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18-*n*+*m* Isomerism in Transition Metal-Main Group Intermetallics:

Chemical Pressure-Directed Configurations of Electronically Viable Structures

By
Amber Lim

A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy
(Chemistry)

At the
UNIVERSITY OF WISCONSIN-MADISON
2024

Date of final oral examination: 04/26/2024

The dissertation is approved by the following members of the Final Oral Committee:
Daniel C. Fredrickson, Professor, Chemistry, Inorganic Path
Yang Yang, Professor, Chemistry, Physical Path
Jason Kawasaki, Professor, Materials Science and Engineering
Song Jin, Professor, Chemistry, Materials Path

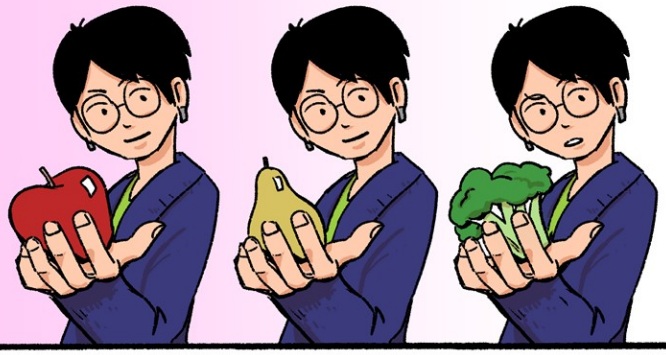

CRYSTAL STRUCTURE SHOWDOWN
ELECTRONICS VS. PACKING EDITION!
VS
aka
A Computational Chemist Narrates How
Nature Decides on a Crystal Structure
by Amber Lim

All too often, when I tell people that I'm in grad school for chemistry, I hear things like,

"Oh. My. God! That's so hard! I could NEVER understand chemistry! So you're going to make medicine, right?"

While their reactions are quite natural, there are two things I want to tell them:

(1): Chemistry encompasses fields beyond medicine--food, geology, space, ecology--just to name a few,



And more importantly, (2): you CAN understand chemistry. You don't need to know every itty-bitty detail. A lot of it is pattern recognition, and humans historically are experts at that.

That's why I wrote and illustrated this chapter.

My research might never intersect with the average person's daily life.

I do computational chemistry, and not only that. I do calculations to understand fundamental, *nerdy* aspects of chemistry. And to top it off, it's chemistry of *metals!*

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> qvasp4 -q fredrickson -np 12 PdSn2_dos
Job 042624 submitted.
> grep TOTEN PdSn2_dos.log
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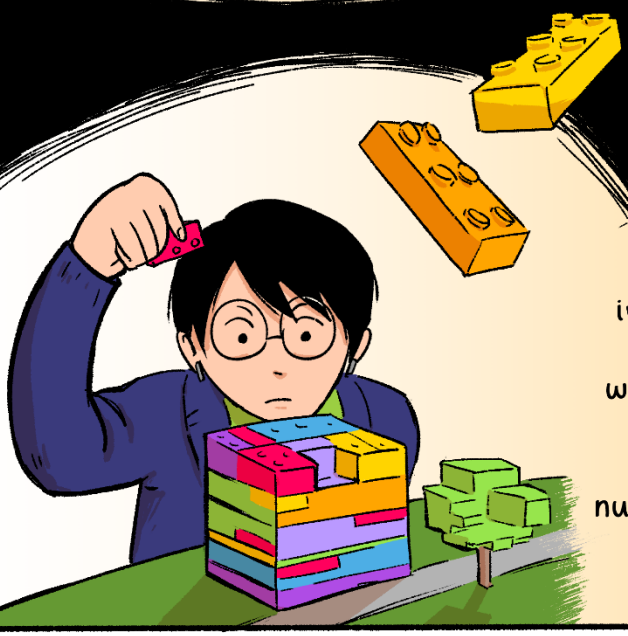


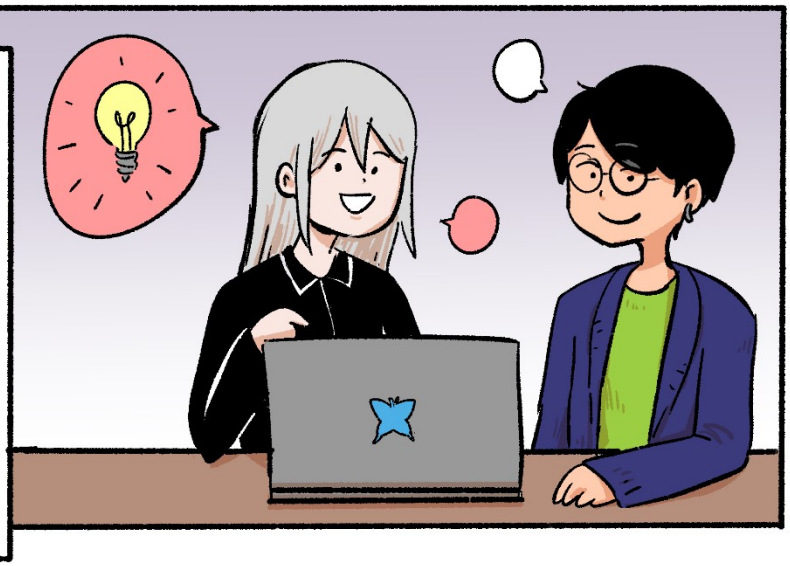
Which makes it all the more important for me to show you-- friends, family, readers-- what I do, and why it's important.

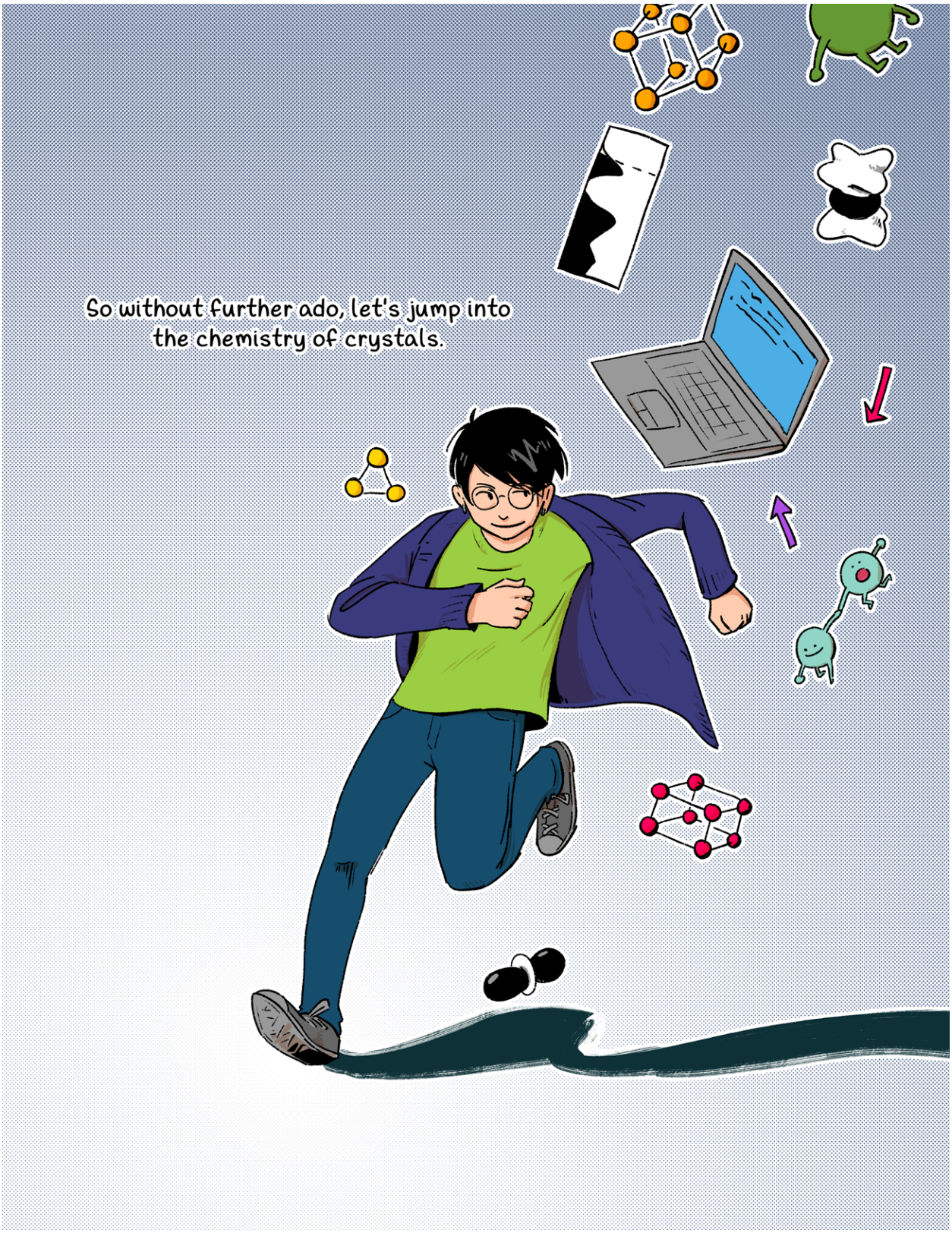
I'm not just crunching numbers--I'm trying to help create conceptual building blocks for future scientists to use.

I fell in love with crystals, like many people. That's part of what sustained my journey in this field.

And through this work, I learned how to run computations, which is part of my next job:

Helping researchers use computers to do heavy calculations-- not only in chemistry, but in other natural sciences, and even social sciences.

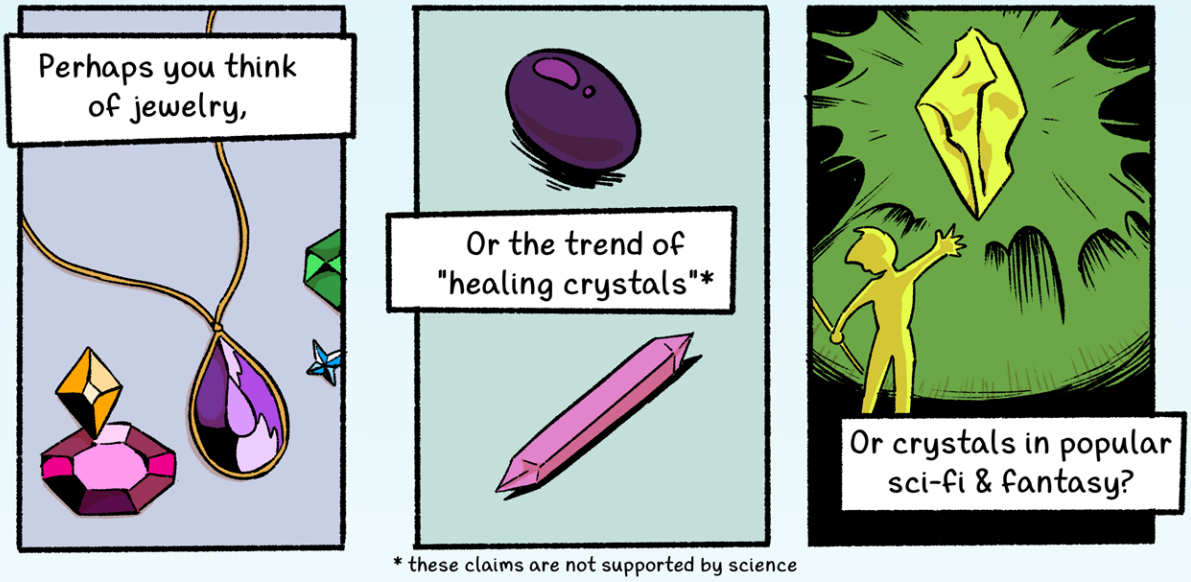



So without further ado, let's jump into the chemistry of crystals.

