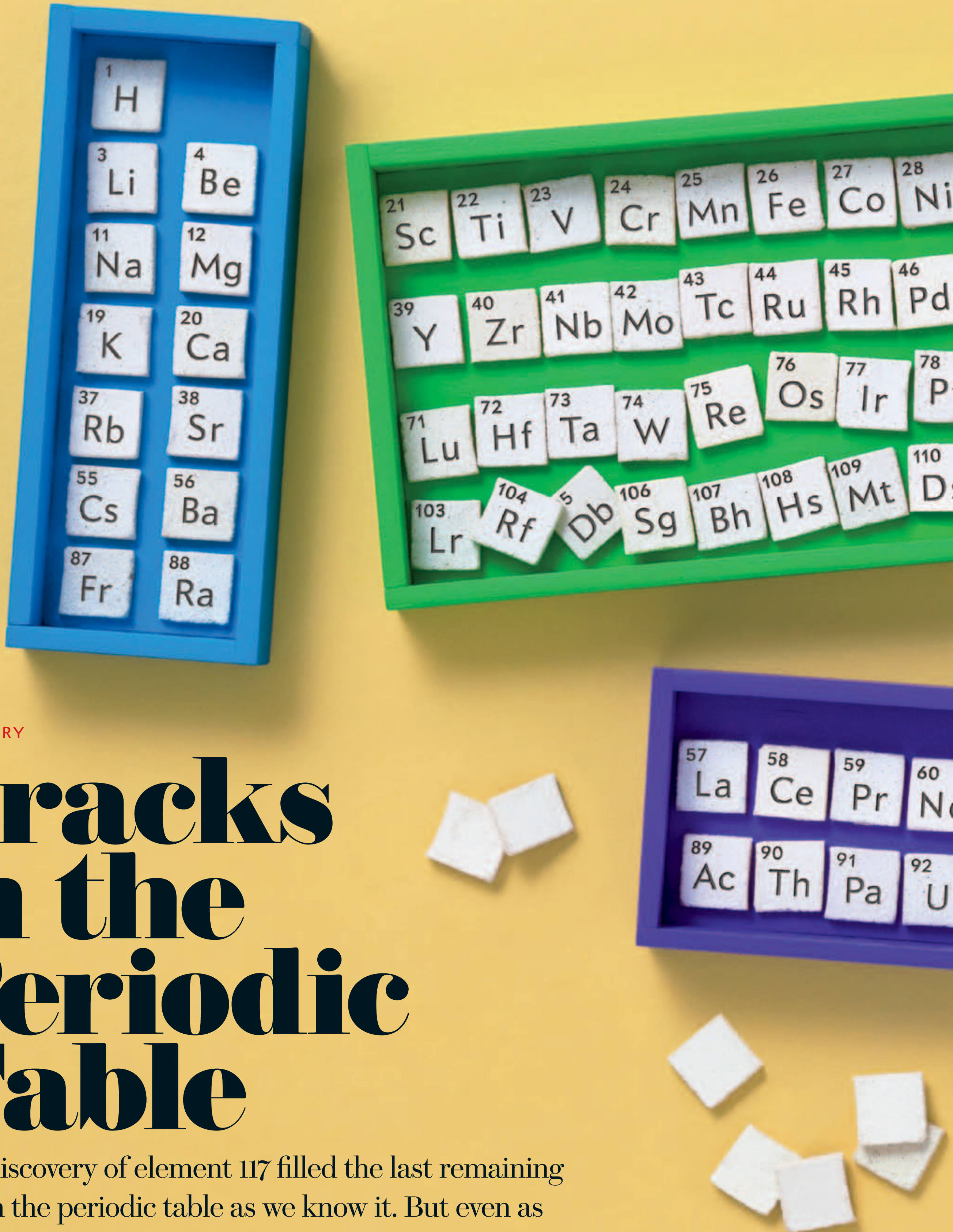
