# Ionic Moduli

## A New Semi-Empirical Model for the Elasticity of Crystalline Ionic Compounds

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*Southern Illinois University*

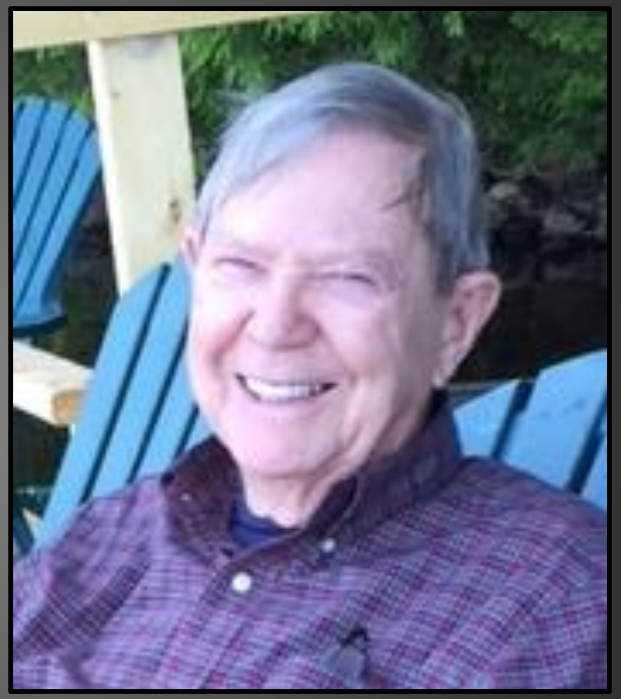


**GSA 2024: MSA Roebling Medal Session for Dr. Nancy Ross**

# Dedicated to

**Nancy Ross**

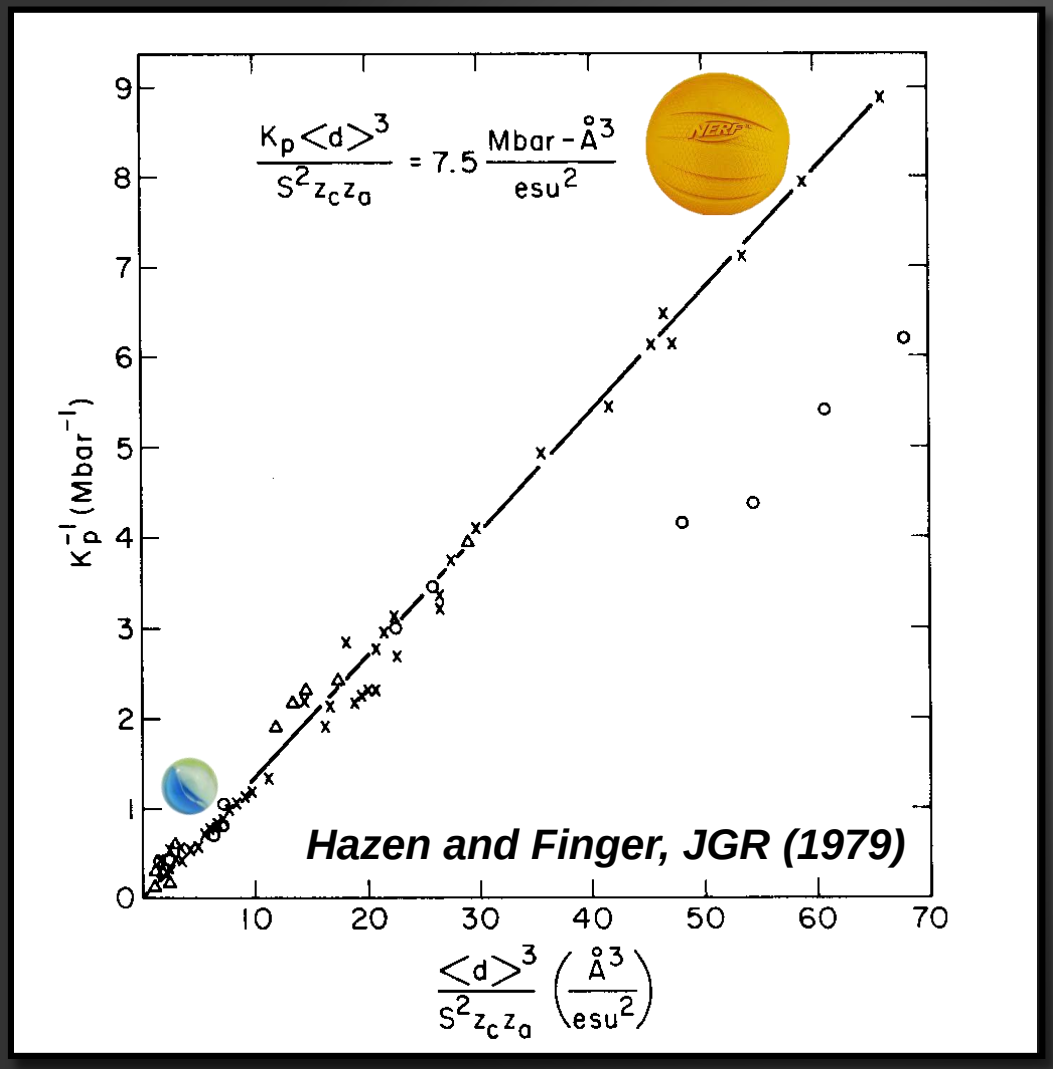
***2024 Roebling Medal Recipient***

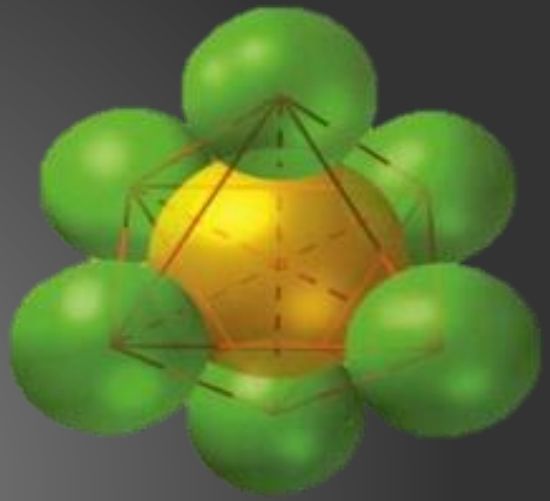


