seem a convenient and direct route to produce particles too small to be easily synthesized by conventional preparation methods. Furthermore, the technique yields a very narrow and reproducible size distribution for the resulting particles. Traditional catalyst preparation methods typically result in a range of particle sizes that is difficult to control, confounding attempts to relate structure to activity in gold catalysis.

What, then, makes gold particles of this size so special? The activity of nanoscale gold has been attributed to the presence of low-coordination sites[6,10,11]: gold atoms at the surface, edge or corner of a particle that have fewer nearest neighbours than bulk atoms, leaving them more free to engage in chemical reactions. The smaller the particle, the larger is the density of these coordinatively unsaturated sites relative to the total number of atoms in the particle. The catalyst particles are also comparable in size to the de Broglie wavelength of an electron. This attribute can radically alter the electronic properties of the particle[12]. Either or both of these phenomena may be responsible for the gold clusters' catalytic dexterity.

To understand why size matters, Turner *et al.*[1] conducted X-ray photoelectron spectroscopic studies of their gold catalysts. The authors found that the electronic properties of the gold in their nano-sized catalyst had altered from those of a bulk gold sample. This modified electronic structure may be the source of the radically different activity of the ~1.5-nanometre particles, but precisely how they can dissociatively adsorb oxygen remains unclear.

The studies of Turner *et al.* open numerous avenues for further exploration. An obvious next step would be to explore other reactions for which these gold particles act as catalysts. It will also be interesting to investigate whether gold nano-clusters are as effective in the gas phase as in the liquid phase. In any case, this work provides a new approach for the consistent synthesis of very small gold nano-clusters and will stimulate activity in the exciting area of gold catalysis. ■

D. Wayne Goodman is in the Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, USA.
e-mail: goodman@mail.chem.tamu.edu

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PHYSIOLOGY

Mutant flies lack magnetic sense

François Rouyer

It seems that fruitflies can detect magnetic fields, but only if they are illuminated with blue light. Mutant flies reveal that a light-responsive receptor underpins this peculiar behaviour.

Animals detect various wavelengths of light, from ultraviolet to red, using photoreceptor proteins. One reason for doing this is to synchronize their circadian clocks with the day–night cycle. In the fruitfly *Drosophila melanogaster*, a vital photoreceptor for this synchronization is cryptochrome, which uses blue light to reset circadian clocks[1]. Reporting on page 1014 of this issue, Gegear *et al.*[2] reveal a new function of this intriguing molecule. They show that both cryptochrome and blue light are required for fruitflies to sense magnetic fields.

Magnetoreception is often found in the animal kingdom, perhaps most notably in migratory species, which use Earth's magnetic field as an aid to navigation. Several mechanisms have been proposed, including electromagnetic induction, in which an electric current is generated in a conductive organ as it passes through a magnetic field; the use of nano-sized crystals of the mineral magnetite as 'compasses'; and the modulation of magnetic-field-dependent biochemical reactions[3]. The biochemical mechanism might rely on the so-called radical-pair model[4], in which the magnetic field modifies the electronic state of paired ions in a reacting molecule, thus altering the product of the reaction.

So which proteins could host a radical-pair mechanism for magnetoreception? Photoreceptors are strong candidates, because several examples of light-dependent magnetoreception have been described[5–7]. Short wavelengths of light seem to be important in these cases, so cryptochrome, which responds to blue light, has been proposed as a candidate molecule[8–10]. This theory is bolstered by the finding that cryptochrome function in plants is affected by magnetic fields[11]. Gegear *et al.*[2] decided to investigate further, using fruitflies as a convenient, genetically modifiable model of other animals.

The authors first set up a simple behavioural test to assay magnetoreception in fruitflies, by making a device in which the flies could choose to enter a tube bathed in a magnetic field or one that was not. They tested several strains of wild-type flies in this way. Only flies from a few of these strains preferentially chose the tube without a magnetic field, indicating that the responses of fruitflies to magnetic fields are strongly influenced by genetic background. This is perhaps unsurprising, because such influences are a recurrent problem in behavioural experiments in general.

Gegear *et al.* therefore decided to motivate the flies to choose between the two tubes, by designing a protocol that trained them to associate magnetic fields with a reward of sugar. The authors starved their experimental subjects for a day, then placed them in a sugar-containing tube in a magnetic field. This treatment proved to be an excellent motivator: when presented with two tubes as before, all the trained flies preferentially chose the tube placed in a magnetic field, regardless of their genetic background.

