

intensive labour that are normally necessary for the seed production of large donor species. Gamete production for a species that has a large body size and long generation time could be carried out in surrogate parents with a smaller body size and shorter generation time. As the cryopreservation of eggs and embryos has so far been unsuccessful for fish, PGC xenotransplantation, in combination with PGC cryopreservation⁸, could be a useful strategy for helping the conservation of endangered salmonid populations.

Yutaka Takeuchi*, Goro Yoshizaki*†, Toshio Takeuchi*

*Department of Marine Biosciences, Tokyo University of Marine Science and Technology, Minato-ku, Tokyo 108-8477, Japan
e-mail: goro@s.kaiyodai.ac.jp

†PRESTO, Japan Science and Technology Corporation, Kawaguchi-shi, Saitama 332-0012, Japan

1. Bella, D. A. *Science* **295**, 1236 (2002).
2. Wylie, C. *Cell* **96**, 165–174 (1999).
3. Lawrence, P. A., Ashburner, M. & Johnston, P. *Genetics* **134**, 1145–1148 (1993).
4. Ono, T., Yokoi, R. & Aoyama, H. *Exp. Anim.* **45**, 347–352 (1996).
5. Takeuchi, Y., Yoshizaki, G., Kobayashi, T. & Takeuchi, T. *Biol. Reprod.* **67**, 1087–1097 (2002).
6. Takeuchi, Y., Yoshizaki, G. & Takeuchi, T. *Biol. Reprod.* **69**, 1142–1149 (2003).
7. McKay, S. J., Devlin, R. H. & Smith, M. J. *Can. J. Fish. Aquat. Sci.* **53**, 1165–1176 (1996).
8. Kobayashi, T., Takeuchi, Y., Yoshizaki, G. & Takeuchi, T. *Fish Physiol. Biochem.* **23**, 479–480 (2003).

Supplementary information accompanies this communication on Nature's website.

Competing financial interests: declared none.

Thin films

Unexpected magnetism in a dielectric oxide

It is generally accepted that magnetic order in an insulator requires the cation to have partially filled shells of *d* or *f* electrons. Here we show that thin films of hafnium dioxide (HfO₂), an insulating oxide better known as a dielectric layer for nanoscale electronic devices, can be ferromagnetic even without doping. This discovery challenges our understanding of magnetism in insulators, because neither Hf⁴⁺ nor O²⁻ are magnetic ions and the *d* and *f* shells of the Hf⁴⁺ ion are either empty or full.

The electronic spins of cations in insulating oxides are normally coupled by nearest-neighbour interactions — either superexchange or double exchange¹. No long-range magnetic order is anticipated below the percolation threshold, because there is no extended network of neighbouring sites occupied by magnetic ions. Controversy has therefore surrounded reports of high-temperature ferromagnetism in thin films of transparent, wide-bandgap oxides, such as zinc oxide, titanium dioxide or tin dioxide, that have been doped with a few per cent of a 3*d* cation such as V³⁺,