**G.V. “Jerry” Gibbs**

***(6/28/1928 - 9/19/2024)***

# Previous Work: Polyhedral Moduli

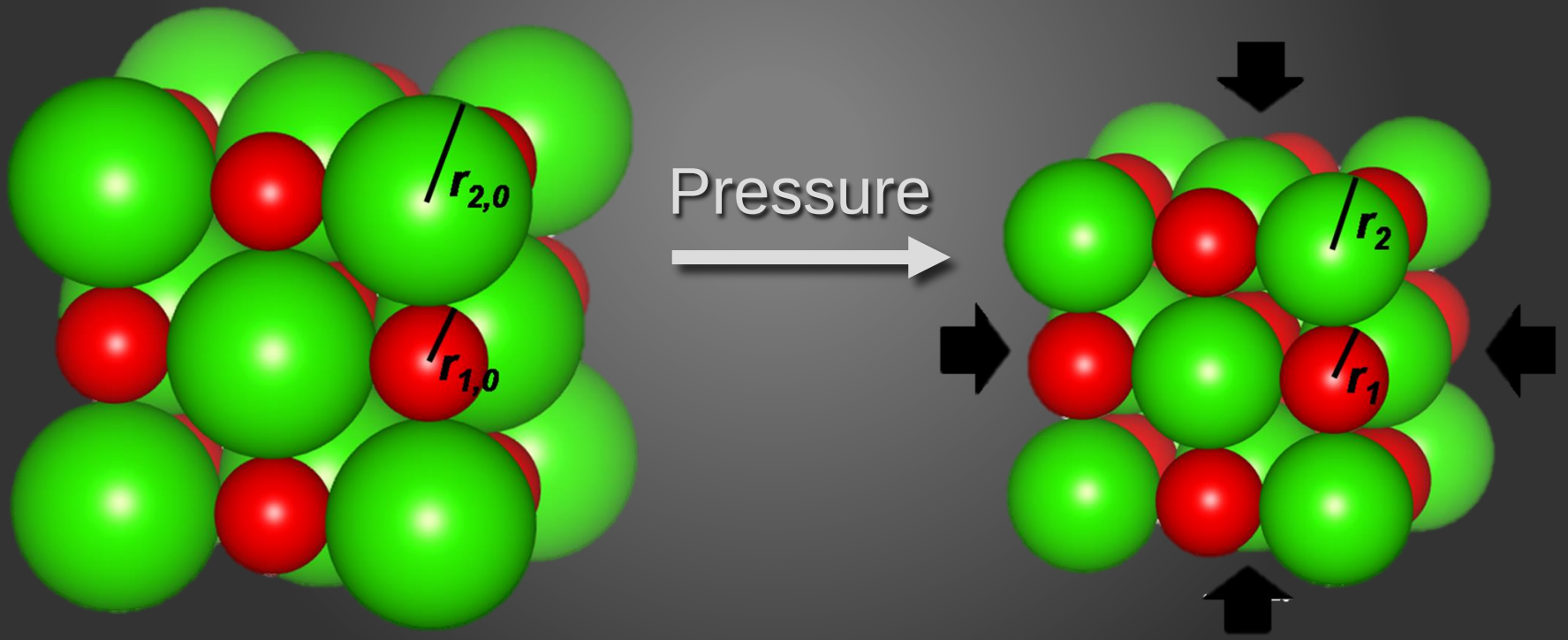


**Compressibility of a polyhedral unit is a linear function of its volume…..**

**(*i.e., fatter atoms are squishier*)**

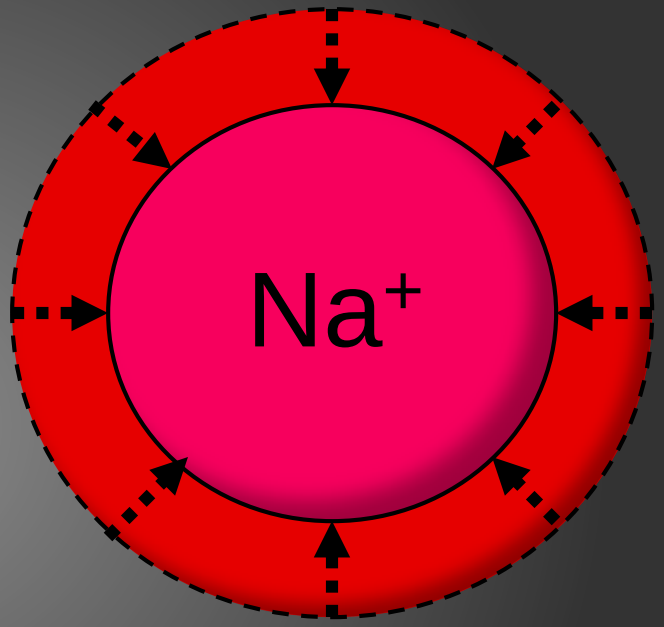
***Can the bulk modulus of an entire material be described in terms of the compression of individual ions?***



# Model Assumptions

1) Each ion is modeled as a compressible sphere.

2) Each ion compresses independently of surrounding ions.