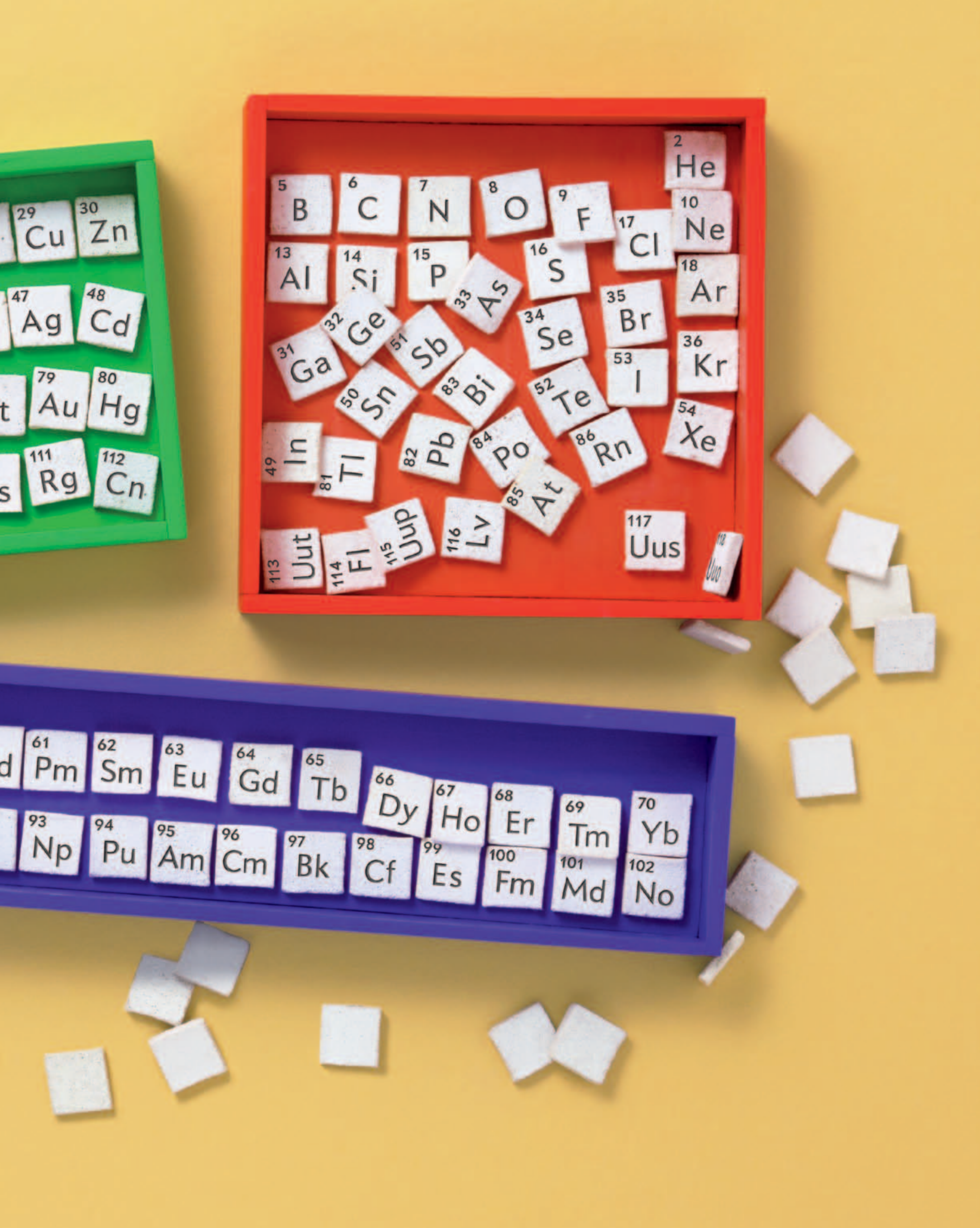


