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# Rare earths in a nutshell

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The elements' electronic configurations help explain why the rare earths are key ingredients in dozens of technological products—cell phones, computer hard drives, and lasers among them.

As a class, the rare-earth elements comprise the 15 silvery-white metals, from lanthanum to lutetium, in the sixth row of the periodic table and the transition metals scandium and yttrium. Despite their name, most rare earths are not actually rare; nearly as many neodymium atoms reside in Earth's crust as nickel atoms, for example. But neither do rare earths congregate in rich metal veins. They are instead widely distributed at low concentrations in mineral and coal deposits, which have made mining efforts difficult (see PHYSICS TODAY, October 2018, page 22).

The heterogeneous distribution notwithstanding, rare earths exert an outsize influence on our daily lives in the common products made with them, including motors, speakers, hard drives, and lasers. Materials that are exploited for their electrical, magnetic, or optical properties often consist of a few distinct types of atoms. Because of that compositional simplicity, their properties can be surmised, at least partially, from the location of their constituent atoms in the periodic table. This Quick Study explores the influence of the rare earths' electronic structure on their properties and applications.

## Lanthanide contraction

The filling and spatial extent of the outer electron (5*d* and 6*s*) shells, which are most important in chemical bonding, are essentially unchanged across the entire rare-earth series. What varies from element to element is the number of electrons in the inner *f* shell. Because the atoms' electronegativities are nearly identical, a compound that incorporates a given rare earth can easily incorporate one of the others as a substitute. Indeed, the rare earths exhibit a linear dependence, known as the lanthanide contraction (see figure 1a), of their atomic radii on atomic number $Z$.

The ability to substitute one rare earth for another produces what's known as chemical pressure on surrounding elements in a material. That pressure is either positive or negative, depending on whether the radius of the substituted element is smaller or larger than the native one. And it allows researchers to finely tune the properties of even a complex compound. A case in point: The magnetic phase of titanium oxide compounds ($RTiO_3$) can be tuned from antiferromagnetic, with $R$ ranging from lanthanum to gadolinium, to ferromagnetic, with $R$ either yttrium or any element between holmium and lutetium.

Electrons in a rare earth occupy shells of either $[Xe]4f^n5d^16s^2$ or $[Xe]4f^{(n+1)}5d^06s^2$. The electrons in the 4*f* energy shell are more localized spatially—by virtue of being held closer to the nucleus—than are the 5*d* or 6*s* electrons. As a result, the orbital angular momentum $L$ of the 4*f* electrons mimics that of a free atom. Such an $L$ is unusual in materials where the crystalline environment is often strongly felt by the outer electrons.

By contrast, the *d* orbitals actually experience that crystalline environment, and their $L$ averages to zero due to its precession in the crystal field. Moreover, the greater spatial extent of outer *d* orbitals in the transition metal ions gives rise to greater variability in their atomic radii and therefore less material control under substitution as compared to the rare earths.

The magnitude of $L$ has important implications for how the spin, or intrinsic angular momentum $S$, of an electron combines with its orbital motion. Einstein's special theory of relativity transforms the electric field of the nucleus into a magnetic field in the reference frame of the electron, which thus couples the electron's orbital motion to its spin. The strength of that spin–orbit coupling is proportional to $Z^4$, so it is especially large in the heavy ($Z$ 56) rare-earth elements.

When the spin–orbit coupling is large, $S$ and $L$ are no longer independent, and the total angular momentum $J = L + S$ be-