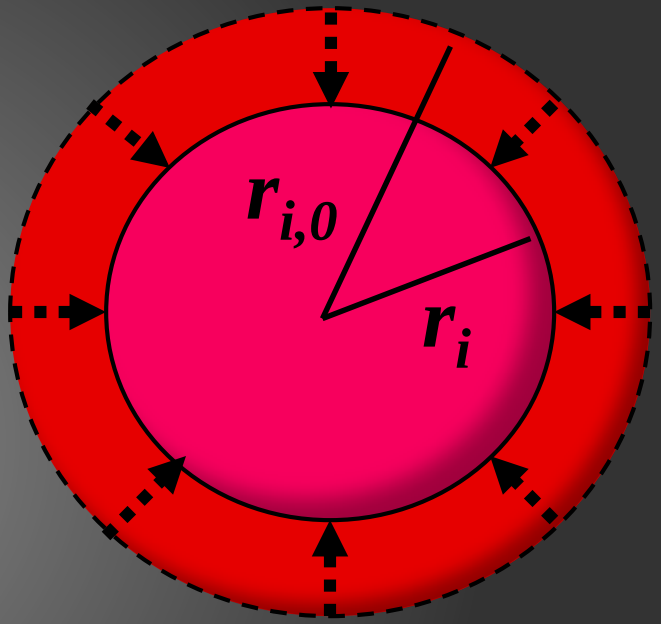



3) Each ion compresses in a reproducible way from one compound to another (i.e., each ion has a unique and reproducible modulus, the **"ionic modulus"**, that is independent of crystal structure).