CHEMISTRY

Cracks in the Periodic Table

The discovery of element 117 filled the last remaining gap in the periodic table as we know it. But even as it is being completed, the table may be losing its power

By Eric Scerri



Photograph by Holly Lindem

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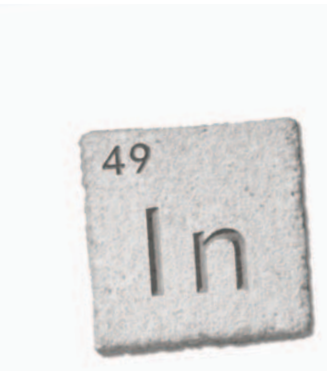


2010 RESEARCHERS IN RUSSIA ANNOUNCED THEY HAD SYNTHESIZED THE FIRST FEW NUCLEI of element 117. This new type of atom does not yet have a name, because the science community traditionally waits for independent confirmation before it christens a new element. But barring any surprises, 117 has now taken its permanent place in the periodic table of elements.

All elements up to 116, plus element 118, had been found previously, and 117 filled the last remaining gap in the bottom row. This achievement marks a unique moment in history. When Dmitri Mendeleev—also Russian—and others created the periodic table in the 1860s, it was the first grand scheme to organize all the elements known to science at the time. Mendeleev left several spaces blank in his table, and he made the bold guess that someday new elements would be discovered that would fill those blanks. Countless revisions of the table followed, but all of them had holes—until now. With element 117, the periodic table is complete for the first time.

The ghost of Mendeleev would probably savor the triumph of his vision—for a while at least, until chemists and nuclear physicists synthesize the next few elements, requiring the addition of new rows and possibly leaving new gaps behind.

Even as the last few pieces of the puzzle were falling into place, however, something more fundamental was beginning to look amiss. And it might undermine the very rationale behind the table's existence: the recurring patterns that give the periodic table its name.

Mendeleev did not just predict the existence of elements yet to be seen; more remarkably, he correctly guessed their chemical properties, based on those recurring patterns. But as the atomic numbers—the number of protons in a nucleus—reached higher, some of the added elements no longer behaved the way the periodic law requires; that is, their chemical interactions, such as the types of bonds they form with other atoms, did not resemble those of other elements in the same column of the table. The reason is that some of the electrons orbiting the heaviest nuclei reach speeds that are a substantial fraction of the speed of light. They become, in physics parlance, "relativistic," causing the atoms' behavior to differ from what is expected from their position in the table. Moreover, predicting exactly how each atom's orbital structure will pan out is extremely challenging. Thus, even as Mendeleev's creation has filled up and scored its successes, it may have begun to lose its explanatory and predictive power.

A COMPLETE SUCCESS

ALTHOUGH MORE THAN 1,000 versions of the periodic table have been published so far, with variations in the arrangement of elements as well as in which elements they contained, all share one essential feature. When the elements are arranged sequentially, based on their atomic number (the first attempts used atomic weights instead), their chemical properties tend to repeat after a particular sequence of elements. For example, if we begin with lithium and move eight places ahead, we reach sodium, which has many similar features—both are metals soft enough to cut with a knife, and both react vigorously with water. If we then

IN BRIEF

The discovery of element 117 in 2010 completed for the first time the periodic table as we know it—at least until new discoveries will force chemists to extend it by adding a new row.

Some recent additions, however, may differ in their chemistry from the elements in the same column, breaking the periodic rule that had defined the table for a century and a half.

The surprising behavior may result from effects described by the special theory of relativity, which make some electron orbits tighter, among other effects.

Nuclear physicists continue in their quest to synthesize new elements, which will have new types of electron orbitals—and to understand their chemistry from studying a handful of short-lived atoms.