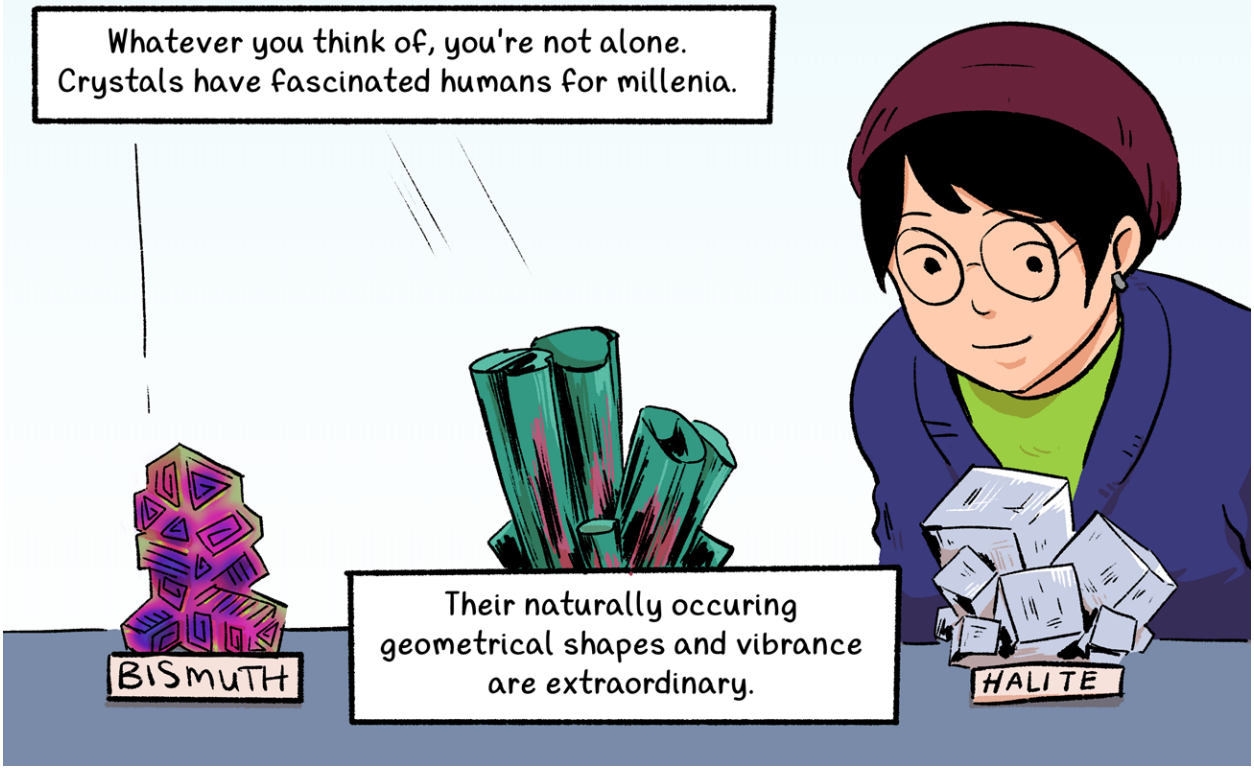
Part 1.

What comes into your mind when you think about

Crystals?



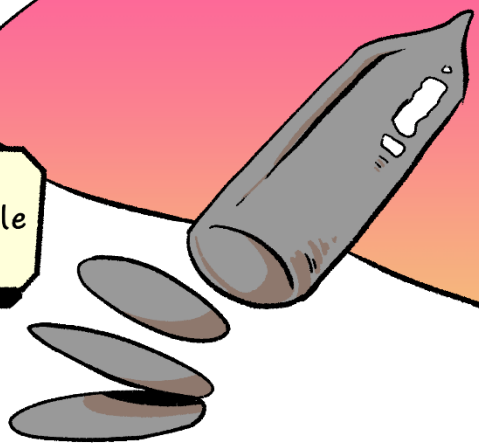
* these claims are not supported by science



But crystals aren't limited to rocks and gemstones.

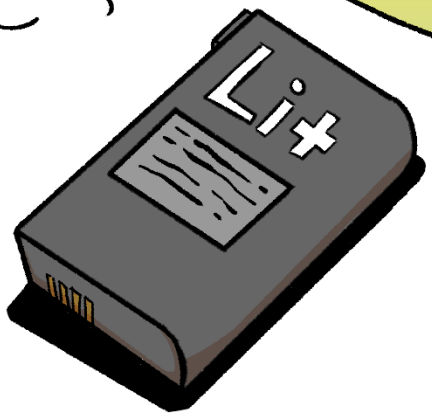
Did you know they are in our devices and electronics?

Circuits used in solar cells are made from single crystals of silicon.



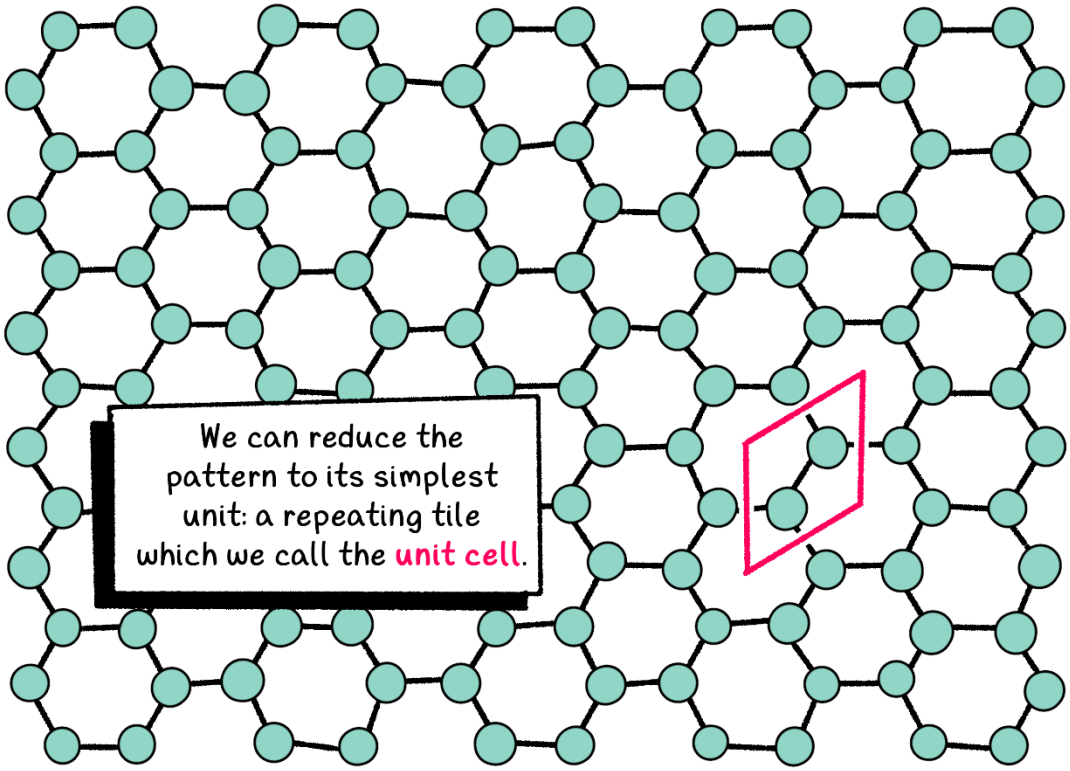
The high-temperature superconductor Yttrium Barium Copper Oxide can levitate magnets.

Crystals in Lithium-ion batteries enable energy storage.



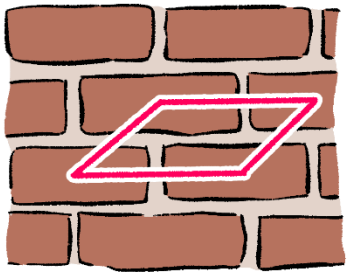
To create and improve these useful materials, researchers need to understand how to design these at the atomic level.

At the atomic level, crystals form ordered patterns.

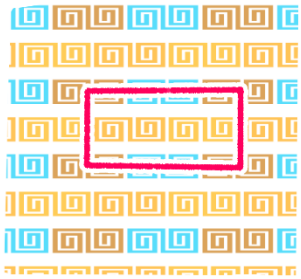


We can reduce the pattern to its simplest unit: a repeating tile which we call the **unit cell**.

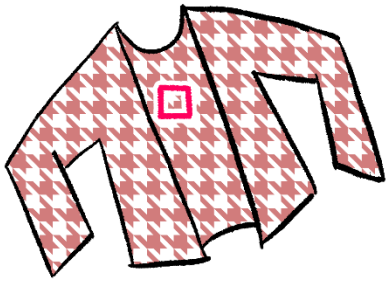
This concept is not limited to science, but we see it anywhere we see repeating patterns, such as in art and design.



In the tiling of bricks,

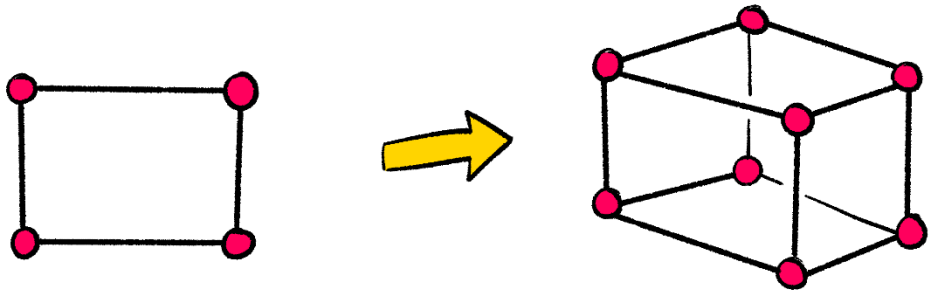


wallpaper,



and prints in fashion.

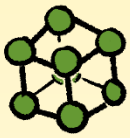
We can expand this concept into 3D,



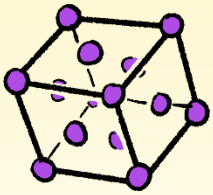
likewise, expanding the possible patterns to higher orders.

Crystals form a multitude of patterns.

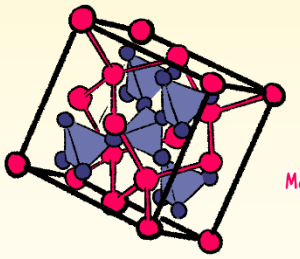
From simple...



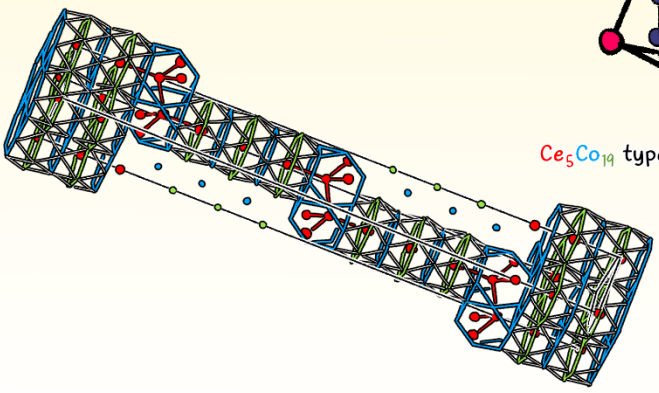
simple cubic



face-centered cubic



$MgCu_2$ type



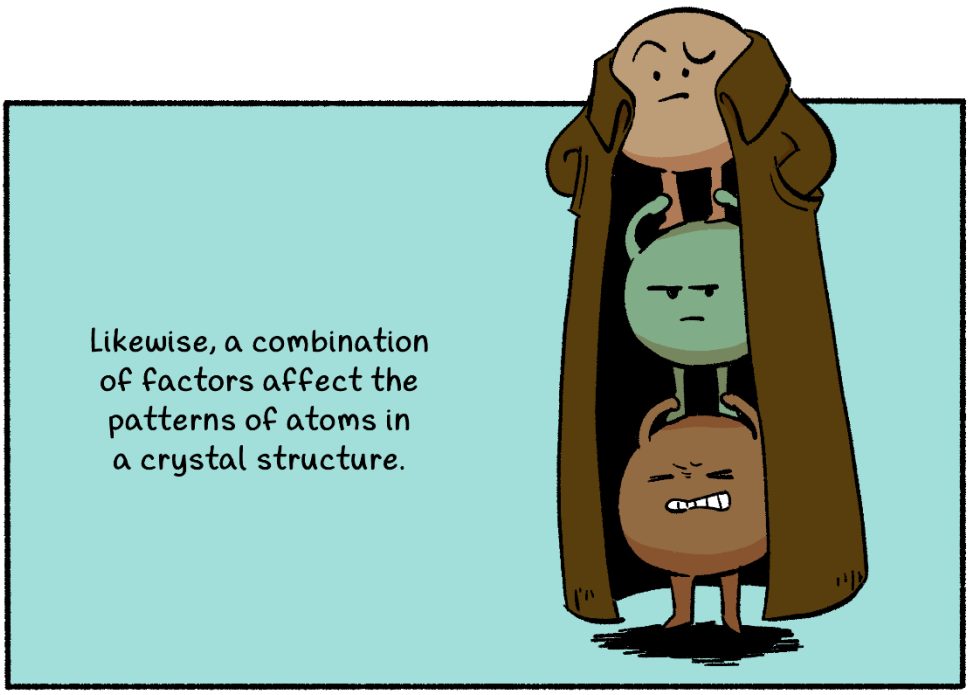
Ce_5Co_{19} type

... to complex.