# Model Formulation

**Ionic Modulus:**

$$K_i = - V_i \frac{\partial P}{\partial V_i}$$




**1st order equation of state for an ion:**

$$V_i = V_0 \, e^{-P / K_i}$$

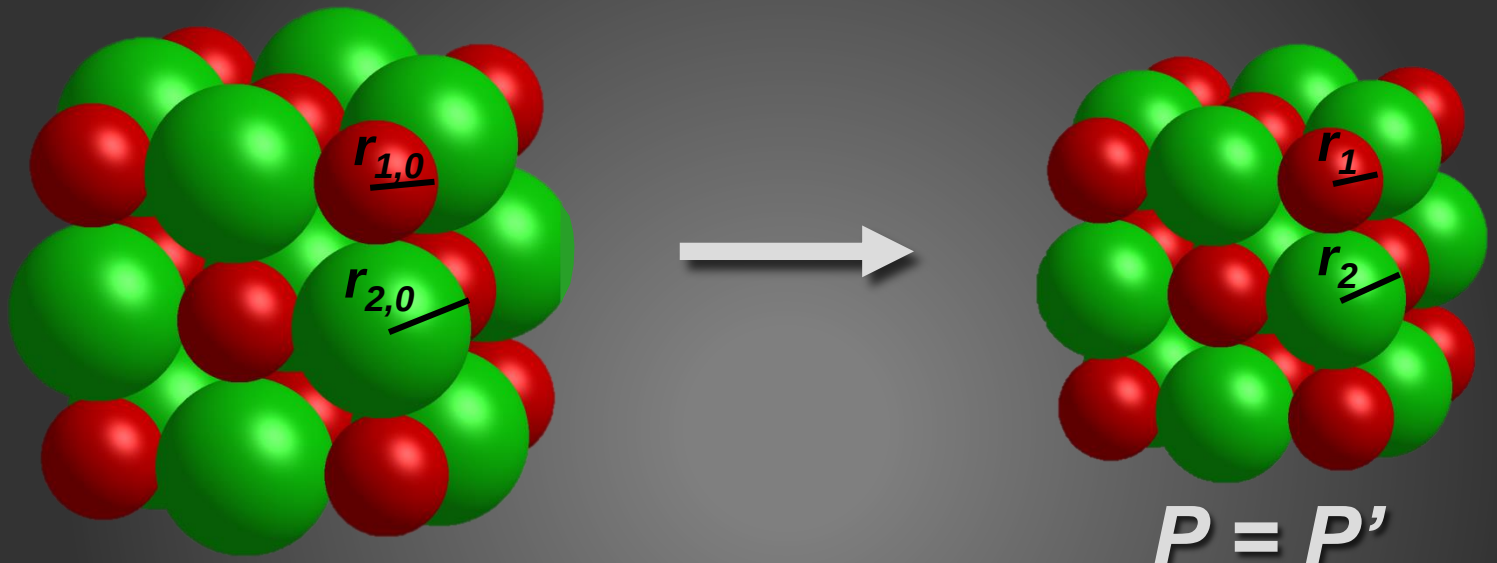
**3 dimensions**

→

$$r_i = r_{i,0} \, e^{-P / 3K_i}$$

**1 dimension**

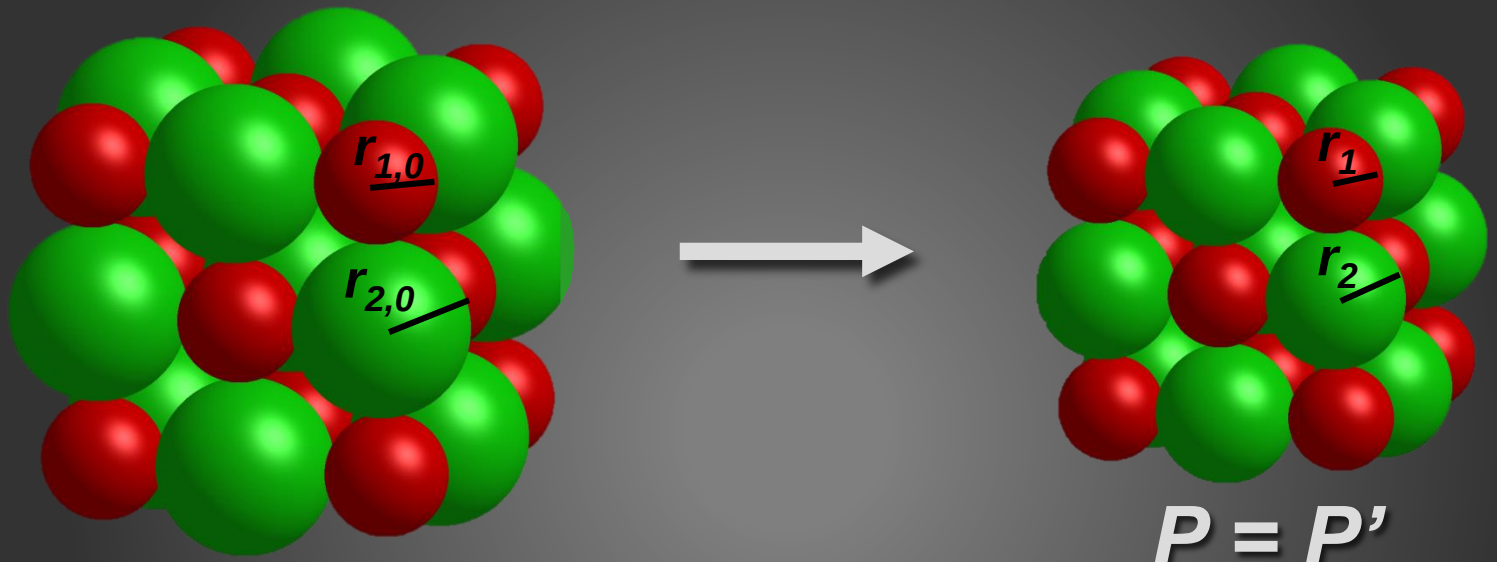
# Model Formulation




For B1 and B2 structures:

$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

# Model Formulation




$P = 0$

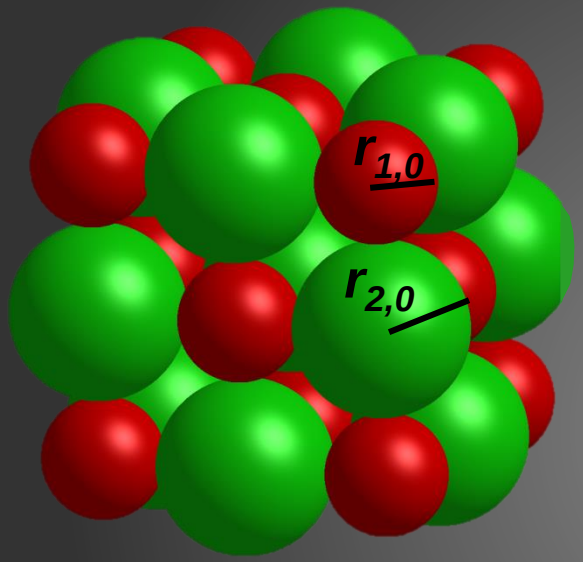
$P = P'$

For B1 and B2 structures:

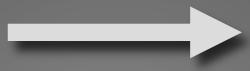
Observable to fit

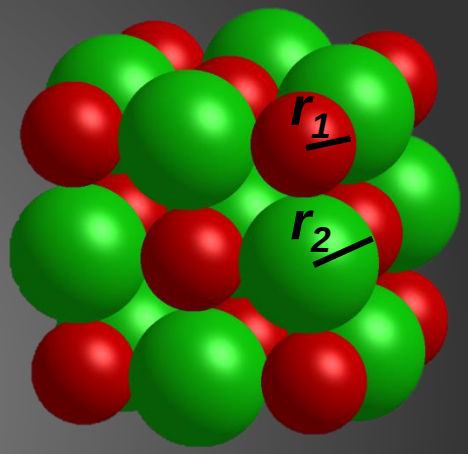
$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

# Model Formulation




$P = 0$






$P = P'$

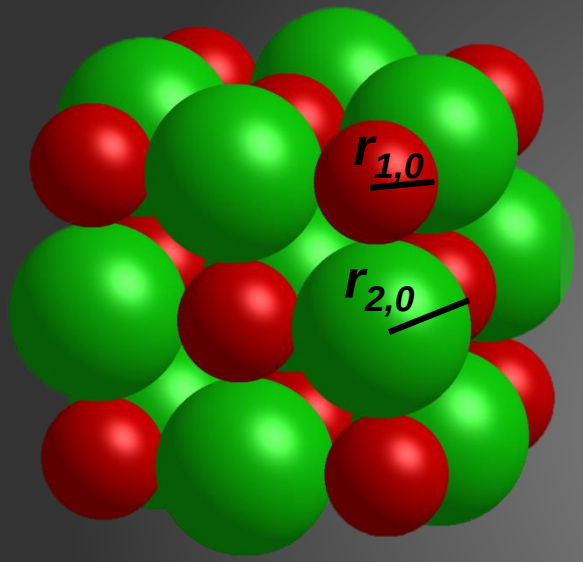
For B1 and B2 structures:

Observable to fit

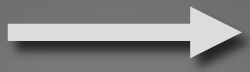
$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

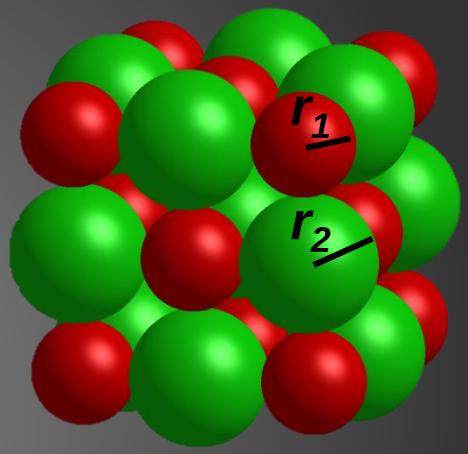
Room pressure radii (Shannon, Prewitt)

# Model Formulation




$P = 0$






$P = P'$

For B1 and B2 structures:

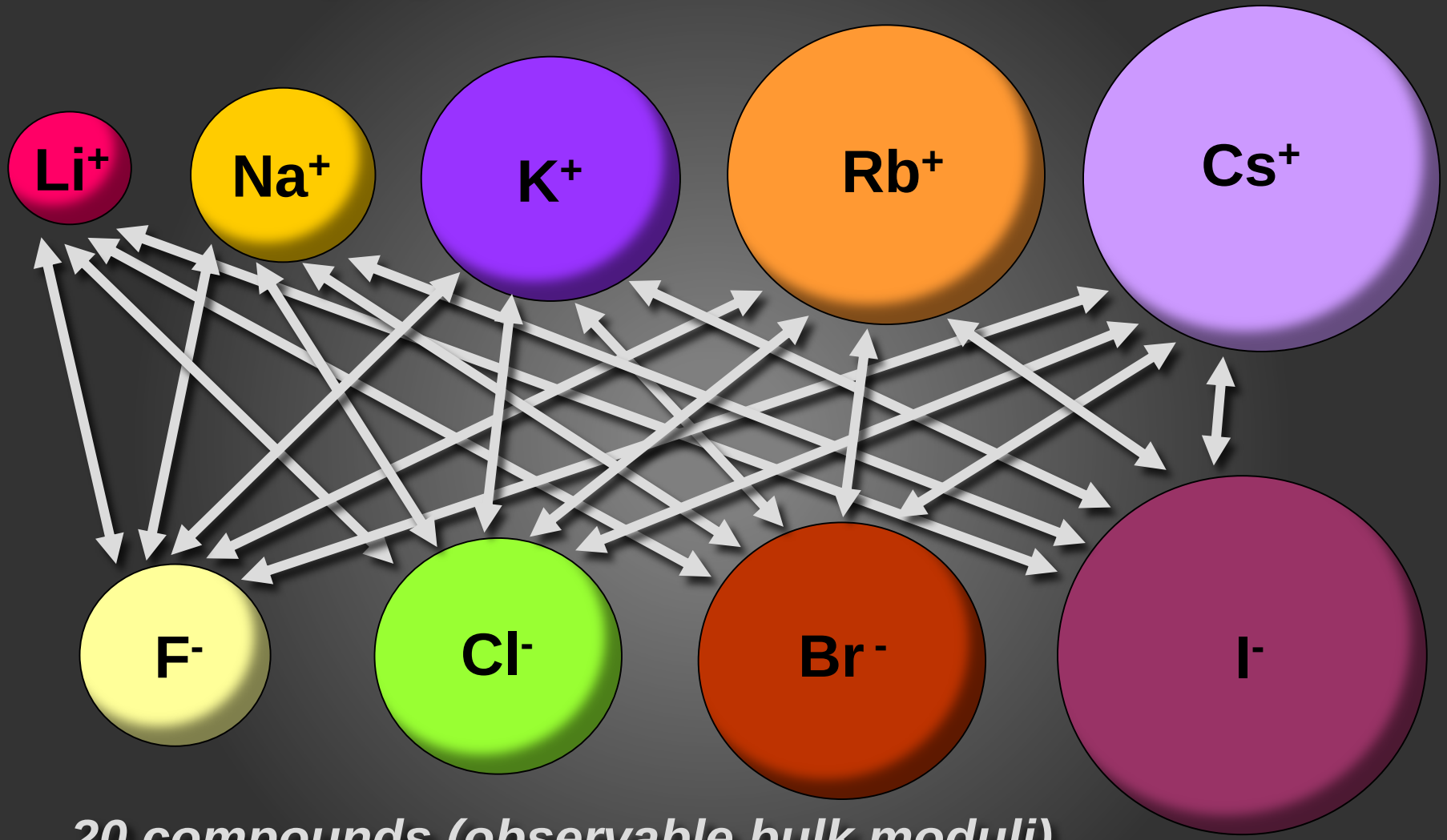
Observable to fit

$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

Room pressure radii (Shannon, Prewitt)

Ionic moduli

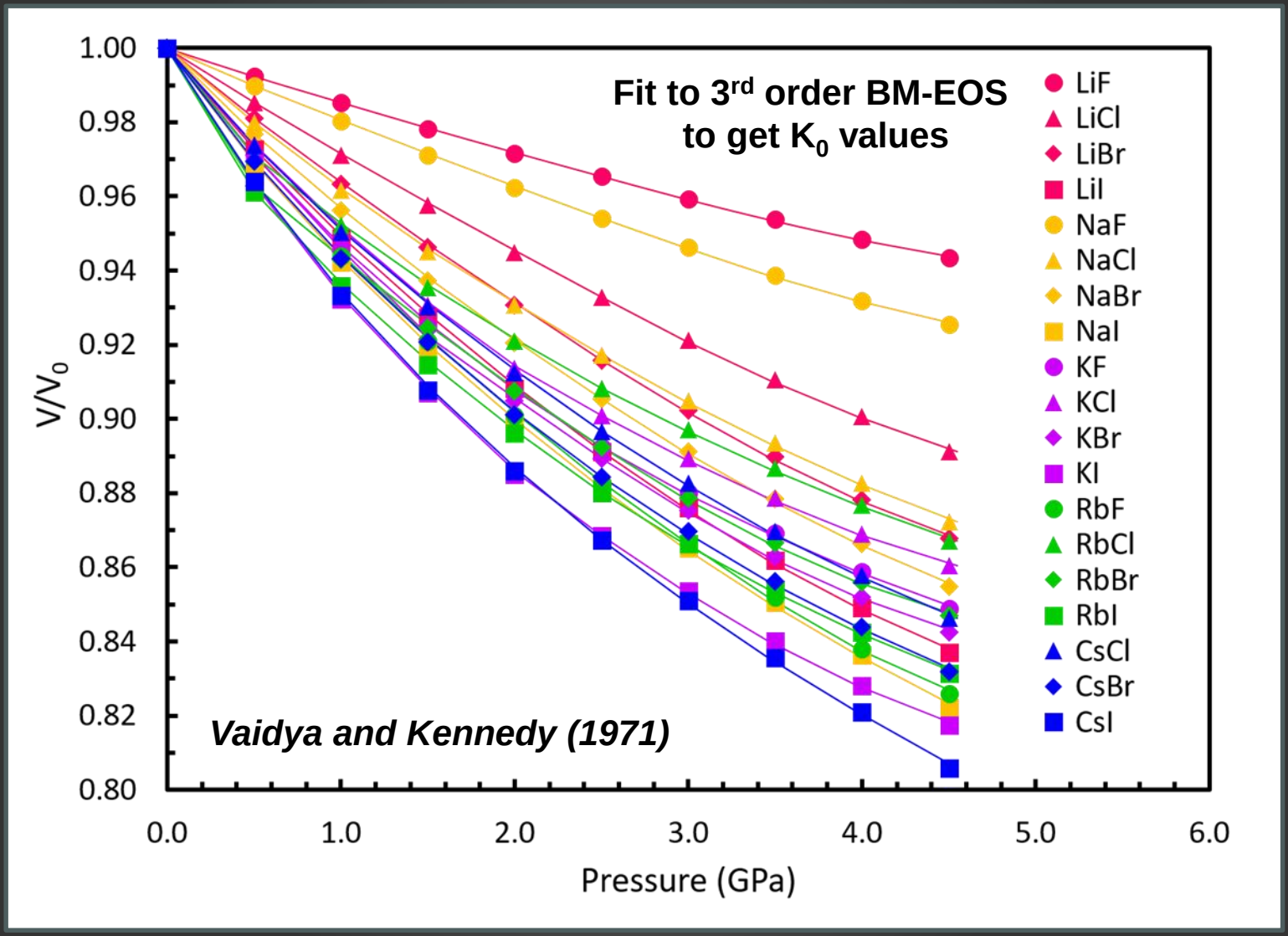
# 9 ions…. (adjustable ionic moduli)