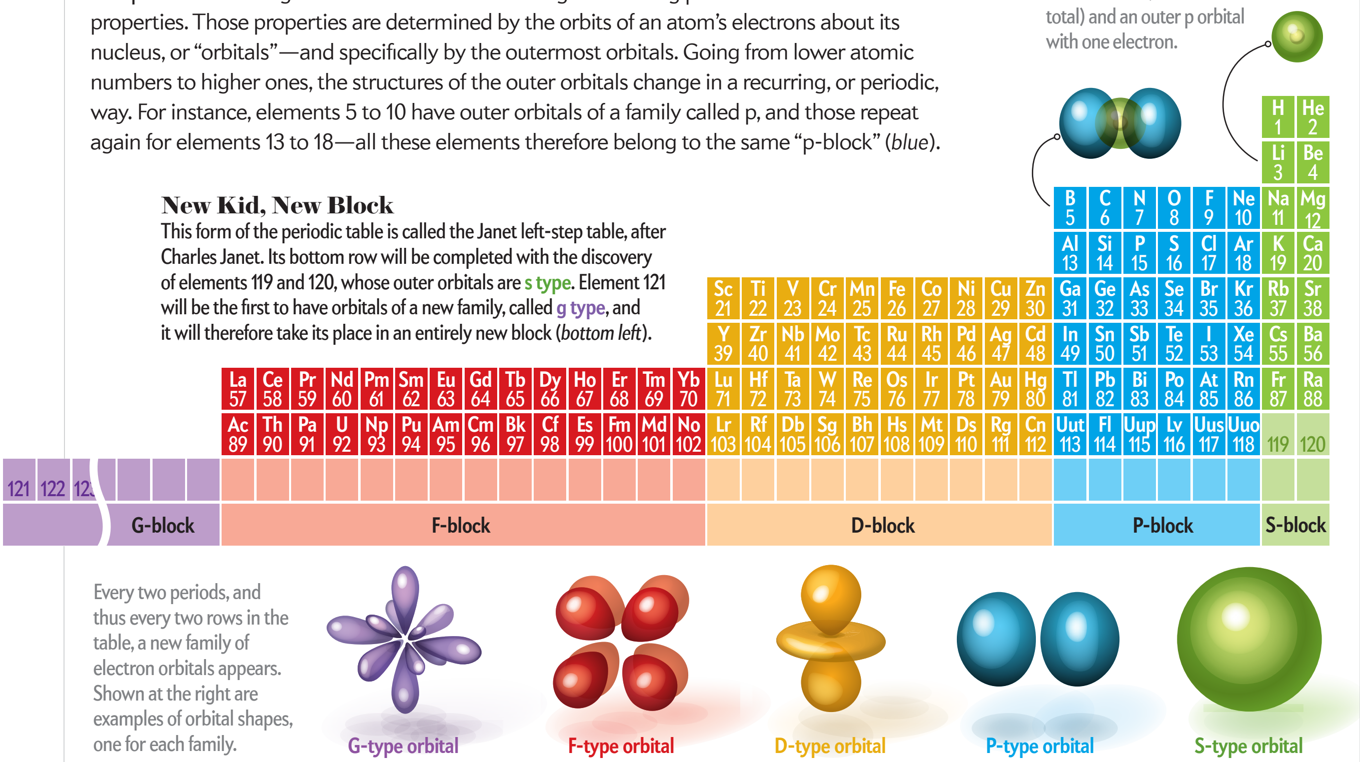
An Ever Growing Cabinet of Chemical Wonders

The periodic table organizes the elements according to recurring patterns in their chemical properties. Those properties are determined by the orbits of an atom's electrons about its nucleus, or "orbitals"—and specifically by the outermost orbitals. Going from lower atomic numbers to higher ones, the structures of the outer orbitals change in a recurring, or periodic, way. For instance, elements 5 to 10 have outer orbitals of a family called p, and those repeat again for elements 13 to 18—all these elements therefore belong to the same "p-block" (*blue*).

Sample structures: Lithium (Li) has two s orbitals, containing three electrons (*not shown*) in total. Boron (B) has two s orbitals (four electrons total) and an outer p orbital with one electron.

New Kid, New Block

This form of the periodic table is called the Janet left-step table, after Charles Janet. Its bottom row will be completed with the discovery of elements 119 and 120, whose outer orbitals are s type. Element 121 will be the first to have orbitals of a new family, called g type, and it will therefore take its place in an entirely new block (*bottom left*).



Every two periods, and thus every two rows in the table, a new family of electron orbitals appears. Shown at the right are examples of orbital shapes, one for each family.

move a further eight places ahead, we reach potassium, which is also soft and reactive with water, and so on.

In the earliest periodic tables, including those designed by Mendeleev but also by others, the length of each period—and thus the length of each row—was always eight. Soon, however, it became clear that the fourth and fifth periods repeated not after eight elements but after 18. Correspondingly, the fourth and fifth rows of the table were wider than the previous ones to accommodate the extra block of elements (the transition metals, which in the familiar view of the periodic table, sit in the middle). The sixth period turned out to be even longer, containing 32 elements, because of the inclusion of a series of 14 elements called the lanthanides—more recently renamed as lanthanoids.