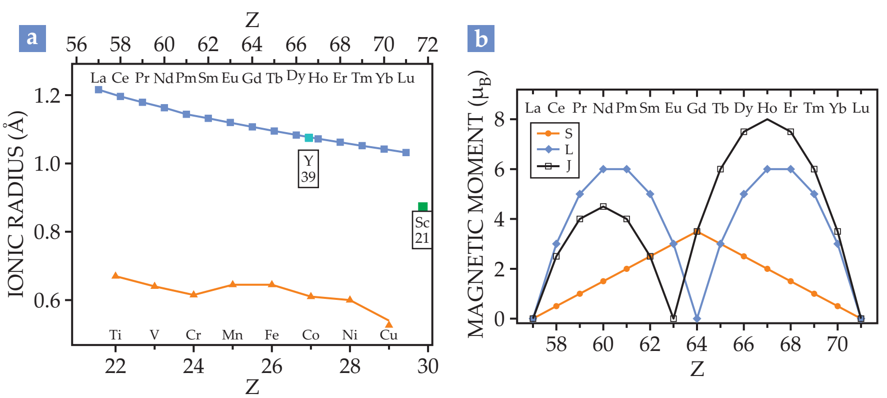


**FIGURE 1. LANTHANIDE CONTRACTION AND SPIN CYCLES. (a)** The ionic radii of rare-earth $R^{3+}$ ions and transition-metal $M^{3+}$ ions are plotted as a function of atomic number $Z$. Compared to the transition metal's *d* orbitals, the rare earths' *f* orbitals have only a weak, indirect effect on bonding. **(b)** The effects of spin $S$, orbital angular momentum $L$, and total moment $J$ on the magnetic moment of rare earth ions are plotted as a function of $Z$. The double-peak structure is a consequence of Hund's rules for atomic-shell filling.

comes a good quantum number. Figure 1b plots the value of *J*, *L*, and *S* as a function of *Z*.

The multiplets of energy levels for electronic states on each rare-earth ion create a rich spectrum of light emission, most of it in the visible range of the electromagnetic spectrum. Moreover, the large magnetic moments of some rare earths and their anisotropy—the moment's preferred direction in the crystal field—make the materials strongly magnetic.