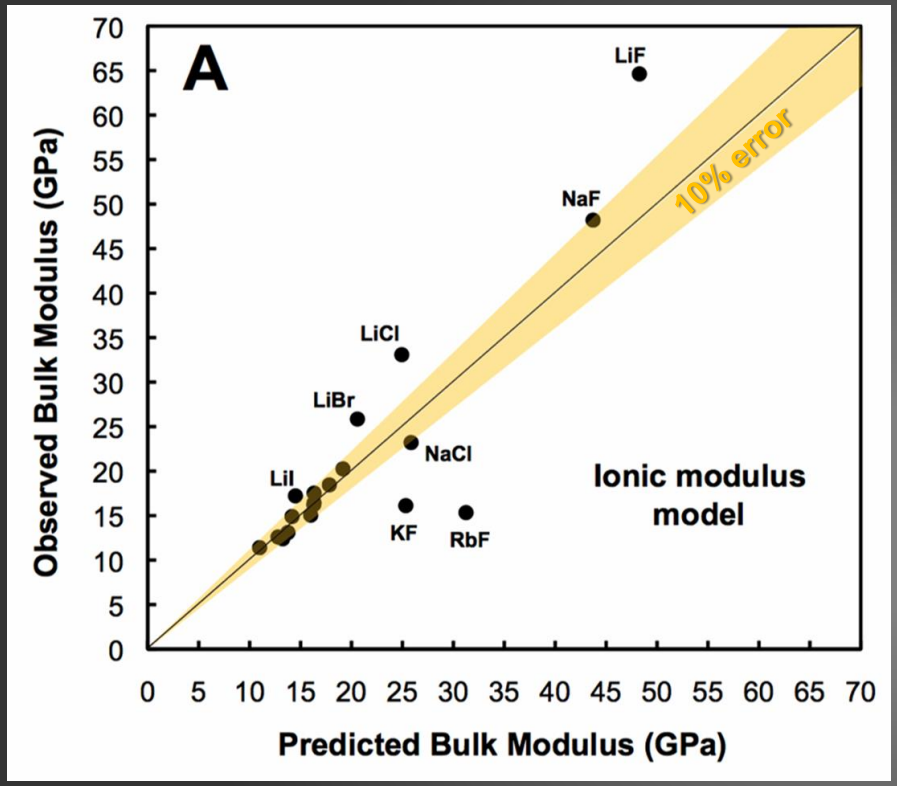

*… 20 compounds (observable bulk moduli)*

**Leave-one-out cross-validation:** Refine ALL ionic moduli to match 19 bulk moduli, then use refined ionic moduli to predict the 20$^{th}$ bulk modulus

# Test with Alkali Halides



# Results with Alkali Halides




## *Ionic Modulus Model*

$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

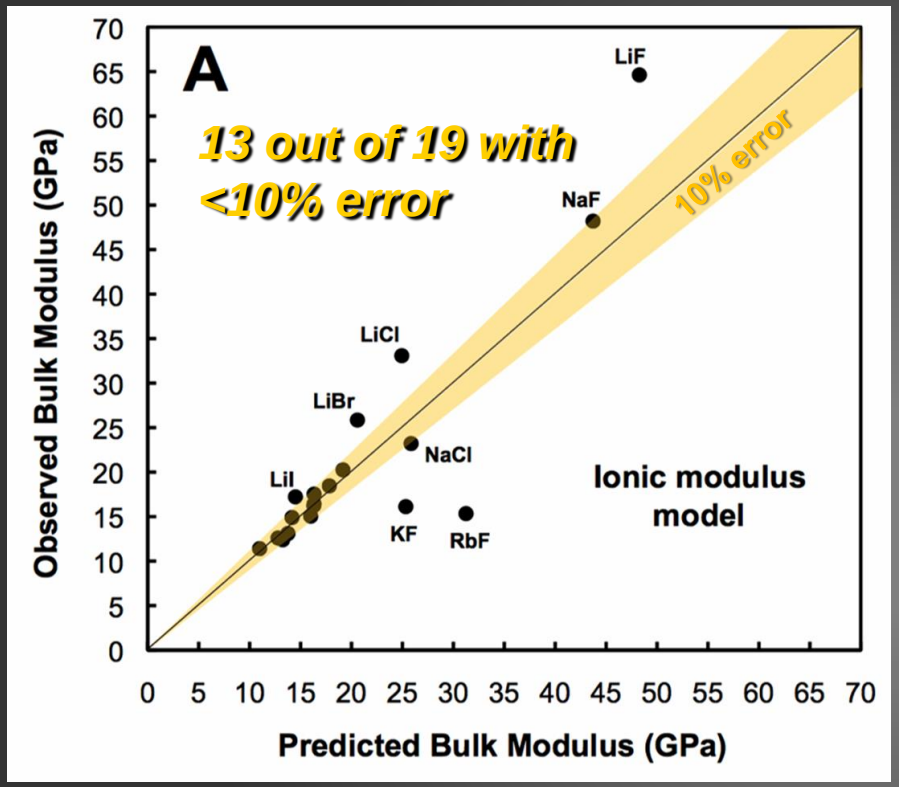
***What if the agreement is just a result of having enough model parameters, and not the validity of the model???***