In 1937 nuclear physicists began to synthesize new elements, starting with technetium. It filled one of four gaps in the table then known, which extended from 1 (hydrogen) to 92 (uranium). The other three missing pieces soon followed, two of them synthesized (astatine and promethium) and the third found in nature (francium). But even as those gaps were being filled, new discoveries were being added to the periodic table beyond uranium, leaving new gaps.

American chemist Glenn Seaborg realized that actinium, thorium and protactinium, together with uranium and the following 10 elements, were part of a new series, which, like the lanthanoids, had 14 elements and which became known as the actinides, or actinoids. (Because the extra elements in these two series would make the table even wider, standard periodic tables display the two 14-element series in a separate block at the bottom.)

As scientists realized in the first half of the 20th century, the periodicity of the elements is rooted in quantum physics and, in particular, in the physics of how electrons orbit the nucleus. The orbits of electrons come in a discrete range of shapes and sizes. Atoms with larger atomic numbers have the same orbit types, or "orbitals," as those of lower numbers, while adding new types. The first period has one type only, named s, which can be occupied by one or two electrons (one for hydrogen; two for helium). The second and third periods each add one more s-type orbital, plus three orbitals of a new type, p. Again, each of these four orbitals can be occupied by one or two electrons, for a potential total of eight electrons—which gives rise to the periodicity of eight in the original versions of the table. The fourth and fifth periods have, in addition to the s and p types, a third kind, d, which adds an extra 10 places for the electrons and thus stretches periods to 18. Finally, the last two cycles have orbitals of types s, p, d and f and have a length of 32 elements (18 + 14).

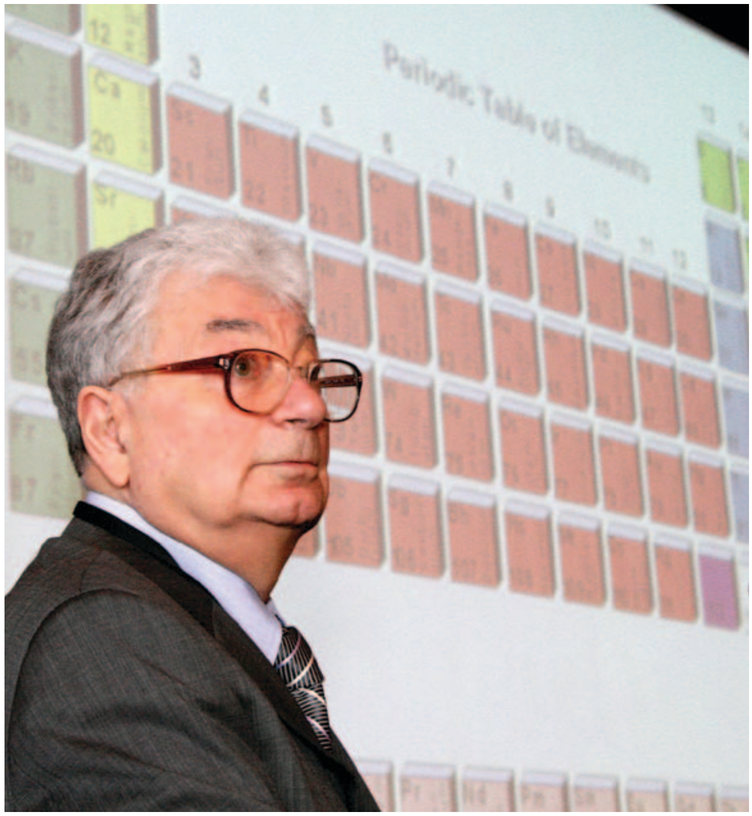
When Yuri Oganessian and his collaborators at the Joint Institute for Nuclear Research near Moscow announced they had synthesized the elusive element 117, all elements in the last row were now in place. The intimate connection between the structure of the table and that of atoms means that the comple-

Illustration by Jen Christiansen

tion of the table was not purely a matter of aesthetics or of organizing information on paper. Element 118 is the only one that has all its s, p, d and f orbitals filled with electrons.