NATURE|Vol 454|21 August 2008

50 YEARS AGO

It has been observed in this laboratory that when aqueous mixtures of dicarboxylic or monocarboxylic acids and certain ammonium salts are irradiated with ultra-violet light, certain amino-acids are obtained.

A cold quartz ultra-violet lamp giving 86 per cent of its output at about 2537 A. was used for irradiated mixtures of succinic, maleic, propionic and acetic acid with a number of ammonium salts ... The irradiation was continued in each case for 24 hr ...

Of all the ammonium compounds investigated only ammonia and ammonium carbonate were active, and of the acids only succinic, maleic and propionic acid gave rise to amino-acids ...

The amino-acids are aspartic acid, alanine and glycine, that is to say, amino-acids with 4, 3 and 2 carbon atoms respectively.

From *Nature* 23 August 1958

100 YEARS AGO

The Rev. J. W. Hayes, of West Thurrock Vicarage, Grays, has directed attention to some old underground workings for chalk at Hemel Hempstead, which in his opinion throw much light on the origin and use of dene-holes generally. It appears that in order to obtain chalk suitable for lime-making it was until recently the practice ... to work the chalk in subterranean chambers reached by deep shafts ... A vertical shaft, of circular section, about 5 feet in diameter, was sunk through superficial deposits until the hard chalk was reached, and from the bottom of the shaft three so-called "arches" were struck out. These arches were chambers, which in some cases were more than 12 feet high. The chalk was mined in these drifts for a length of twenty to twenty-five yards, and when the distance of the working face from the bottom of the shaft became inconveniently great, or when the roof proved unsound, a new pit would be sunk.

From *Nature* 20 August 1908

50 & 100 YEARS AGO

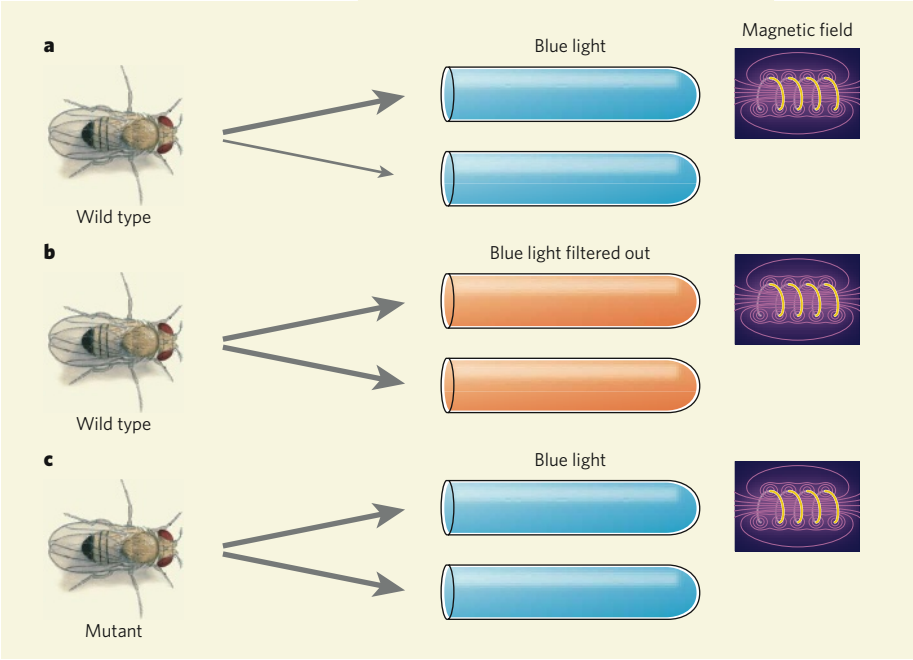

Figure 1 | Magnetoreception in fruitflies. Gegear *et al.*[2] studied the ability of fruitflies to detect a magnetic field. **a**, When trained to associate a magnetic field with a reward of sugar, wild-type flies preferentially choose to enter a tube that is bathed in a magnetic field, rather than one that is not, so long as blue light illuminates the experiment. **b**, The trained flies demonstrate no preference for the tubes if blue light is filtered out of the illumination. **c**, Genetically modified flies that lack the photoreceptor cryptochrome (which responds to blue light) do not recognize the magnetic field, even in the presence of blue light, showing that cryptochrome is essential for magnetoreception in fruitflies.