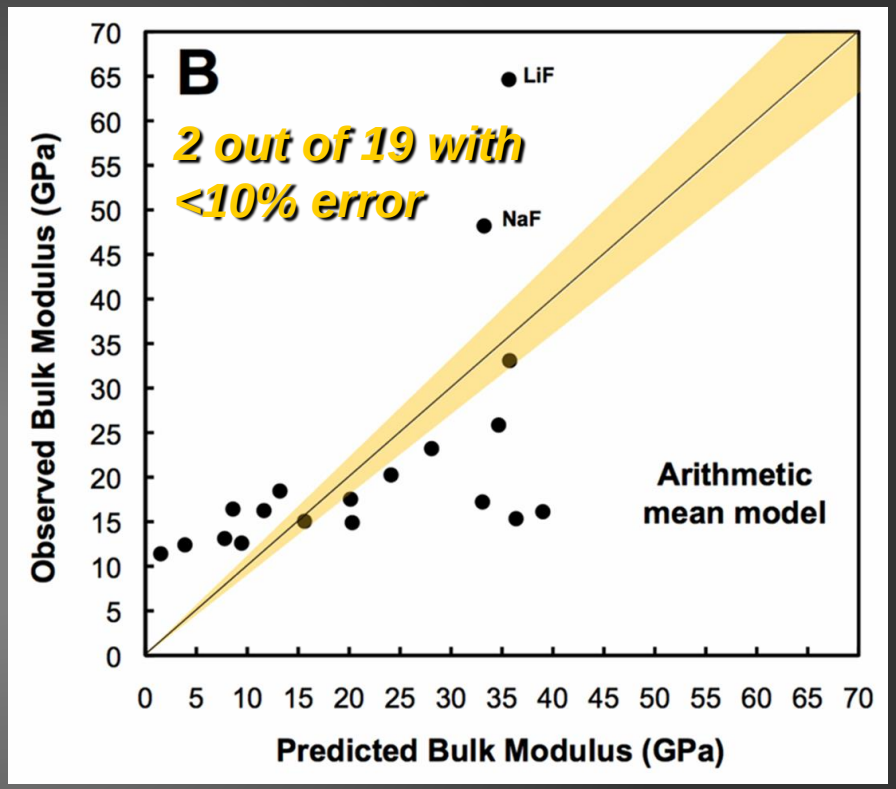
- **Predict bulk moduli of the *same* compounds with a *bogus* model….**