If more elements are ever synthesized, they will take their place on an entirely new row of the table. Element 119, the one that is most likely to appear next [*see box on preceding page*], would start a new cycle—again with the simplest type of orbital, the s orbital. Element 119 and the following element 120 would occupy the first two slots in the new eighth period. But with element 121, a wholly new block would start, at least in principle, which would involve orbitals never encountered before: the g orbitals. As before, the new orbital types add new possibilities for the electrons and thus lengthen the periodicity, raising the number of columns. This block of elements would broaden the table to as many as 50 columns (although chemists have already devised more compact ways of arranging such an expanded table).

A completed table—one with all its rows filled in—would seem to be the ultimate fulfillment of Mendeleev's dream. And it might have been, were it not for Albert Einstein and his special theory of relativity.



YURI OGANESSIAN led the team that created element 117 and is now set to attempt the synthesis of the next novel element, 119.

COURTESY OF FLEROV LABORATORY

BREAKING BAD?

AS WE MOVE FROM LOWER to higher atomic numbers, nuclear charge increases because of the additional protons. As nuclear charge increases, so does the speed of the electrons in the inner orbitals—to the point that the special theory of relativity begins to play a bigger role in explaining their behavior. This effect causes a contraction in the size of the inner orbitals and makes them more stable. That tightening has a knock-on effect on the other s and p orbitals, which also tighten, including the "valence" orbitals, the outermost ones, which govern the chemical properties.

All these phenomena come under the name of the direct relativistic effect, which, broadly speaking, increases with the charge on the nucleus of each atom. Some competing effects, however, make things more complicated. Whereas the direct relativistic effect stabilizes certain orbitals, another, "indirect" relativistic effect destabilizes the d and f orbitals. It is a kind of electrostatic screening by the s and p electrons, whose negative charges partially neutralize the attraction from the positive charge of the nucleus as measured from farther out. Thus, to distant electrons the nucleus appears to have less, not more, electrostatic pull.

Some relativistic effects on elements are apparent in everyday life. For example, they explain the color of gold, which sets it apart from the colorless elements surrounding it in the d-orbital block of the periodic table—such as silver, which lies directly above gold.

An atom of a d-block metal, when hit by a photon of the right wavelength, undergoes a transition. It absorbs the photon, and the photon's energy makes an electron jump from a d orbital to the s orbital directly above it. In silver, this gap between orbital energies is rather large, so that it takes a photon in the ultraviolet region of the spectrum to trigger the transition. But photons in the spectrum of visible light, having lower energy than ultraviolet rays, just bounce off, so that to our eyes the material appears to act as a nearly perfect mirror.

In gold, the relativistic contraction lowers the energy of the s orbitals even as it raises the energy of the d orbitals, thus narrowing the gap between the two levels. Now the transition requires less energy—exactly that carried by a photon in the blue part of the spectrum. Photons of all other colors still bounce off, however, and we observe white light minus blue light—which yields the characteristic golden-yellow color.

Pekka Pyykkö of the University of Helsinki and others went on to predict a number of effects that relativity has on gold, including the fact that it could bind to other atoms in surprising new ways. The compounds they expected to result from such interactions were subsequently discovered, a feat that somewhat paralleled the exploits of Mendeleev in anticipating new elements. Pyykkö's successful predictions included bonds between gold and the noble gas xenon—which is usually extremely inert—and triple bonds between gold and carbon. Another success was a spherical molecule involving one atom of the metal tungsten and 12 atoms of gold and resembling the all-carbon "fullerenes," better known as buckyballs. This gold fullerene forms quite spontaneously when tungsten and gold are vaporized in the presence of helium gas.

Relativistic quantum-mechanical calculations have also proved indispensable in studying how gold clusters can act as catalysts—for example, to break down toxic chemicals typical of car exhaust—even though bulk gold is notoriously inert.

SUPERHEAVY SURPRISES

EVEN WITH THE EMERGENCE of relativistic effects, elements such as gold still do not deviate too far from the character expected. Until recently, novel elements by and large matched the properties that were anticipated based on their position in the periodic table. But worse (or perhaps more interesting) surprises were yet to come. Some tests on the chemistry of the most recently discovered elements have begun to show what could be serious cracks in the periodic law.