Previous studies[6] have shown that fruitflies respond differently to magnetic fields depending on the wavelength of light that they are exposed to. Gegear *et al.* therefore investigated the influence of different light colours on the behaviour of their trained flies, concentrating on the blue end of the spectrum for the reasons mentioned earlier. Their results indicate that light is indeed required for fruitfly magnetosensitivity — the flies were unable to detect magnetic fields in the absence of light of short wavelength (less than 420 nanometres; Fig. 1). This is close to the region of the spectrum that is absorbed by cryptochrome, suggesting that the photoreceptor might be involved in this behaviour.

To confirm the role of cryptochrome in magnetoreception, the authors tested mutant cry^0 flies, which lack the photoreceptor, in their behavioural assay. They found that untrained wild-type flies that have the same genetic background as cry^0 flies are attracted to magnetic fields. But the cry^0 mutants showed no response to the magnetic field, even if they had been through the training protocol. Moreover, flies that carried a different cryptochrome mutation — one that disrupts most of the photoreceptor's function without deleting the protein completely — were also unresponsive to the magnetic field. This strongly bolsters the idea that cryptochrome is a vital component of light-dependent magnetoreception in fruitflies.

Because cryptochrome is involved in setting the circadian clock in flies' brains, and could also have a clock-gene function in other tissues[1], Gegear *et al.* checked to see whether the flies' magnetoreceptive response depended on having a functional circadian clock. The answer was no. Even in conditions that caused the flies to be circadianly arrhythmic, wild-type flies retained their ability to detect a magnetic field, supporting the idea that magnetoreception in fruitflies is independent of their body clocks.

Clearly, cryptochrome is required for magnetoreception in fruitflies, but more sophisticated behavioural assays will be needed to understand the type of information that flies glean from magnetic fields. It also remains to be seen whether the receptor itself is the magnetosensitive molecule.

It has been proposed[4] that, in birds, Earth's magnetic field causes variations in signals from precisely oriented photoreceptors, thus providing a three-dimensional map of the field to the bird's brain. This raises the question of where cryptochrome localizes in the body. In fruitflies, the precisely organized compound eye seems a likely candidate. But fruitfly larvae also seem to sense magnetic fields[7], yet they don't have compound eyes. The finding of cryptochrome in the nerve fibres of some circadian-clock neurons[12] in fruitflies suggests that sites might exist in the brain for oriented placement of these receptors. Further studies with genetically engineered fruitflies will certainly provide us with some answers to these questions.

It is not clear why fruitflies, which do not migrate and usually spend their summers flying around rotten fruit, should care about Earth's magnetic field. The magnetoreceptive function

of their cryptochrome raises the possibility that vertebrate cryptochrome does the same job, and might even explain why the light-detecting properties of the protein have been evolutionarily conserved in mammals[13]. In any case, Gegear and colleagues' results open a new avenue of investigation for magnetoreception — that of genetic and molecular analysis. ■

François Rouyer is at the Institut de Neurobiologie Alfred Fessard, CNRS UPR2216, 91198 Gif-sur-Yvette, France.
e-mail: francois.rouyer@inaf.cnrs-gif.fr

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MATERIALS SCIENCE

A metal left spinning

Zachary Fisk and Stephan von Molnár

Conductors and semiconductors usually behave like conduits for fluids of electrons. But sometimes the electrons' spins conspire to produce unconventional behaviours that can be turned off and on with magnets.

The theory of Landau–Fermi liquids is a remarkably simple but effective model to describe the behaviour of conventional metals. It views metals as consisting of a liquid of independent, mobile electrons with spin and charge, responding to applied magnetic and electric fields. That individual electrons strongly repel each other as a result of their identical electronic charges is accommodated in this picture by an adjustment to the effective electron mass. Semiconductors doped with atoms carrying either more or fewer electrons than the host atoms a re also explained by this model. Instances in which this picture fails are therefore of considerable interest, and understanding how to produce such materials has both fundamental and technological potential. The possibility of a systematic method of inducing non-Landau–Fermi-liquid states is the claim in the paper by Manyala *et al.*[1] on page 976 of this issue.