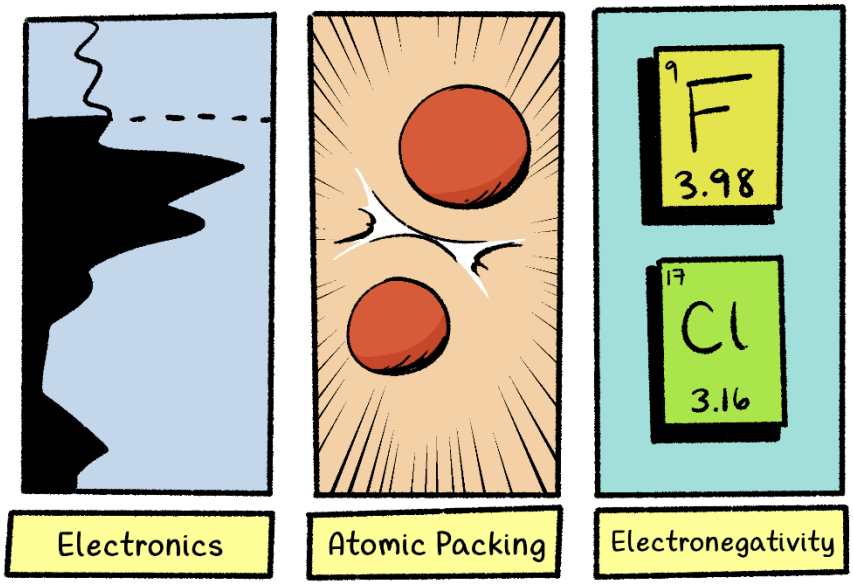
But how does nature decide what crystal structure is best?
This is where my research in computational chemistry comes in.


Part 2. How to decide on a crystal structure.
When picking your outfit for the day, how do you decide what to wear?
You might take some factors into account, like personal style,
your sense of comfort,
or the weather.

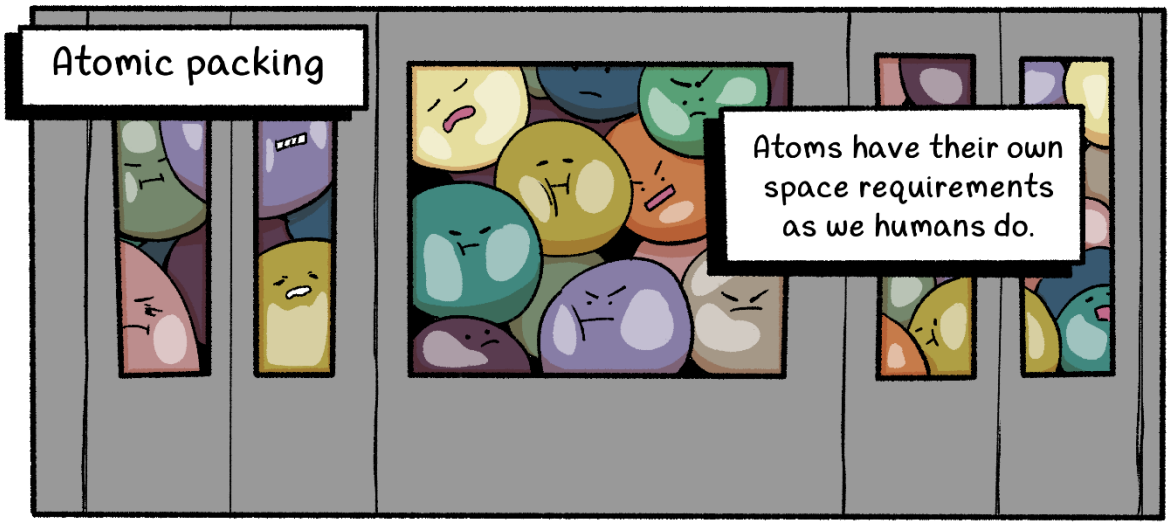

Most of the time, you don't just pick one of these factors (or you might end up wearing something strange), but take a combination of these into account.



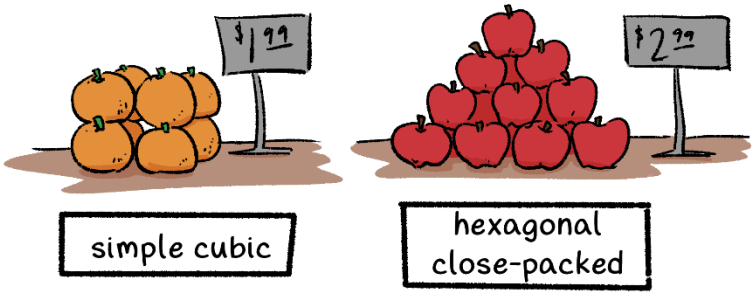
We call these the ***Hume-Rothery factors***, named after the scientist William Hume-Rothery who pioneered metallurgical research in the 20th century.



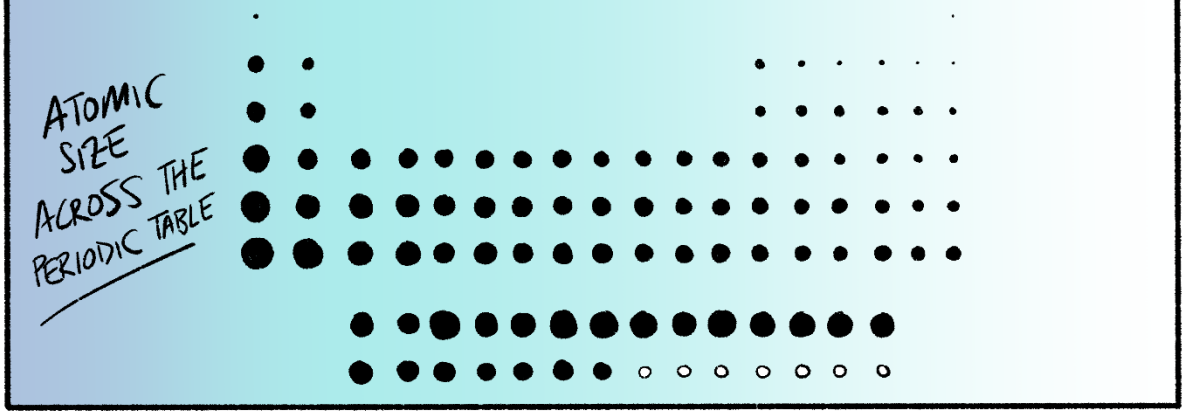
In my research, we focus on electronic and atomic packing effects. Let's see how these can affect crystal structures.



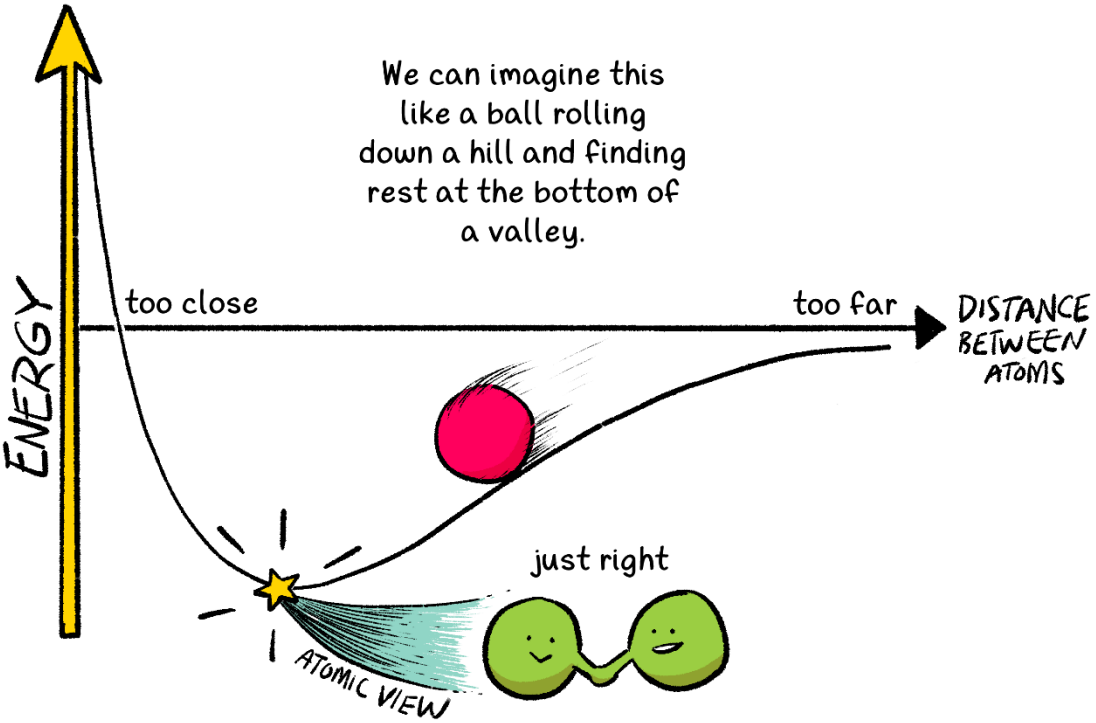
Atoms can be modeled as simple spheres and pack accordingly. Perhaps you've seen some simple sphere packings at the grocery store.



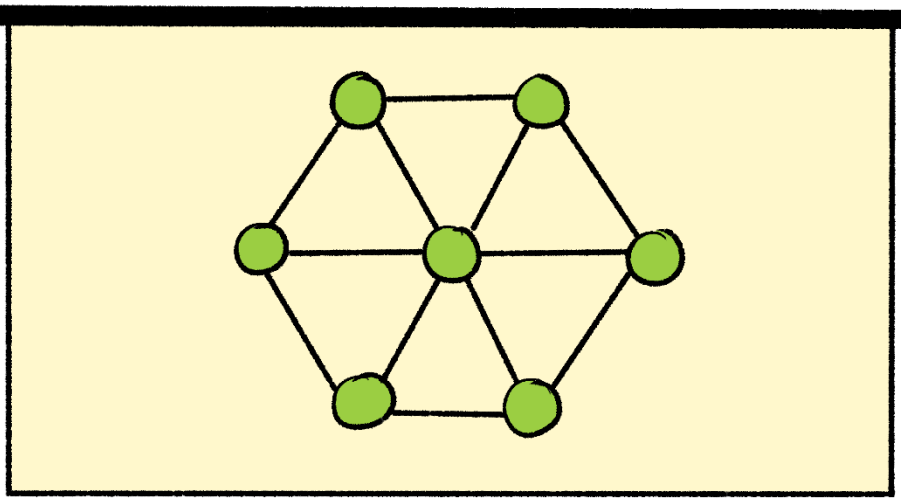
Packing is relatively easy when spheres are the same size, but elements have a variety of sizes.