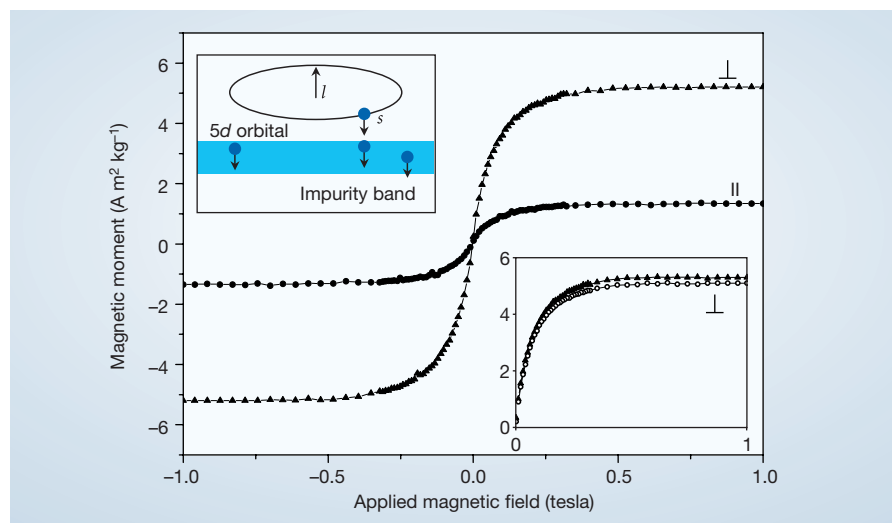


Figure 1 Magnetization curves for a thin film of hafnium dioxide measured in a superconducting quantum interference device (SQUID) magnetometer with the field parallel (||) or perpendicular (⊥) to the plane of an R-cut sapphire substrate. These room-temperature data are corrected for background diamagnetism of the substrate ($-1.8 \times 10^{-7} \text{ A m}^2 \text{ T}^{-1}$). Insets: top left, proposed coupling scheme for orbital, spin and impurity-band magnetism in hafnium dioxide (blue circles represent electrons, arrows show direction of their spin moment, the orbital and spin moments *l* and *s* of an electron in a 5*d* state couple antiparallel to form a $j = 3/2$ state); bottom right, magnetization curves at different temperatures (triangles, 5 K; circles, 400 K).

Mn²⁺, Fe³⁺ or Co²⁺ (ref. 2). The moments in these ferromagnets, which may be insulating or conducting, are sometimes too large to be explained by any impurity phase. An indirect exchange mechanism involving donor electrons in a spin-split impurity band has been proposed for such materials having a high dielectric constant (our unpublished results).

The Hf⁴⁺ ion has a closed shell [Xe]4*f*¹⁴ configuration, with no unpaired electrons. We deposited thin films of hafnium dioxide by conventional pulsed-laser deposition from a sintered target on to substrates maintained at 750 °C. The target was 99.95% pure, with zirconium as the main metallic impurity. Iron, cobalt and nickel were below 10⁻² wt%. Substrates were sapphire or silicon. The excimer laser wavelength and fluence were 248 nm and 1.8 J cm⁻², respectively. Oxygen pressure during deposition was varied from 10⁻⁴ to 1 millibar. Films were 45–135 nm thick, transparent, colourless and insulating; in a typical film, the *c*-planes of the monoclinic hafnium dioxide structure were oriented parallel to the surface of the R-cut sapphire substrate.

These films are ferromagnetic, with a Curie temperature exceeding 500 K and a magnetic moment of about 0.15 bohr magnetons per HfO₂ formula unit (Fig. 1). The magnetization is remarkably anisotropic, being up to three times greater when the magnetic field is applied perpendicularly to the plane of the film than when it is applied in the parallel direction. Coercivity at 5 K was about 5 millitesla. Results were reproduced in films of different thicknesses prepared at different oxygen pressures and on different substrates. No ferromagnetism was found in similarly prepared films of zinc or tin oxides.

These results confound our understanding of magnetism in solids. What in hafnium dioxide could possibly be magnetic? Lattice defects may be the key. In view of the preparation conditions, oxygen vacancies may be expected³, leading to *n*-type doping of the material. The electrons associated with defects in oxides having a high dielectric constant occupy large Bohr orbitals and tend to form an impurity band where they may be localized by correlations and local potential fluctuations⁴ to give the observed insulating behaviour. By allowing the impurity band to mix with the empty 5*d* states of hafnium and to transfer a fraction of an electron for each vacancy, the 5*d* states would in turn polarize the impurity band and provide the necessary ferromagnetic coupling. The anisotropy suggests a large orbital contribution to the 5*d* moment, with electrons in a spin-orbit coupled $j = 3/2$ state (Fig. 1, top-left inset).

Whatever the explanation, our discovery of anisotropic high-temperature *d*⁰ ferromagnetism in a transparent oxide is challenging for the theory of magnetism and propitious for the future of spin electronics, provided that the spin-polarized electrons can be mobilized.

M. Venkatesan, C. B. Fitzgerald, J. M. D. Coey

SFI-Trinity Nanoscience Laboratory, Physics Department, Trinity College, Dublin 2, Ireland
e-mail: jcoey@tcd.ie

1. Goodenough, J. B. *Magnetism and the Chemical Bond* (Interscience, New York, 1963).
2. Prellier, W., Fouchet, A. & Mercey, B. *J. Phys. Cond. Mat.* **15**, R1583–R1601 (2003).
3. Foster, A. S., Lopez-Gejo, F., Shluger, A. L. & Nieminen, R. M. *Phys. Rev. B* **65**, 174117 (2002).
4. Mott, N. F. *Conduction in Noncrystalline Materials* (Clarendon, Oxford, 1987).

Competing financial interests: declared none.