

Anisotropic dysprosium

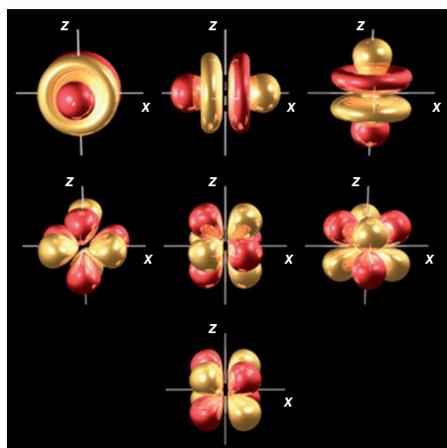
Beginning with its origins as the archetypal and eponymously elusive rare-earth element, **Dante Gatteschi** explains why dysprosium and other lanthanides have cornered the market in molecular magnetism.

Why should one be interested in dysprosium? As a member of the rare-earth elements it has been, as Giuseppe Verdi and Francesco Maria Piave described love in *La Traviata*, *croce e delizia*: a curse and a blessing. The similarity in the chemical properties of rare-earth compounds made the separation of their elements a difficult task, demanding the use of large amounts of mineral. The laboratory of Luigi Rolla at the University of Florence in the 1920s and 1930s was one of the places where the separation of the rare earths was actively pursued. There was also a claim to have isolated another element, number 61, tentatively called florentium, but the attempts to confirm its presence in pure form failed. It is to this difficulty in isolation that dysprosium, for which 2011 is the 125th anniversary, owes its name: from the Greek *dys* meaning 'hard' and *prositos* meaning 'to get at'.

The magnetic properties of rare earths, like their chemical ones, depend on the nature of the $4f$ orbitals (pictured) that interact only weakly with the environment. The magnetic properties of electrons are due to spin and orbital components. Spin is isotropic, whereas the orbital component reflects the symmetry of the system and can be anisotropic. For f electrons, the orbital moment is largely unquenched and the magnetic properties are therefore highly anisotropic.

Dysprosium is a good example of how anisotropic interactions induce interesting properties, which can then be used in applications. Its alloy with iron and terbium has the highest magnetostriction at room temperature — that is, it changes size when exposed to a magnetic field. The magnetic properties of dysprosium can also be exploited in magnetic resonance imaging — it can be used as a contrast agent when combined with chelating ligands.

Recently, the interest in magnetic properties of the dysprosium(III) ion has



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increased in parallel with the interest towards molecular magnetism. In the 1990s, my and other groups were involved in the design of molecule-based magnets: bulk magnets based on molecules rather than on the metals and oxides that are found in nature.

Remembering the Florence tradition in rare earths 60 years before, we decided to try to exploit the magnetic properties of the lanthanides. We started with gadolinium, whose orbital contribution is completely quenched, and dysprosium as an example of an anisotropic ion. Why dysprosium and not, say, thulium? There was not much rational design: one of them simply had to be first. With some surprise we found that the dysprosium-based material ordered as a bulk magnet at a temperature very close to that of the manganese-based material (C. Benelli, A. Caneschi, D. Gatteschi and R. Sessoli *Adv. Mater.* **4**, 504–505; 1992). The manganese-based material was expected to have stronger interactions between the magnetic building blocks, so these results gave an indication of the role that dysprosium anisotropy plays in the magnetic properties of molecular magnets.

Among the possible types of magnetic anisotropy that favour the orientation of magnetization along an easy axis, the Ising anisotropy showed its relevance in 'single-molecule magnets' (SMMs) — molecular

systems in which the large anisotropy blocks the relaxation of the magnetization, transforming each molecule into a tiny magnet. There was a 'gold rush', and lanthanides were in the forefront when it was discovered that dysprosium ions sandwiched between two phthalocyaninate rings behave as SMMs (N. Ishikawa *Polyhedron* **26**, 2147–2153; 2007). Other systems containing up to three dysprosium ions showed unique features associated with the anisotropy being larger than the exchange interaction. This opens new possibilities to store information in the chirality of the spin arrangement without any net magnetic moment.

The results showed the potential of dysprosium in molecular magnetism, highlighting the fact that although the interactions involving lanthanides are weak, magnetic anisotropy can yield novel properties. These properties are now actively investigated in the frame of molecular spintronics — the exploration of the opportunities for developing new electronics using molecules. However, to get to the *delizia* of using these molecules for new spintronic applications, one has to go through the *croce* of detailed quantum mechanical investigations to rationalize the electronic and magnetic structure of the rare earths.

The initial question "why should one be interested in dysprosium?" has become "why should one be interested in magnetic anisotropy?" My firm view is that chemists must tackle all aspects of the correlations between structure and properties. The rationalization of, say, room-temperature magnetic moments of metal ions seemed to be exotic at the time molecular magnetism was discovered. More complex phenomena must be tackled and chemistry is needed to transform concepts like magnetic anisotropy into real objects. □

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