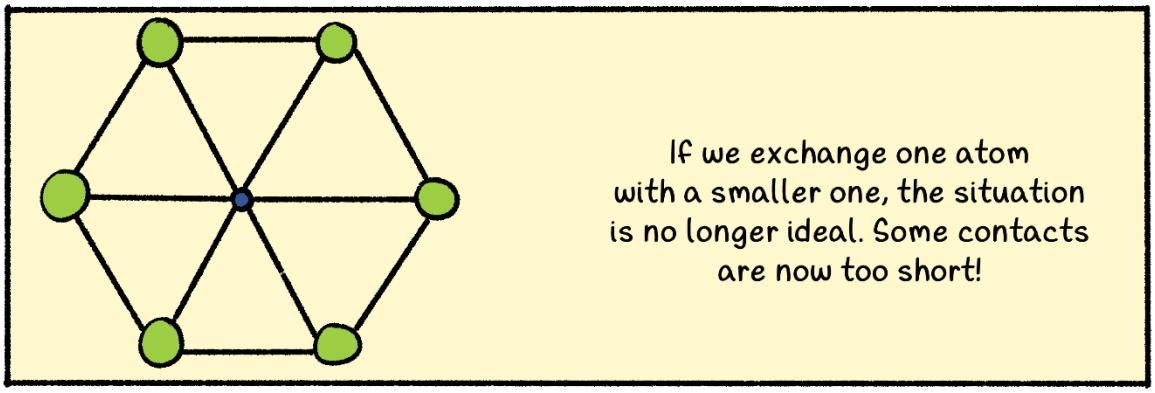


The best distance for two atoms to be next to each other occurs at the **lowest energy**.



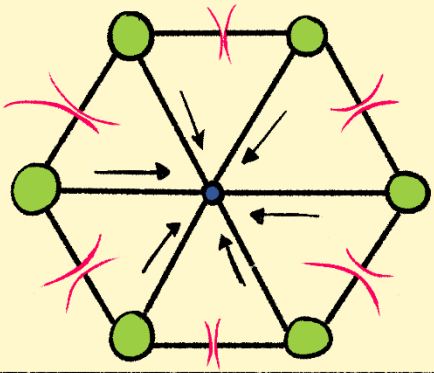
If we have an arrangement of atoms at the equilibrium distance...



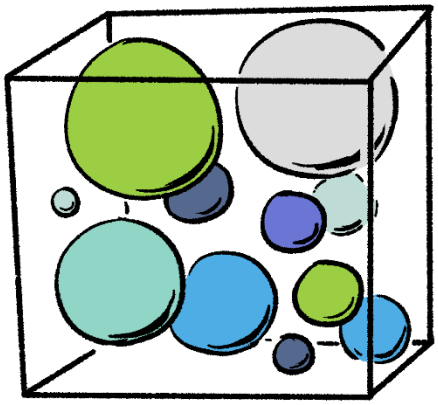


If we exchange one atom with a smaller one, the situation is no longer ideal. Some contacts are now too short!

But if we shorten those contacts, we make others shorter than they prefer to be.

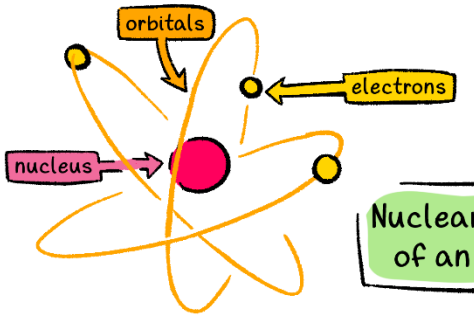


In this way, the structure needs to compromise between the two types of contacts.



So when we add lots of different elements, the situation becomes very complex!

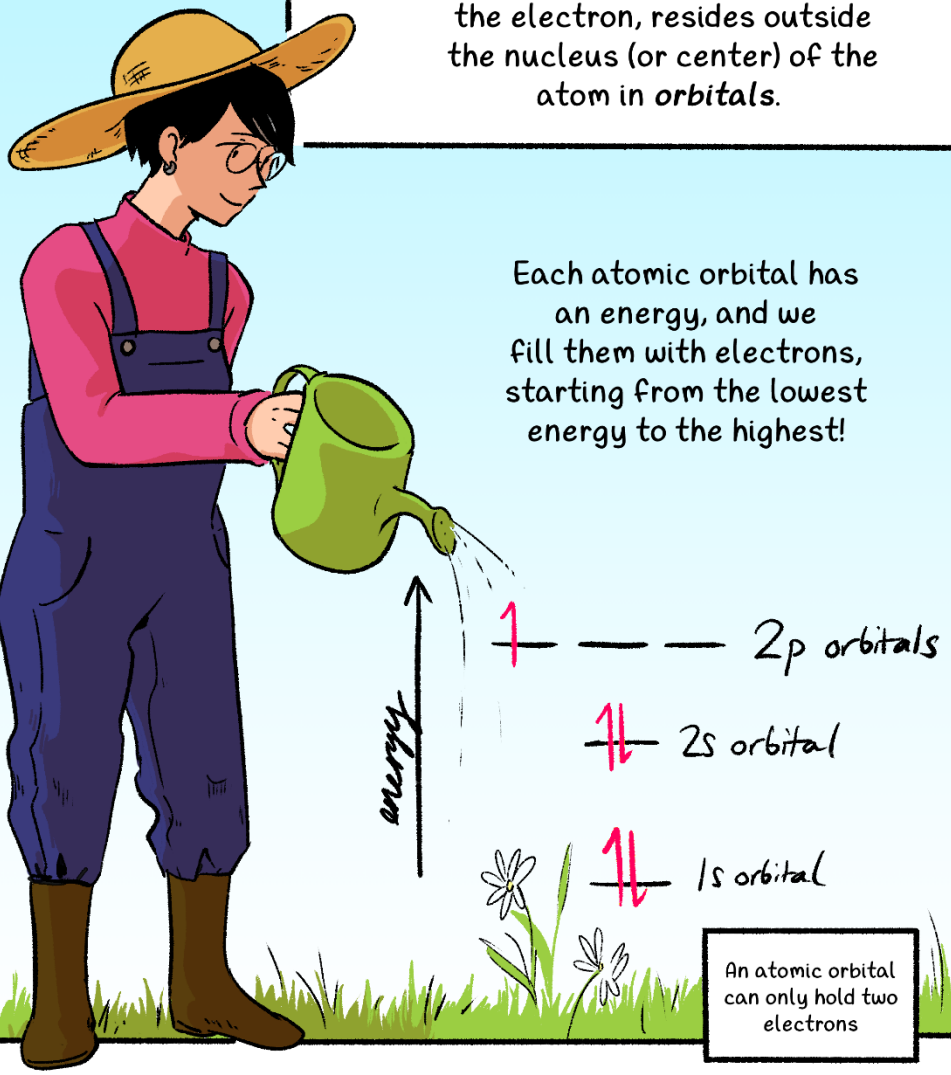
The electronic structure of a compound is another *key* factor for crystal structures.



Nuclear model of an atom

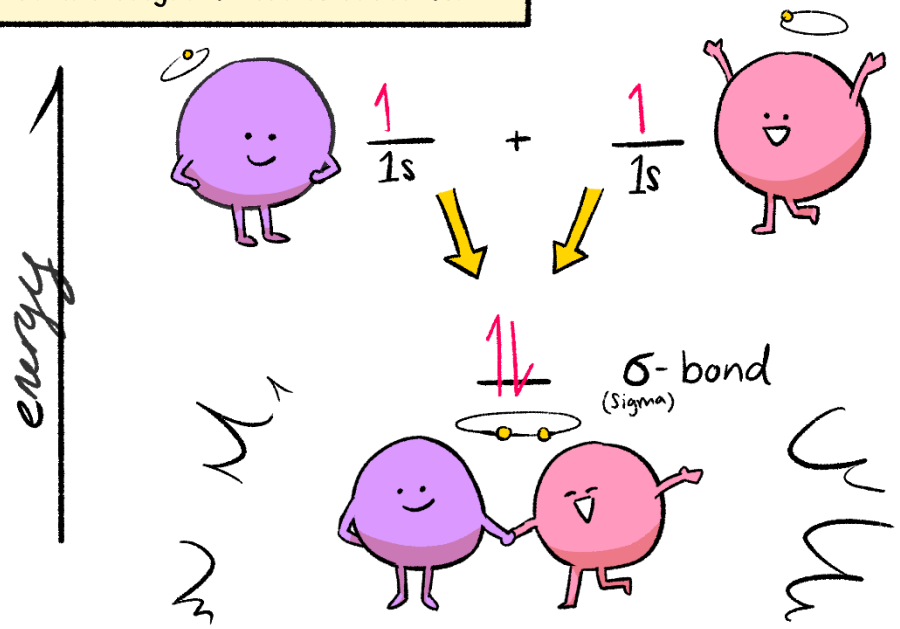
Atoms are made of tiny particles. One of these types of particles, the electron, resides outside the nucleus (or center) of the atom in ***orbitals***.

Each atomic orbital has an energy, and we fill them with electrons, starting from the lowest energy to the highest!



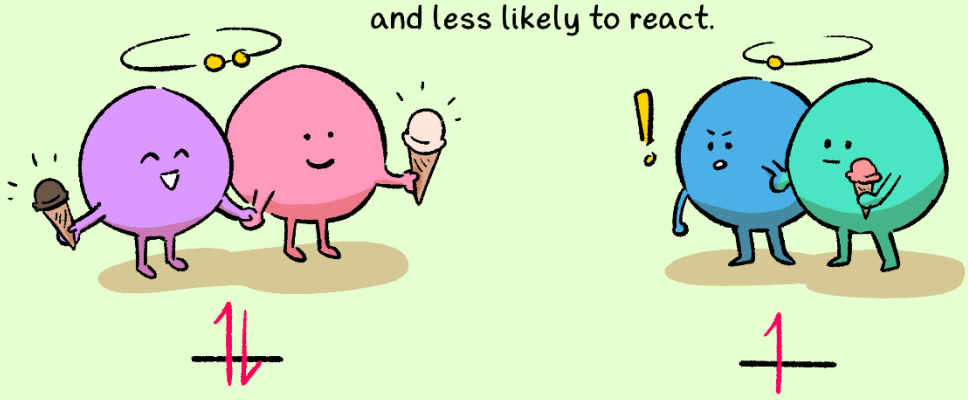
An atomic orbital can only hold two electrons

When atoms form covalent bonds, their atomic orbitals combine to create new molecular orbitals that are lower in energy than that of the original atomic orbitals.

