

V for vanadium

Andrea Taroni shares his experience with vanadium — a colourful element with a rich chemistry (and physics!) that is emblematic of all transition metals.

Quite why I chose to study chemistry at university is a mystery, even to me. I mostly got the general principles, but it was as if its details — oxidation, reduction; *cis*, *trans*; *R*, *S* — or rather which way around those details went, had been designed to consistently make me feel like I couldn't tell my right hand from my left. It is fair to say I wasn't a natural at the subject.

One of the first elements I remember encountering in the lab — by attempting to work with it, as opposed to simply acknowledging its existence — is vanadium. My inorganic chemistry lab practical involved the synthesis and analysis of the five-coordinate complex $\text{VO}(\text{acac})_2$ (where *acac* is acetylacetonate) and I soon got a vivid demonstration of just how colourful chemistry could be.

The fascinating chemical and physical properties of vanadium all stem from the rich behaviour of its *d* electrons.

Like most transition metals, vanadium exists in a wide range of oxidation states — most commonly from +2 to +5, but all states from -1 to +5 exist and even the rare -3 is known, in $\text{V}(\text{CO})_5^{3-}$ — and can therefore take part in all manner of electron-transfer processes. In a coordination complex, these can occur in the form of charge-transfer transitions from the metal ion to the ligand (or vice versa). As the excitation energies of these transitions occur in the visible region of the electromagnetic spectrum, absorption of light produces a characteristic intense colour — blue in the case of $\text{VO}(\text{acac})_2$.

Changing a metal's oxidation state, typically by adding or swapping a ligand, affects its coordination environment, in turn altering the energetics of the charge-transfer transitions it is involved in, thereby

changing the colour of the complex. The rest of my undergraduate practical required me to determine the oxidation states of vanadium upon reducing my solution with various agents. I vividly recall the sudden changes in colour that came with each oxidation state switch, and I like to think this gave me a greater appreciation for the inspired decision to name the element after Vanadis, the Norse goddess more commonly known as Freyja, whose attributes include beauty.

In fact, many transition metal compounds have spectacular colours (pictured), making them ideal for pigments. Their rich redox chemistry is also key to their application in biological systems (think manganese in photosynthesis). Redox reactions are also, of course, central in electrochemistry, and vanadium flow batteries have been devised that store energy in liquid electrolytes instead of electrodes. These work using $\text{V}^{4+}/\text{V}^{5+}$ and $\text{V}^{2+}/\text{V}^{3+}$ aqueous sulfate solutions as cathode- and anode-side electrolytes separated by an ion-exchange membrane.

Transition metals give rise to exciting physics too. When bound together in the solid state, forming what condensed-matter physicists call a strongly correlated electron system, remarkable properties become manifest.

The conductivity and ferromagnetic nature of iron — an element that has been exploited to the extent that an entire epoch of human history is named after it — are two examples that have been used since antiquity; for example in magnetite-based compass needles. In the mid-1980s, it was realized that certain copper oxides can be made to superconduct when cooled with liquid nitrogen, a discovery for which J. Georg Bednorz and K. Alex Müller were awarded the 1987 Nobel Prize in Physics. In the same decade, thin Fe-Cr films were found to display a giant electrical response to applied magnetic fields, an effect now known as giant magnetoresistance, which underpins much of the memory storage technology in use today



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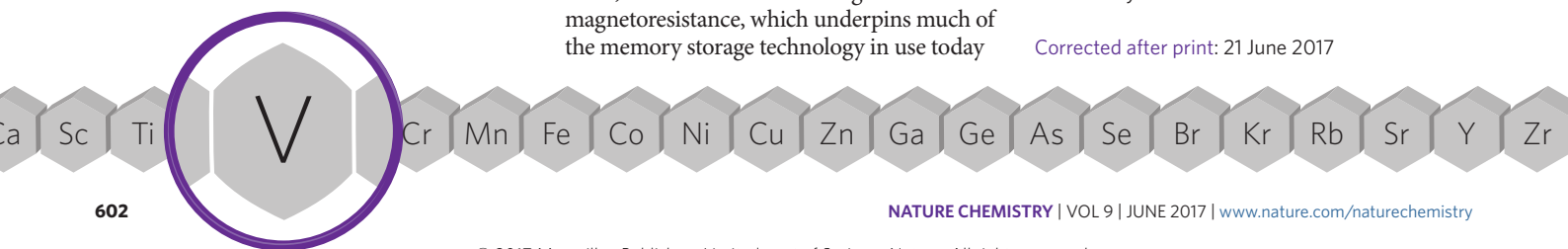
(earning Albert Fert and Peter Grünberg the 2007 Nobel Prize in Physics in the process). All of these properties arise from the different choreographies that the electrons of these systems can be made to arrange in — a seemingly limitless set that material scientists are becoming ever more adept at manipulating.

Naturally, element 23 also displays its own set of intriguing, yet useful, properties in the solid state. Vanadium dioxide, for instance, is the textbook example of an oxide that undergoes a transition from a conducting metal to a non-conducting insulator as it is cooled below room temperature. In fact, this metal-insulator transition can be controlled using a range of external parameters such as pressure, doping and applied electric fields, and as it is accompanied by huge changes in resistivity and opacity, VO_2 is widely used in coatings and sensors.

Like the rest of the transition metal elements, the fascinating chemical and physical properties of vanadium all stem from the rich behaviour of its *d* electrons. Back in my undergraduate chemistry days, where I got a small, albeit spectacular demonstration of this, I never would have guessed that these strongly correlated electron systems would go on to dominate my own research interests as a physicist. □

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Corrected after print: 21 June 2017



Correction

A sentence in the fifth paragraph of the In Your Element article 'V for vanadium' (*Nat. Chem.* **9**, 602; 2017) incorrectly mentioned magnesium, it should have read: "Their rich redox chemistry is also key to their application in biological systems (think manganese in photosynthesis)". This has been corrected after print 21 June 2017.