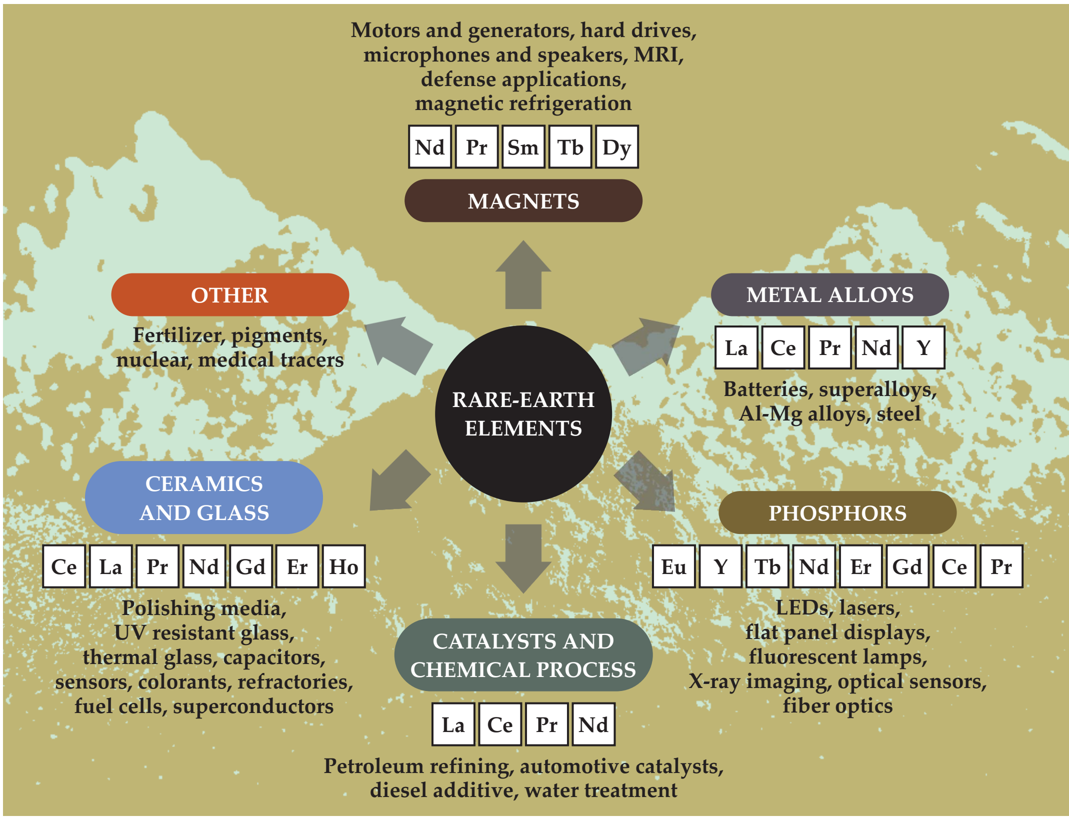


**FIGURE 2. DOZENS OF APPLICATIONS** use rare-earth elements as key ingredients.

## Lasers and magnets

The lanthanide contraction, the identical nature of the outer electronic structure, and the spin–orbit coupling in the rare earths are exploited in a variety of applications. This Quick Study focuses on just two. Yttrium aluminum garnet (YAG) is a hard, durable, and transparent crystal widely used in lasers because of its high gain. The material's lasing transition occurs between two energy levels of an $Nd^{3+}$ ion in a Nd:YAG laser. In a YAG crystal co-doped with $Er^{3+}$ and $Ho^{3+}$, even more efficient lasing occurs because of the more favorable energy transfer between those ions.

Yttrium lithium fluoride is another popular host crystal for lasers. Because of their identical outer electronic structure and similar ionic size, Eu, Tm, and Yb make ready substitutes for $Y^{3+}$ in the material. Other rare earths serve important functions in yet other laser systems. For example, carbon dioxide lasers produce IR light from transitions between molecular vibration levels. During high-power operation, some of the $CO_2$ converts into CO, which often causes the laser to fail. Lanthanum strontium cobalt oxide is a rare-earth oxide that, when used as an electrode in the laser, catalyzes the conversion of CO back to $CO_2$ and significantly extends the laser's life span. Without La, the catalyst is unstable.

Magnetic applications benefit from the rare earths' strong spin–orbit coupling. The interactions between the magnetic moments of electrons in partially filled 3*d* and 4*f* orbitals produce especially strong ferromagnetism. The magnets' most impressive feature is their extremely large coercive field ($\mathbf{H}_c$), a measure of their ability to resist demagnetization. That field in rare-earth ferromagnets is an order of magnitude higher than it is in traditional permanent magnets such as iron, and results from the spin–orbit-coupling induced magnetic anisotropies in the rare earths.

Popular rare-earth and transition-metal permanent magnets include samarium cobalt, neodymium iron boron, terbium iron, and gadolinium cobalt. Nd, Sm, Tb, and Gd have some of the largest moments of any rare earths (see figure 1b). And their alloys offer such advantages as a high Curie temperature and coercive field. They commonly replace traditional permanent magnets and are often found in wind generators, electric-car motors, data recorders, and voice-coil actuators. (Figure 2 lists some of the dozens of applications that use rare-earth elements.)

The bonding mismatch in a complex compound can cause a structural distortion. One can systematically tune that distortion or correct for it through rare-earth substitutions. In the orthorhombic $RMO_3$ perovskites, for instance, the electron kinetic energy is proportional to the deviation of the bond angle *M*-O-*M* from 180°, where *M* represents a transition metal. A rare earth in the series from $Lu^{3+}$ to $La^{3+}$ widens the deviation from 145° to 165° in $RNiO_3$. As a result, the perovskite changes from a metal to an insulator; and during that phase transition the strength of electronic correlations can be tuned over a broad range. Indeed, $RNiO_3$ is a classic system for studying electronic correlations in solids.

Near the crossover from strong to weak correlations, exotic properties such as colossal magnetoresistance in the manganese oxides and high-temperature superconductivity in the copper oxides can be observed. And in those oxides, the lanthanide contraction is a key knob for tuning their electronic states.

## Additional resources


▶ J. M. D. Coey, *Magnetism and Magnetic Materials*, Cambridge U. Press (2009).
▶ *Handbook on the Physics and Chemistry of Rare Earths*, vols. 1–43, Elsevier (1978–2013).
▶ J. H. L. Voncken, *The Rare Earth Elements: An Introduction*, Springer (2016).
▶ A. R. Jha, *Rare Earth Materials: Properties and Applications*, CRC Press, Boca Raton (2016).

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