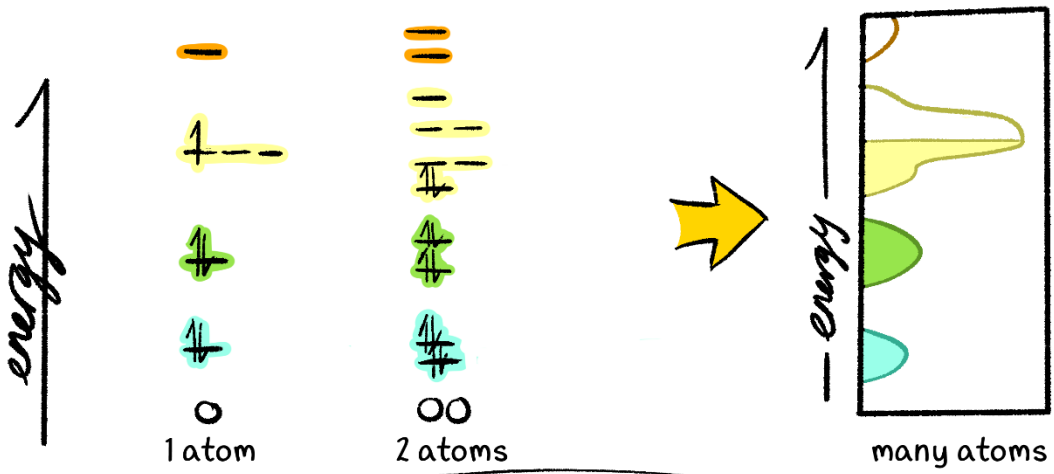


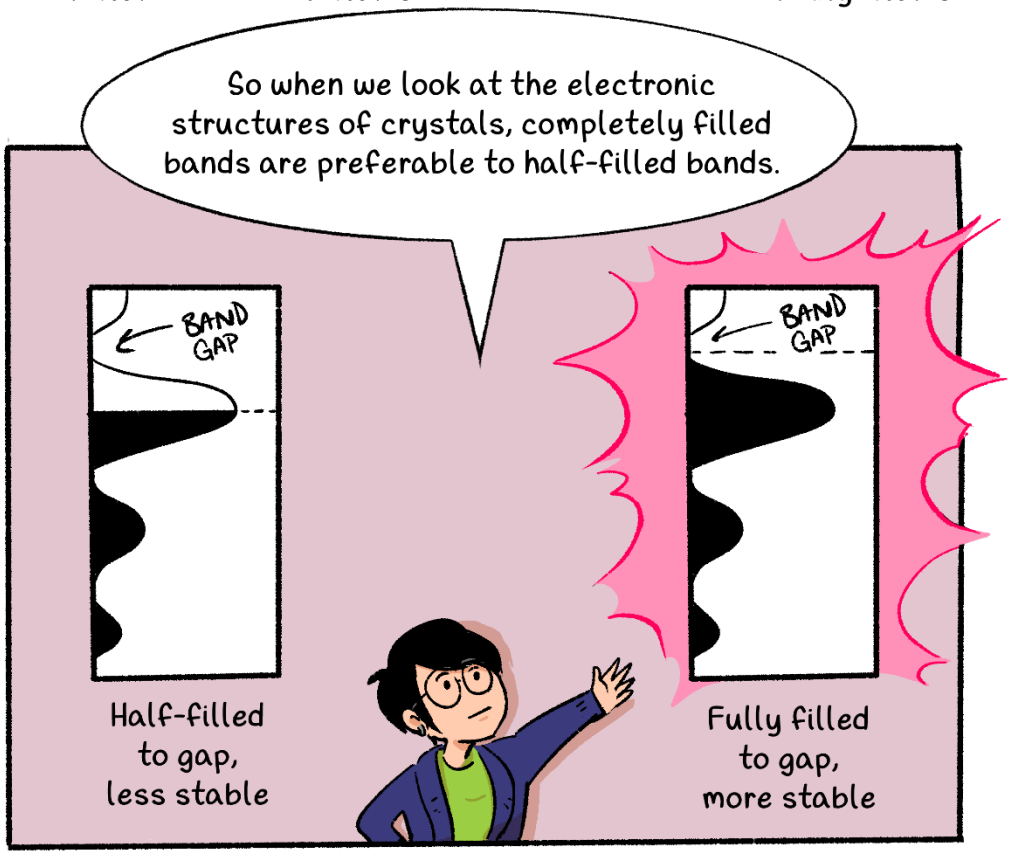
Work in the 20th century by chemistry giants like Lewis, Mulliken, and Pauling helped us understand why atoms bond.

And electronic structures with filled orbitals are preferable to those that are partially filled because they're more stable and less likely to react.



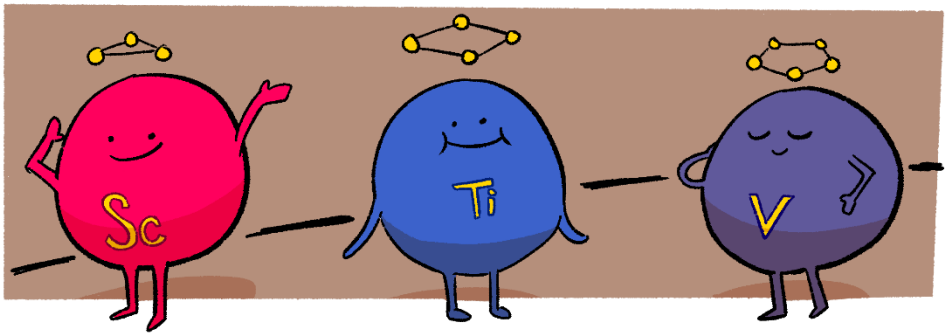
As crystals contain a lot of atoms, their orbitals add up and mix. Because they're not discrete anymore, they become "bands" instead.



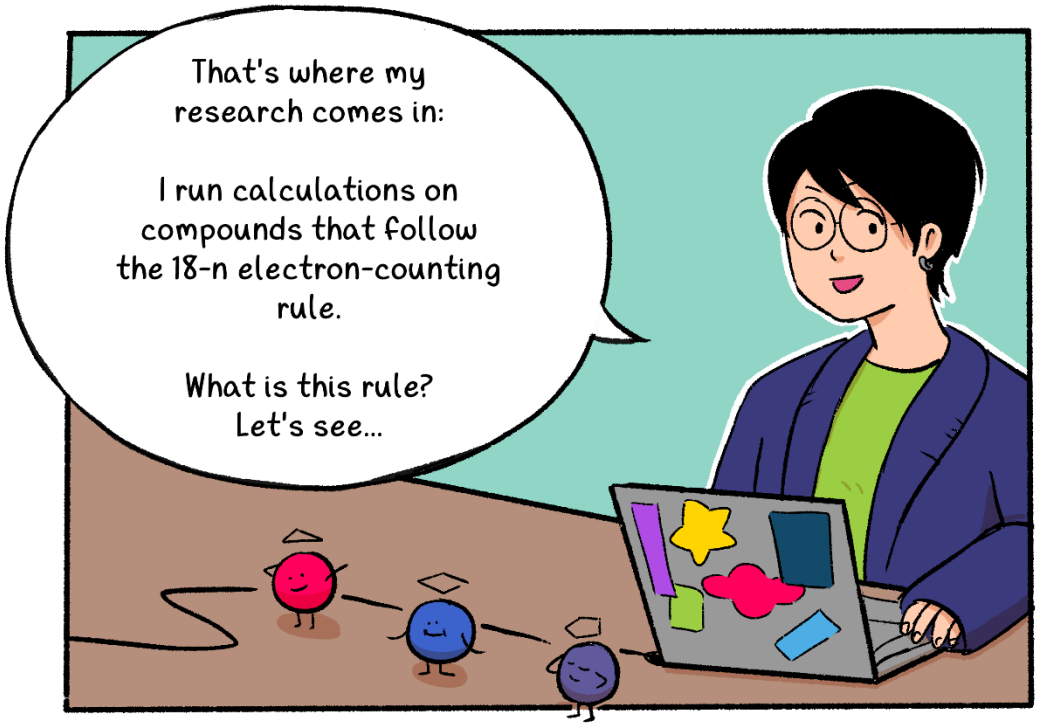


That means in order to fill the bands completely, the crystal prefers a certain number of electrons.

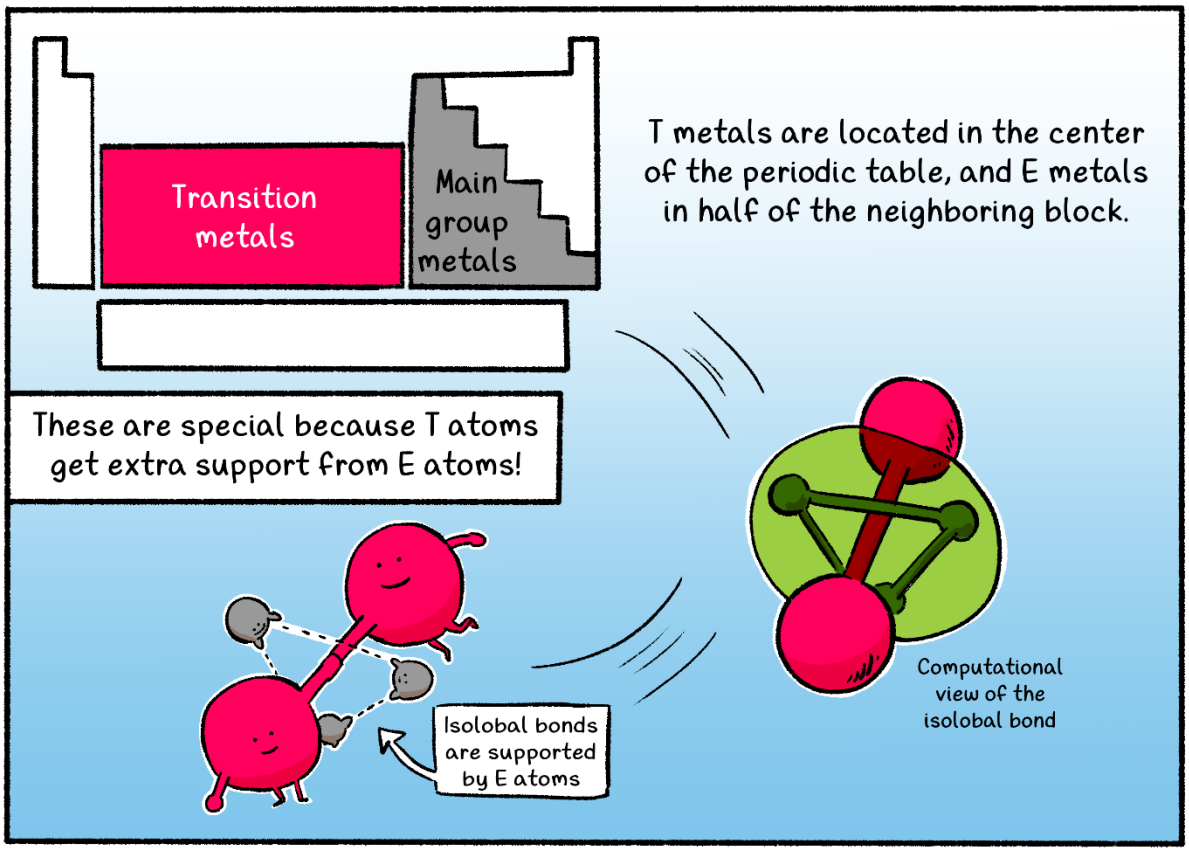
We use electron-counting rules to rationalize and design these crystal structures.



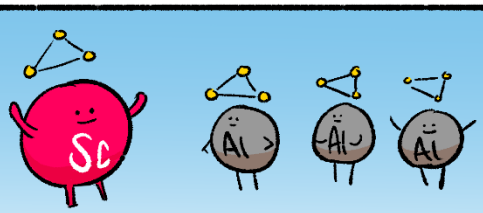
This can help scientists select which element to use based off the number of electrons. However, electron-counting rules don't describe every compound in every context.



The 18-*n* rule applies to crystals made of transition metals (T) and main group metals (E)!



The number of isolobal bonds, *n*, is related to the total number of electrons available for bonding, represented by 18-*n*.

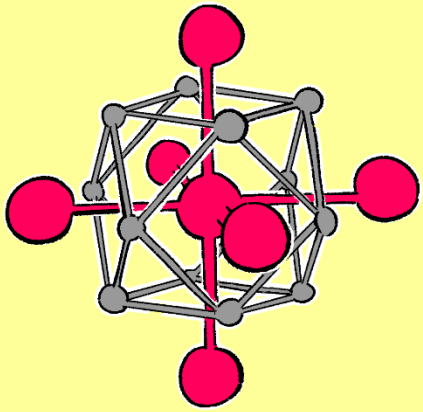


For example, the compound Scandium Trialuminide ($ScAl_3$) has 12 electrons.

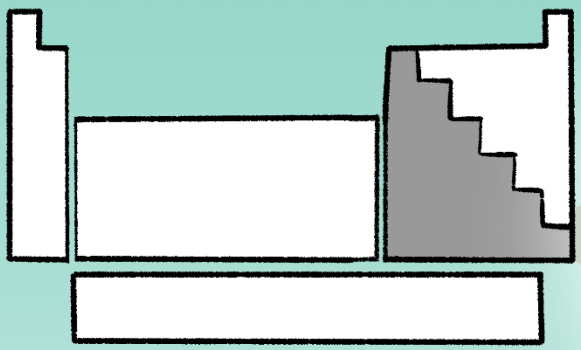
18-*n* = 12

so *n* = 6!

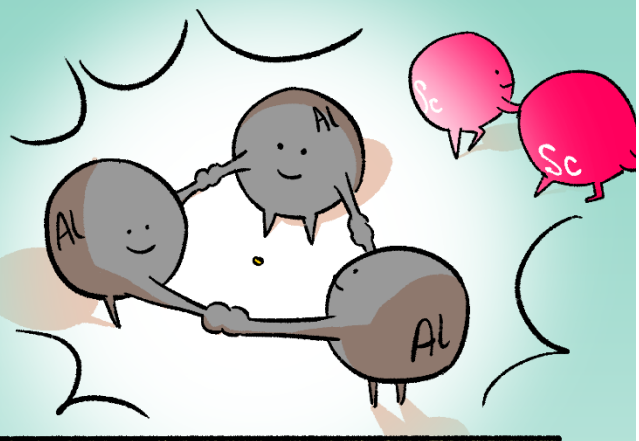
And we do see 6 Sc-Sc bonds in the crystal structure!