The authors have taken the semiconductor ferrosilicon (FeSi) and replaced a few per cent of its iron atoms with manganese (Mn). This element comes just before Fe in the periodic table, having one less electron than Fe in its outer shell. Replacing an Fe atom with Mn in the semiconductor's cubic lattice introduces a 'missing electron', known as a hole. Holes act like electrons but with positive charges; a collection of holes will act exactly like a collection of electrons, apart from moving in the opposite direction in applied electric fields. As with electrons, holes have a spin of 1/2 with an associated magnetic moment.

Manganese atoms carry their own magnetic moment corresponding to a spin of 1 in the FeSi semiconductor. In metals containing atoms from first-row transition elements (scandium to zinc, which includes Mn and Fe) that have local atomic moments, the spin of any mobile electrons or holes (collectively known as carriers) and the local moment preferentially line up anti-parallel, because the carrier attempts to compensate for the local atomic moment. When Mn substitutes for Fe, there are not enough carrier spins to balance the Mn atom's spin completely, because each spin-1 Mn atom appears in the lattice accompanied by a single spin-1/2 hole. A pair of carriers would be needed to compensate for this spin-1 moment, but then the moment of a Mn atom elsewhere would be left uncompensated.

The detailed experiments of Manyala *et al.*[1] show that Mn-doped FeSi does not behave in the manner expected of the standard metallic state of a doped semiconductor; for example, it has an anomalous relationship between electrical resistance and temperature. This non-Landau–Fermi behaviour arises because, even at temperatures below 2 kelvins, undercompensated atomic spins interact with the spins of the free carriers, affecting their degrees of freedom. However, Manyala and colleagues found that applying a sufficiently large magnetic field at low temperature froze the free spins in a single orientation, restoring the expected metallic behaviour.

The suggestion that undercompensated doping provides a general route to non-Landau–Fermi behaviour is a seductively simple idea. But FeSi is an unusual semiconductor whose low-temperature semiconducting state has developed out of a solid with strongly temperature-dependent magnetic properties. This may or may not be relevant. FeSi could simply be an easily accessed venue into which a dopant carrying a local moment incompletely balanced by the net carrier moment can be introduced. It is therefore important for the studies of Manyala *et al.*[1] to be repeated in a more conventional semiconductor.

One might wonder whether similar effects to those occurring with Mn doping of FeSi might occur when doping with cobalt (Co). This is the element just to the right of Fe in the periodic table, and so would provide additional electrons rather than removing them. Cobalt even has a larger atomic moment (of spin 3/2). However, Manyala *et al.*[1] found that Co-doped FeSi becomes magnetically ordered at low temperatures, abolishing all the spin degrees of freedom associated with local moments, leaving no source for behaviour as a non-Landau–Fermi liquid. There are also atoms with local moments that couple to carrier spins in a non-compensating fashion, a process known as preferential spin alignment. Most of the rare earth metals are of this character, including gadolinium, which has a 7/2 spin moment. But no known non-Landau–Fermi liquid associated with this non-compensating situation has yet been seen.

Manyala and colleagues propose that doped semiconductors based on elements in groups III and V (for example gallium arsenide, GaAs) could be used to produce non-Landau–Fermi liquids. There is a considerable volume of literature on low-level doping with Mn in these semiconductors, especially in indium arsenide[2–4] . The extreme of doping, MnAs, is a ferromagnet (as is MnSi) but transition metals do not incorporate well or to high levels with group III–V elements, in contrast with the ease with which Mn dopes FeSi. Magnetic measurements indicate that with Mn replacing between 2% and 18% of the indium atoms, the sum of all spin exchange interactions produces antiferromagnetic behaviour (the moments align in a regular way, cancelling each other out and leaving the material with no overall magnetic moment), the strength of which decreases with decreasing Mn content. For materials with less than 2% Mn the exchanges result in ferromagnetic behaviour (individual moments align to reinforce each other)[3,4]. When Mn doping falls below 1.8%, corresponding to less than 2.2×10^{19} holes per cubic centimetre, the materials display long-range ferromagnetism with a transition temperature (around 7 kelvins) above which ferromagnetism breaks down[3].

It seems that group III–V semiconductors with Mn doping near 2%, where the exchange between local and carrier spin is small, could provide favourable conditions in which to find systems lying between Landau–Fermi liquid and non-Landau–Fermi liquid states. In these semiconductors Mn has a spin of 5/2. In addition, the concentrations of free electrons and/or holes can be controlled independently of Mn content by the addition of impurities, which allows the preparation of materials close