Using particle accelerators to smash heavy nuclei together, nuclear physicists are able to produce "superheavy" elements—those beyond atomic number 103. Early experiments in the 1990s on rutherfordium (104) and dubnium (105) already suggested that these elements did not have the properties expected for them according to their positions in the periodic table. For example, Ken Czerwinski and his colleagues at the University of California, Berkeley, found that in solution, rutherfordium reacted in ways similar to plutonium, an element that is quite distant in the periodic table. Similarly, dubnium was showing signs of behaving more like the element protactinium, which is again rather distant in the periodic table. According to the periodic law, these two elements should have behaved instead like those directly above them in the periodic table, namely, hafnium and tantalum.

It is not clear yet whether the principle that elements in the same column in the periodic table behave similarly remains valid for very heavy atoms.

In more recent work, scientists have been able to synthesize new superheavy elements in only extremely small numbers: the discovery of element 117 was based on the observation of just six atoms. Superheavy elements also tend to be very unstable, decaying into lighter elements in a fraction of a second. Experts mostly are left to observe the debris of this nuclear decay, which yields information on the physics and chemistry of their nuclei. In this state of affairs, investigating chemical properties through traditional "wet" chemistry—put the stuff into a flask and watch it react with other chemicals—is out of the question. And yet scientists have come up with ingenious techniques to study the chemistry of these elements one atom at a time.

Chemical experiments carried out on the next two elements were, compared with those on 104 and 105, disappointing. Seaborgium (106) and bohrium (107) seemed to act just the way Mendeleev would have guessed, inspiring researchers to give titles such as "Oddly Ordinary Seaborgium" and "Boring Bohrium" to their scholarly papers. The periodic law seemed to be back in business.

In the case of element 112, chemists and physicists have been trying to assess whether the element behaves more like mercury, which sits directly above it in the periodic table, or like the noble gas radon, as some relativistic calculations predict. In such experiments, teams synthesize atoms of 112, along with some heavy isotopes of mercury and radon. (Although mercury and radon occur naturally in substantial amounts, investigators use synthetic ones because they can produce them in conditions identical to those that give rise to the heavier elements, rather than relying on data that apply to the macroscopic properties of the more abundant lighter elements.)

The experimenters then allow all these atoms to deposit on a surface kept at very low temperature and coated partly with gold and partly with ice. If element 112 truly behaves like a metal, it will bind to gold. If it is more like the noble gas radon, it will tend to deposit on the ice. To date, different laboratories have obtained different results, and the situation is still far from settled.

The effects of relativity on element 114 also remain to be seen. Initial results reported by Robert Eichler and his group at the Paul Scherrer Institute in Switzerland indicate some genuine surprises here, given that the disagreement with the theory is quite pronounced.

New additions to the periodic table will surely follow, and research into the chemistry of those elements will help clarify the dilemma. A more general question is whether there is an end to the periodic table. The overall consensus is that when the number of protons becomes too large, nuclei will not form, even for a fleeting instant. But opinions seem to differ as to where the new elements will stop. In calculations that assume the nucleus is pointlike, the limit appears to be at element 137. Other experts who have taken account of the volume of the nucleus estimate the final element to have an atomic number of 172 or 173.

It is simply not yet clear whether the principle that elements in the same column in the periodic table behave similarly remains valid for very heavy atoms. That question is of no great practical consequence, at least for the foreseeable future. The loss of predictive power in the superheavy realm will not affect the usefulness of the rest of the table. And the typical chemist will never get to play with any of the elements of highest atomic numbers: these elements' nuclei are all very unstable, which means that they decay into lighter elements instants after being created.

Still, the question of special relativity's effect strikes at the very heart of chemistry as a discipline. If the periodic law does lose its power, then chemistry will be in a sense more reliant on physics, whereas a periodic law that holds up would help the field maintain a certain level of independence. In the meantime, perhaps, Mendeleev's ghost should just kick back and marvel at the success of his favorite brainchild. SA

MORE TO EXPLORE

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SCIENTIFIC AMERICAN ONLINE
See a slide show of the many shapes the periodic table has taken throughout history, plus more multimedia content, at **ScientificAmerican.com/jun2013/periodic-table**