However, electrons can also be put in bonds made solely of main group metals.



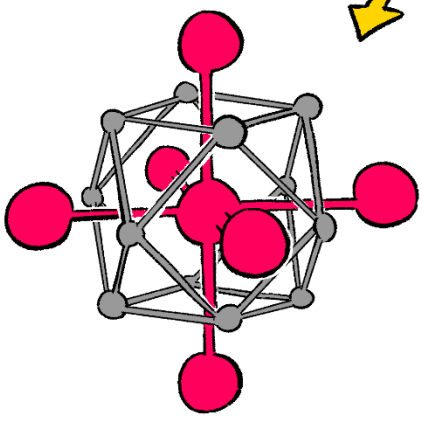
We use the letter m to count these electrons.



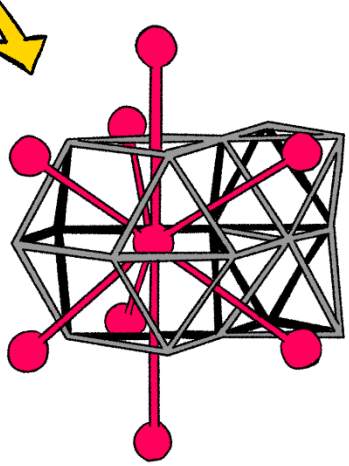
In that case, the number of electrons must equal

$$18-n+m$$

We can divide up the electrons between *n* and m in different ways.

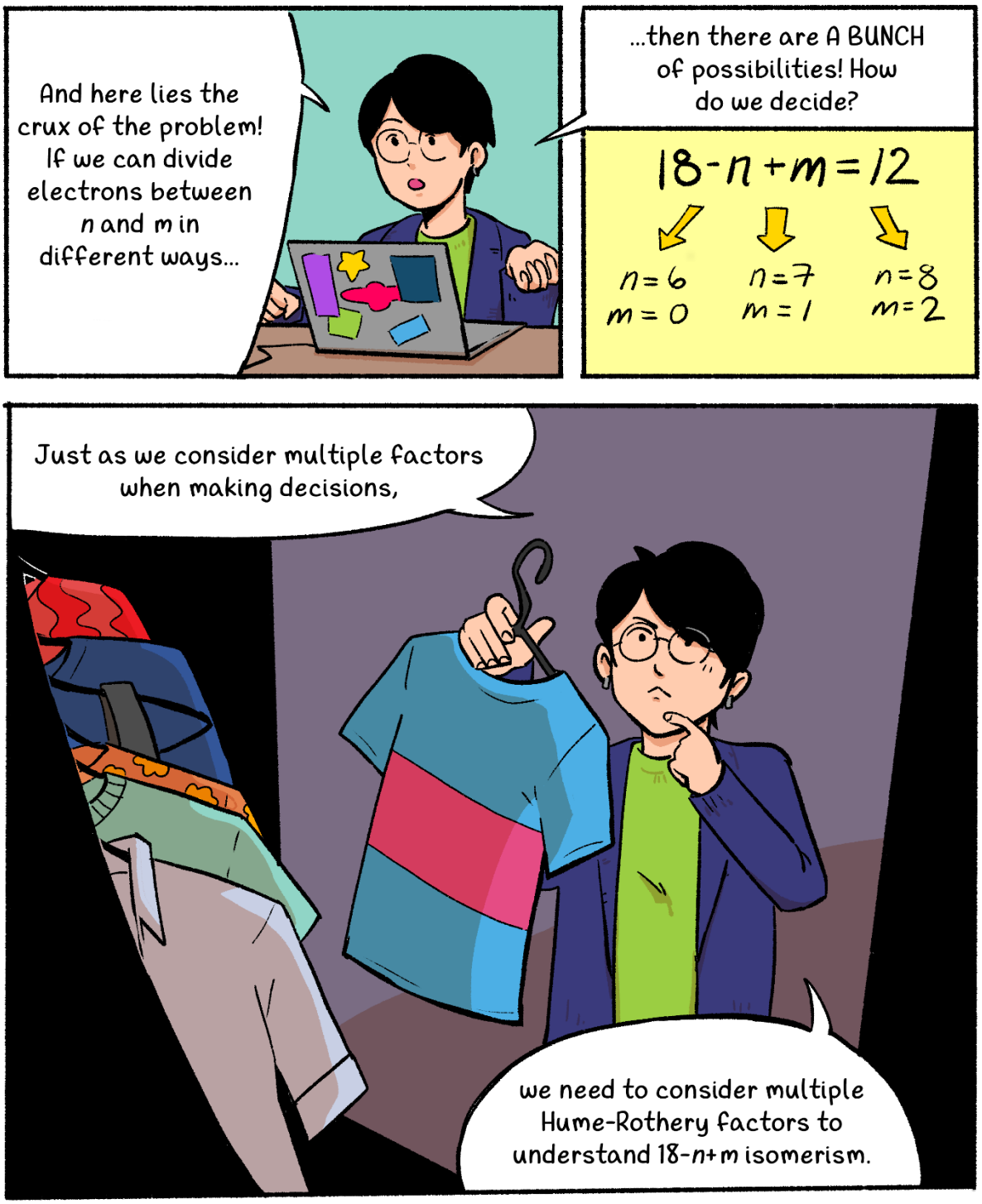


For 12 electrons, we can have 18-6+0, like in $ScAl_3$.



Or we can have 18-7+1, like in YAl_3 (Yttrium trialuminide).

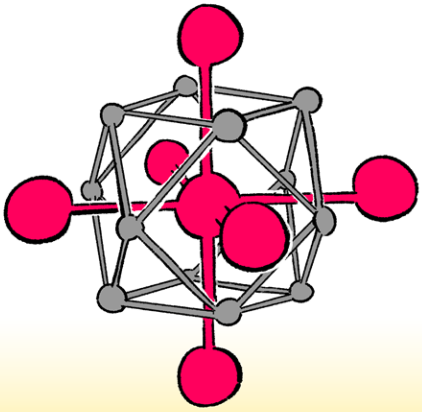
We call these potential structure 18-*n*+m isomers.



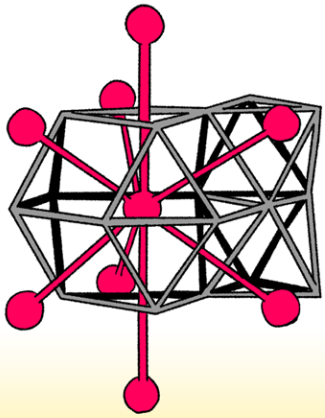
Next, I'll show you how I use computational work to tackle this problem!

Part 3. 18-*n*+*m* isomerism in Scandium & Yttrium Trialuminides $ScAl_3$ and YAl_3

In previous section, we saw how $ScAl_3$ and YAl_3 divide their 12 electrons differently. We call this phenomena "18-*n*+*m* isomerism," since they have the same (iso) number of electrons but different structures.

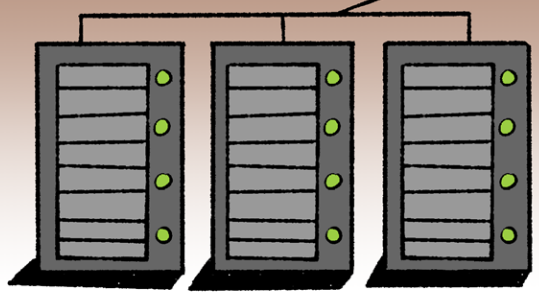


(*n*,*m*) = (6,0)

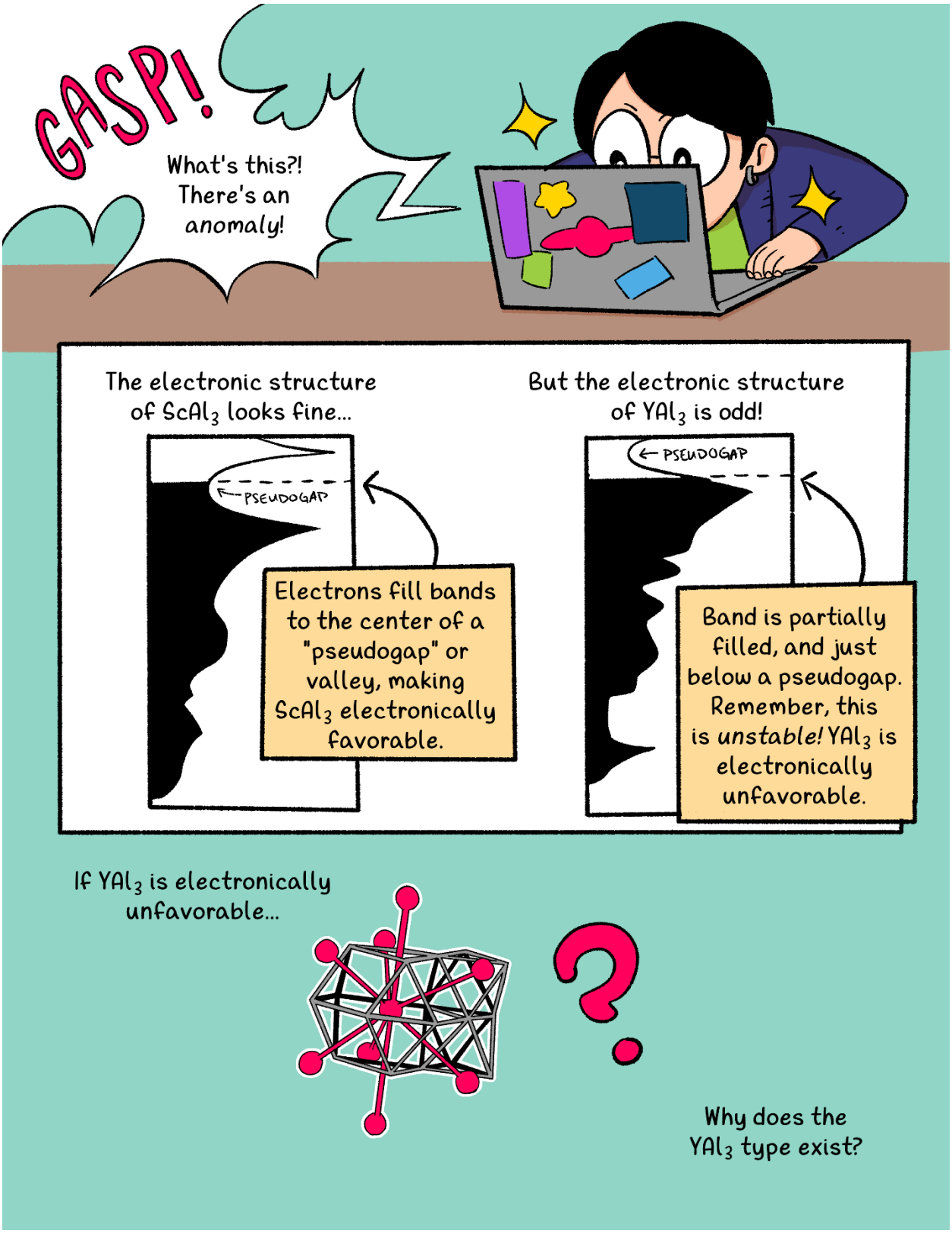


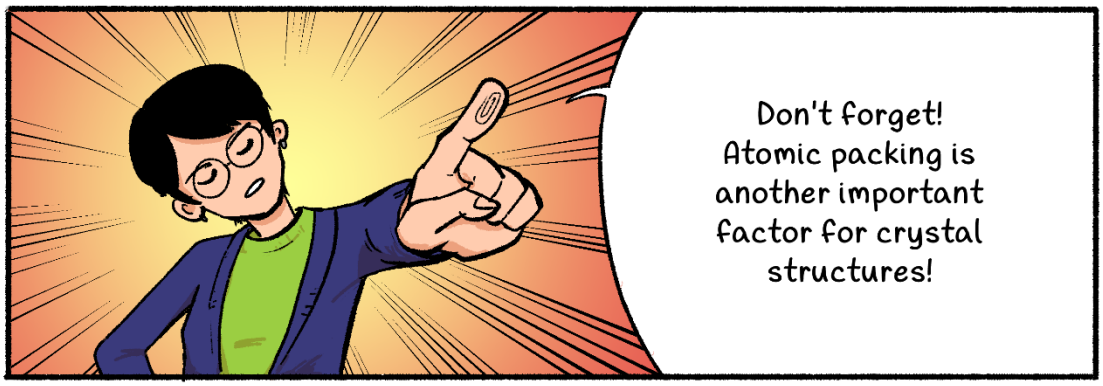
(*n*,*m*) = (7,1)

