Elucidating how asymmetry confers chemical properties

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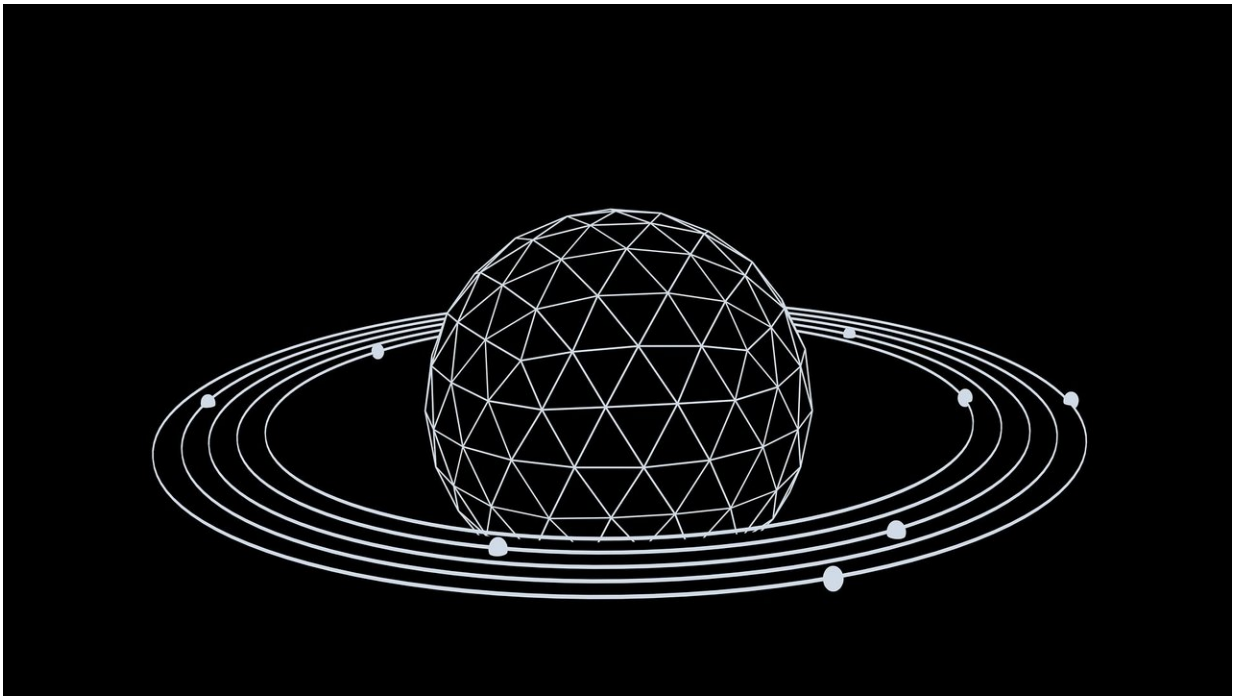

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You've heard the expression 'form follows function'? In materials science, function follows form.

New research by Carnegie's Olivier Gagné and collaborator Frank Hawthorne of the University of Manitoba categorizes the causes of structural asymmetry, some surprising, which underpin useful properties

of crystals, including ferroelectricity, photoluminescence, and photovoltaic ability. Their findings are published this week as a lead article in the *International Union of Crystallography Journal*.

"Understanding how different bond arrangements convey various useful attributes is central to the materials sciences" explained Gagné. "For this project, we were particularly interested in what variations in bond lengths mean for a material's most-exciting characteristics, and in how to create a framework for their optimization."

This was the fifth and final installment in a series of papers by Gagné and Hawthorne examining variability in bond lengths of crystalline structures. This time around they focused on compounds made up of oxygen and elements from the category called transition metals.

Picture the periodic table. The transition metals make up its central block—forming a bridge linking the taller towers of elements on the left and right sides.

Like all metals, they can conduct an electrical current. They also have a tremendous range of chemical and physical properties, including the emission of visible light, malleability, and magnetism. Many, like gold, platinum, and silver are prized for their value. Others, including iron, nickel, copper, and titanium are crucial for tools and technologies.

The transition metals' ability to form a variety of useful compounds is owed in large part to the particular three-dimensional configuration of their electrons. As such, the bonds they form in compounds can be widely asymmetrical. But Gagné and Hawthorne wanted to understand whether other causes for bond-length variation were in play.

"It's a century old problem" Gagné explained. "The likes of Linus Pauling and Victor Goldschmidt made this topic one of their prime

research interests; however, the data simply weren't there at the time."

Gagné and Hawthorne analyzed data on the bond lengths of 63 different transition metal ions bonded to oxygen in 147 configurations from 3,814 crystal structures and developed two new indices for contextualizing asymmetrical bonding.

"These indices allow us to pinpoint the different reasons underlying asymmetrical bonding arrangements, which will hopefully allow us to harness the properties that they convey when predicting and synthesizing new materials," Hawthorne explained.

To their surprise, they found that the internal structure of crystals often spontaneously distorts as a sole function of the connectivity of its bond network, an effect which they show occurs more frequently than distortion caused by electronic effects or any other factors.

"We suspected some bond-length variation originated from crystal-structure controls, but we didn't expect it to be the primary factor underlying bond-length variation in inorganic solids," Gagné explained. "It's a mechanism that is entirely separate and unaccounted for by current notions of solid-state chemistry; it that has been overlooked since the early days of crystallography."

More information: Olivier Charles Gagné et al, Bond-length distributions for ions bonded to oxygen: results for the transition metals and quantification of the factors underlying bond-length variation in inorganic solids, *IUCrJ* (2020). DOI: 10.1107/S2052252520005928

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