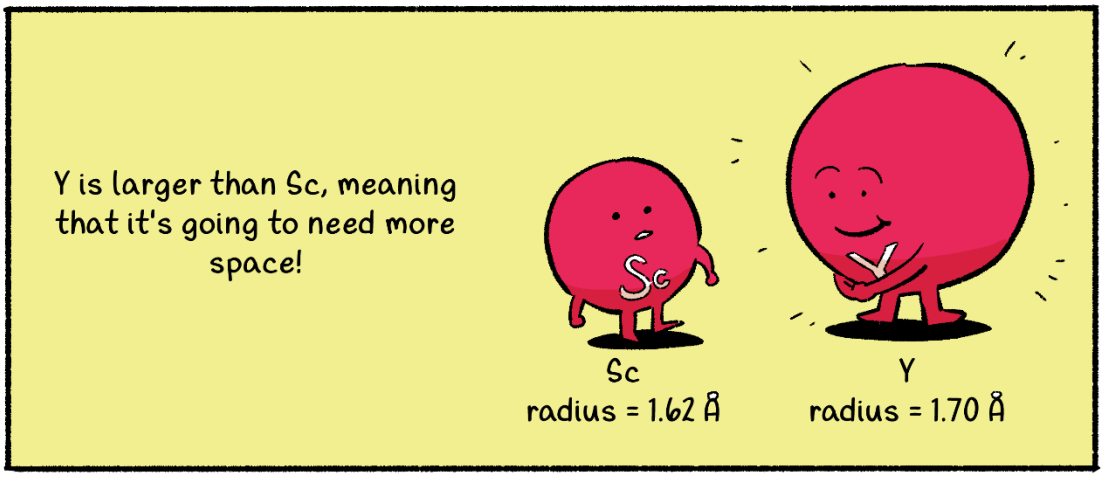
Their 18-*n*+*m* electronic schemes make sense, but let's run some calculations to ground it in data.

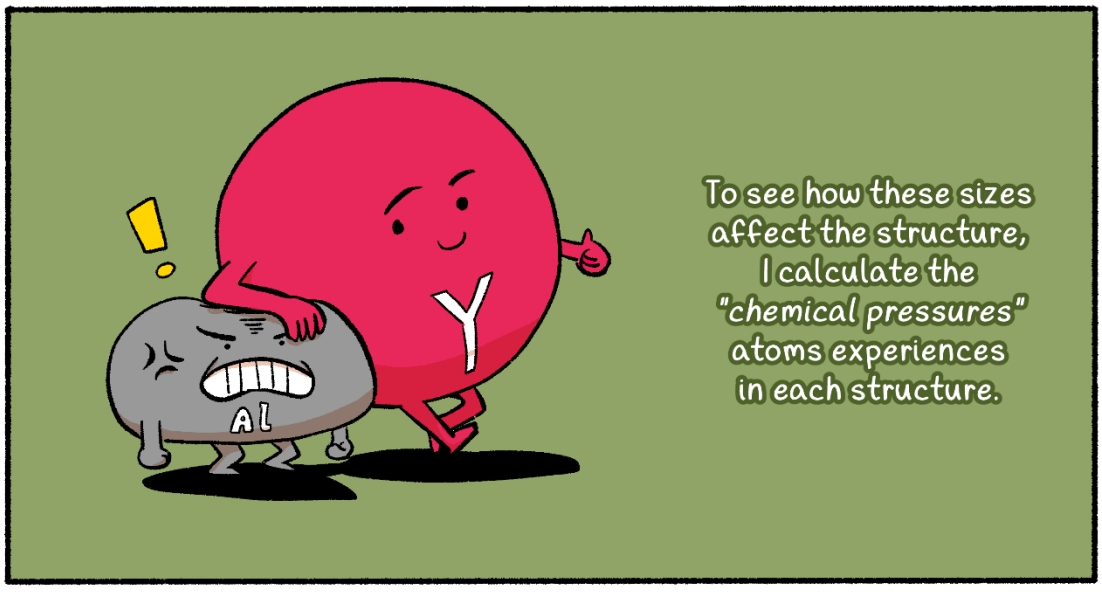


I connect to a powerful computing system to calculate the electronic structure of our crystals with a modelling method called Density Functional Theory.


GASP!
What's this?! There's an anomaly!
The electronic structure of $ScAl_3$ looks fine...
PSEUDOGAP
Electrons fill bands to the center of a "pseudogap" or valley, making $ScAl_3$ electronically favorable.
But the electronic structure of YAl_3 is odd!
PSEUDOGAP
Band is partially filled, and just below a pseudogap. Remember, this is *unstable!* YAl_3 is electronically unfavorable.
If YAl_3 is electronically unfavorable...
?
Why does the YAl_3 type exist?


Don't forget!
Atomic packing is another important factor for crystal structures!


Y is larger than Sc, meaning that it's going to need more space!
Sc
Y
Sc
radius = 1.62 Å
Y
radius = 1.70 Å

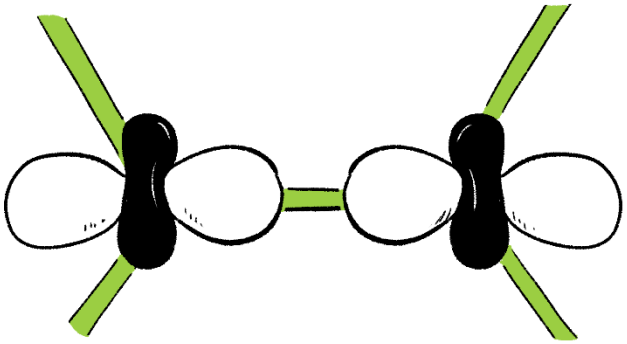

Y
Al
To see how these sizes affect the structure, I calculate the "chemical pressures" atoms experiences in each structure.

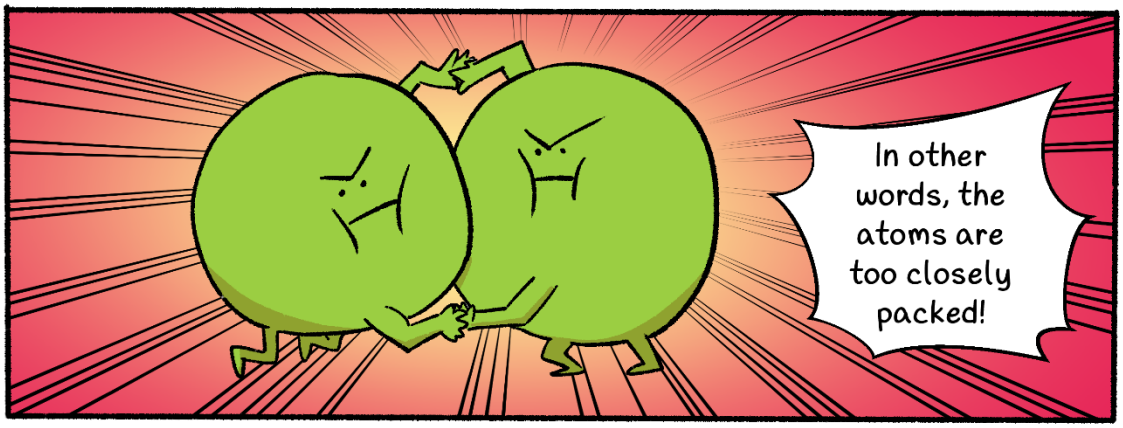
Chemical pressure is defined as the change in energy over change in volume.

$$CP = \frac{\Delta E}{\Delta V}$$

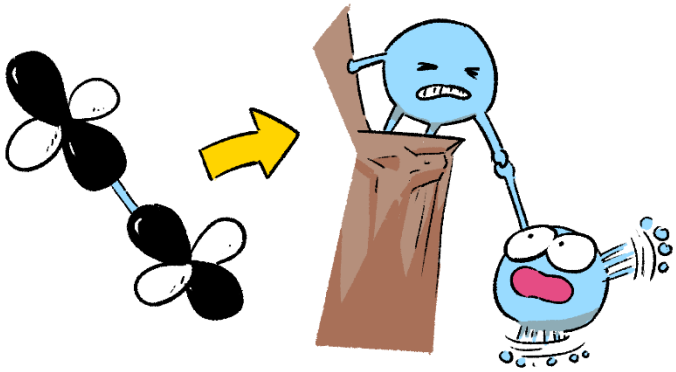
These chemical pressures between atoms are visualized with black and white lobes.

White lobes between atoms represent positive pressure, where energy increases if the atoms get closer.





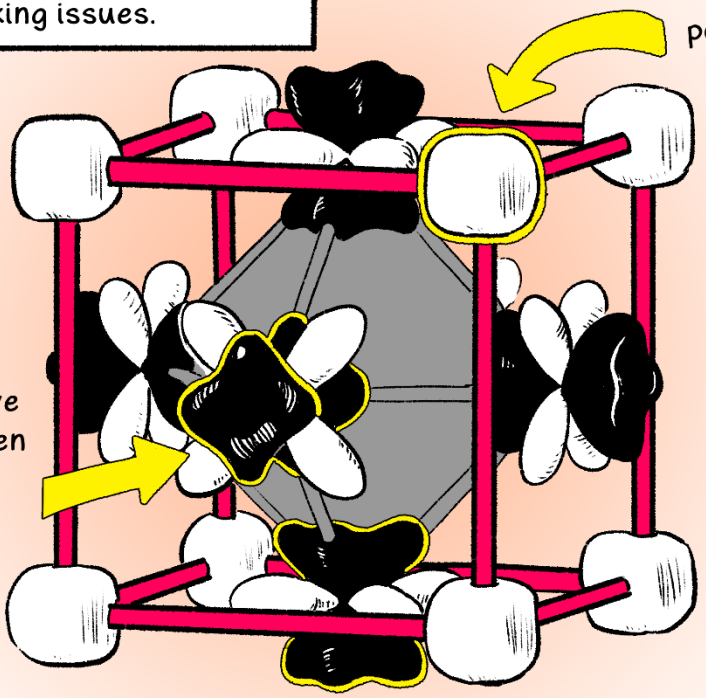
Black lobes between atoms represent negative pressure, and atoms are too far apart!



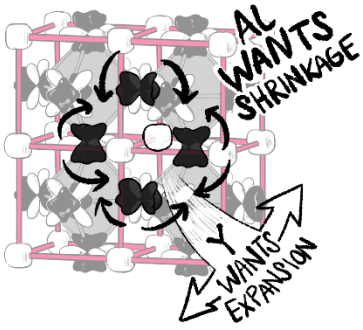
Let's apply this to YAl_3!
YAl_3 doesn't form in the crystal structure as $ScAl_3$.
Why?

If we calculate the chemical pressure scheme of YAl_3 in the same type of crystal structure as $ScAl_3$, we can see some packing issues.

Spherical positive pressures on Y tell me it's being squeezed on all sides.



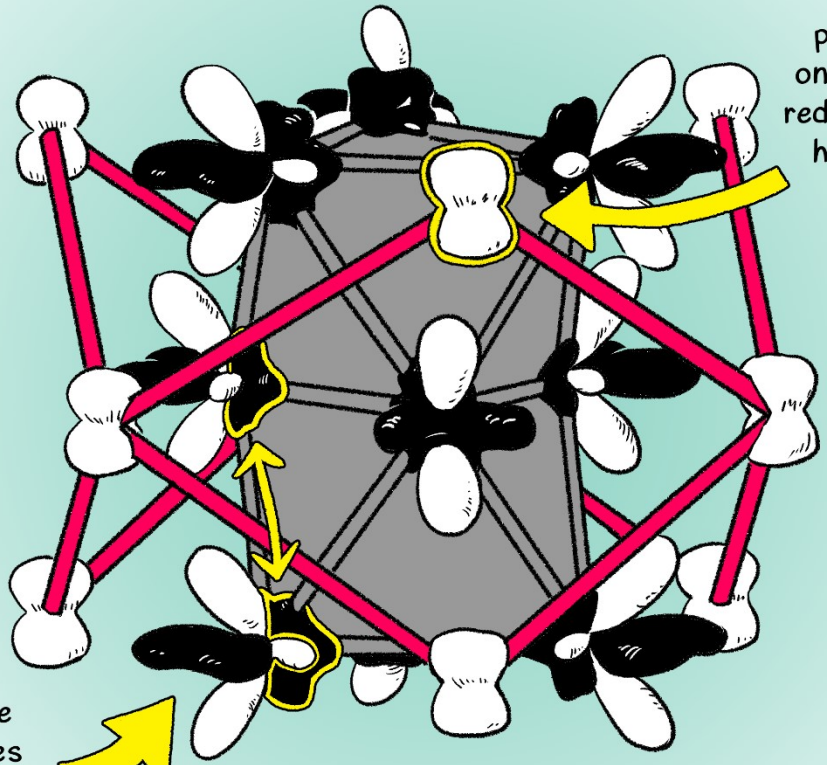
However, negative pressures between Al atoms mean they're too far apart.



The Y atom would like to expand its environment...
But the repeating unit shows us that the Y atoms are embedded in the Al-Al network.

It'll have to stretch the Al-Al network that's already overstretched!
This is a pretty tense packing situation.

What about the crystal structure that YAl_3 actually forms?

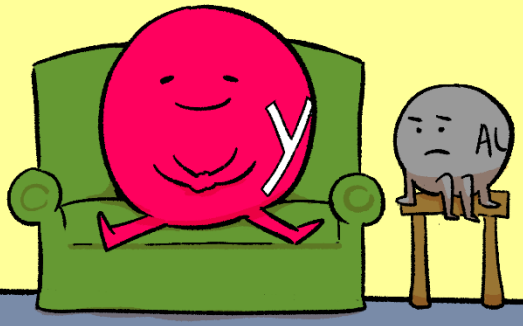


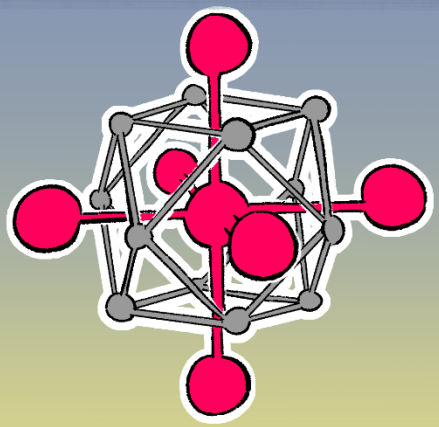
Positive pressures on Y are now reduced in the horizontal layer

Negative pressures between Al atoms in columns are smaller

In this type, we are able to simultaneously expand the coordination environment of the Y atom and shorten some of the Al-Al contacts!

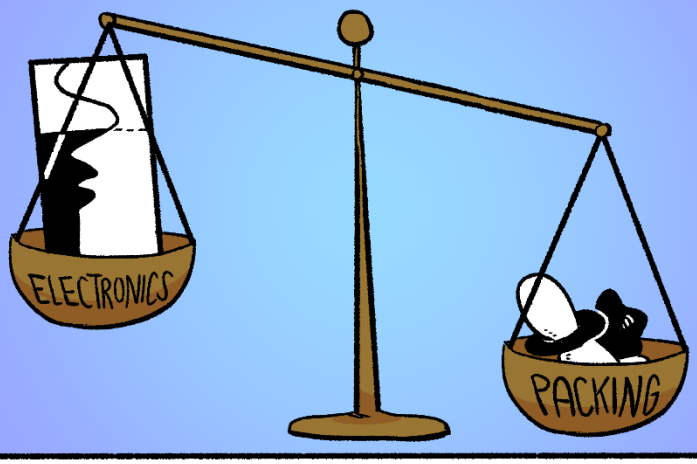
In YAl_3, packing tensions are the most important, so it opts for more room for the Y atom, even if it means having an unfavorable electronic structure.



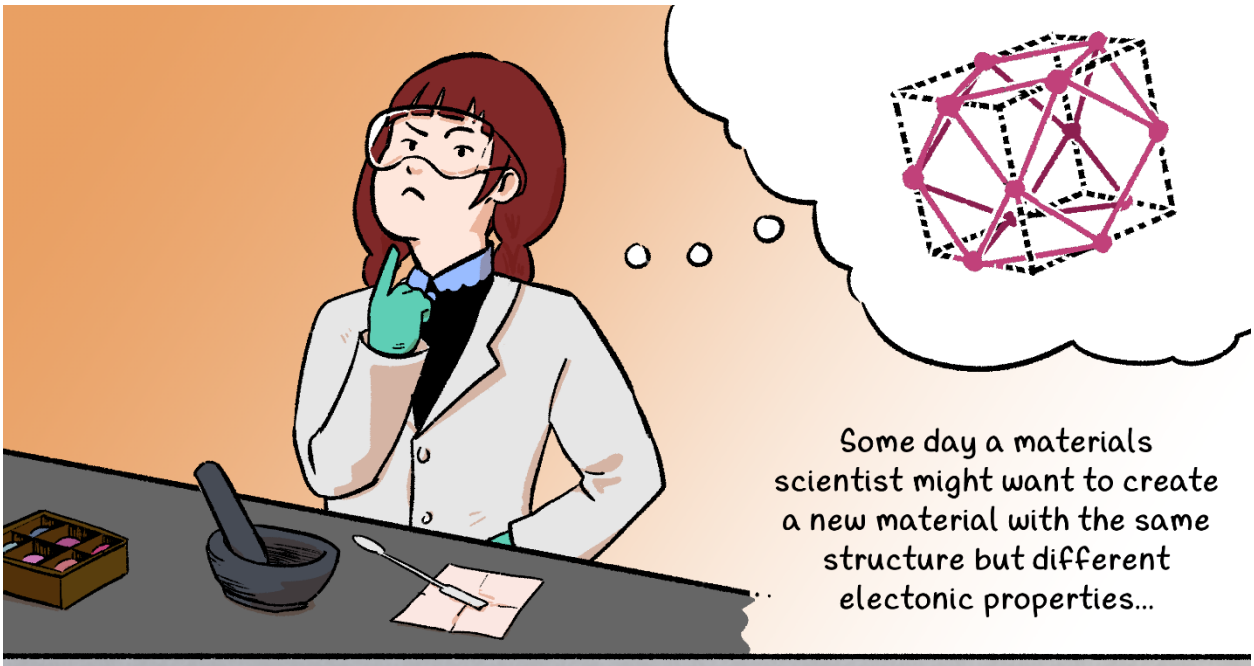


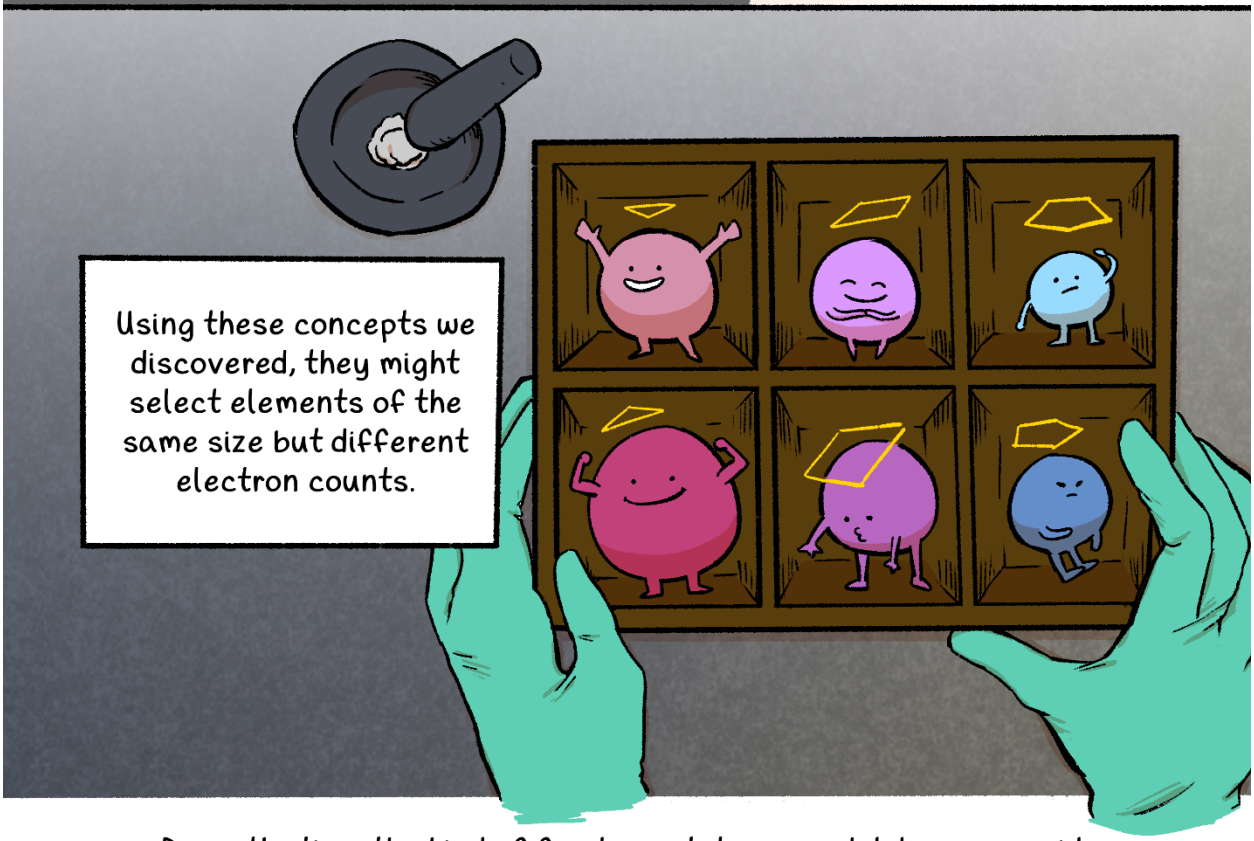
In $ScAl_3$, since Sc is smaller, packing tensions aren't as bad, so the structure type with 6 isolobal bonds is preferred.

We can see how electronic and atomic packing factors compete, creating this situation of 18-*n*+*m* isomerism.



The computational tools I used helped us unravel this mystery, and can help us understand why other crystal structures form.

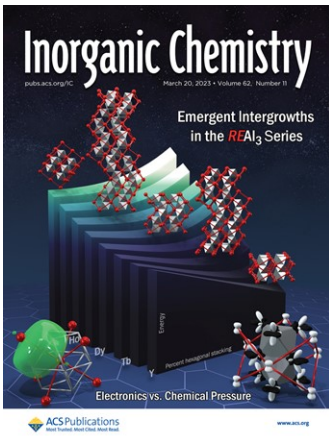




Down the line, the kind of fundamental research I do can provide guidelines in discovering the next greatest material!

Afterword and acknowledgements

This work is based off my first paper in *Inorganic Chemistry*, "Emergent Transitions: Discord between Electronic and Chemical Pressure Effects in the $RE Al_3$ (RE = Sc, Y, Lanthanides) Series." Dr. Katie Hilleke performed the initial calculations on this system, and my PI, Prof. Danny Fredrickson, guided the overall project. There's a lot of cool things about this system that I had to omit from this comic, so go read it! My research was funded by the National Science Foundation through Grant DMR-2127349. Thank you!



I designed the cover for the issue of *Inorganic Chemistry* it was published in!

Amber Lim, Katerina P. Hilleke, and Daniel C. Fredrickson. *Inorg. Chem.* **2023**, *62*, 4405-4416.
DOI: https://doi.org/10.1021/acs.inorgchem.2c03393

The complex Ce_5Co_{19} type figure in Part 1 is based off this work:

Kyana M. Sanders, Jonathan S. Van Buskirk, Katerina P. Hilleke, and Daniel C. Fredrickson. *J. Chem. Theory Comput.* **2023**, 19, 4273-4285
DOI: https://doi.org/10.1021/acs.jctc.3c00368

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https://www.scifun.org/Thesis_Awards/thesis_awards.html

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And thank you to my family for always being there.

Amber Lim

April 2024