**…. but do the regressions in the same way**

$$K_0 = \frac{K_1 + K_2}{2}$$

# Results with Alkali Halides



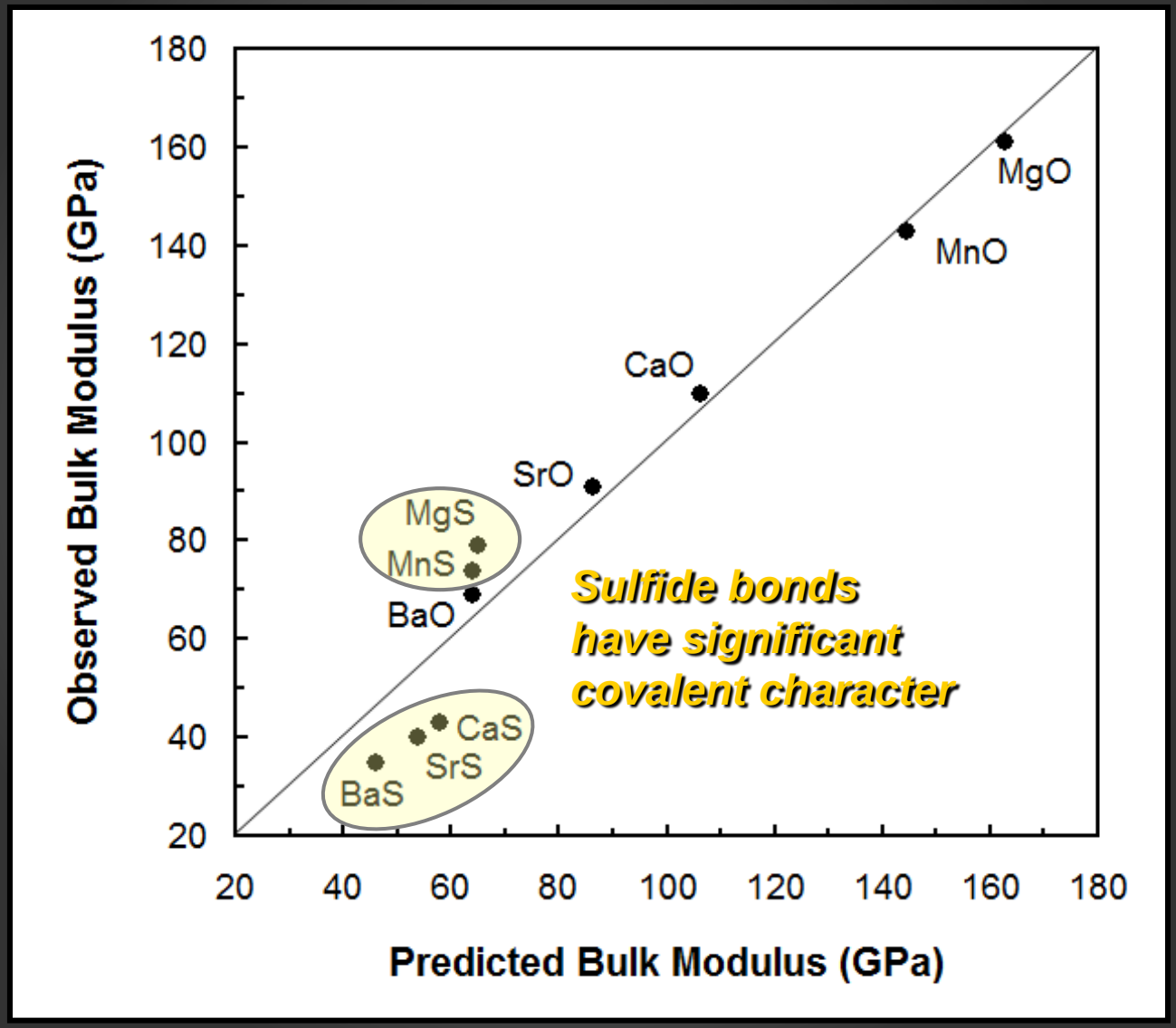

## *Ionic Modulus Model*

$$K_0 = \frac{r_{1,0} + r_{2,0}}{\frac{1}{K_1} r_{1,0} + \frac{1}{K_2} r_{2,0}}$$

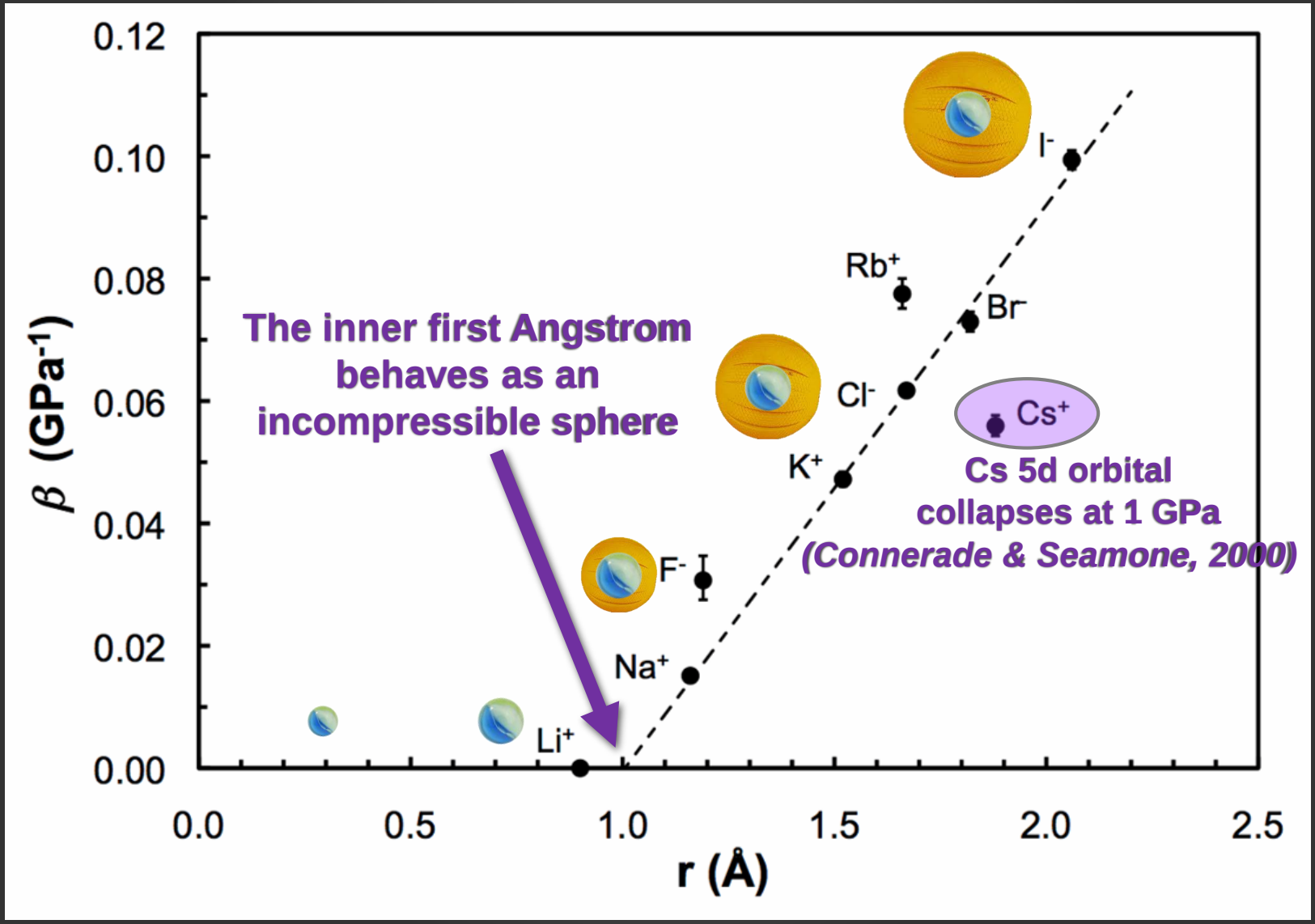
## *Dumb Model*

$$K_0 = \frac{K_1 + K_2}{2}$$

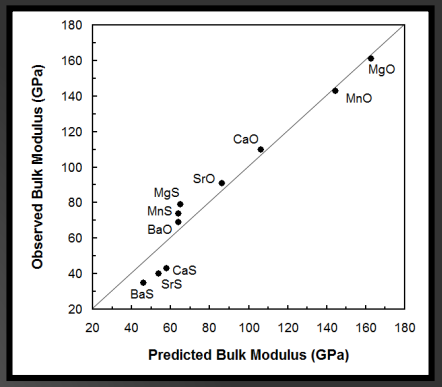
# Results with Oxides and Sulfides



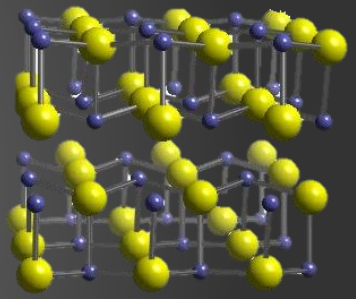
# Results for Ionic Moduli



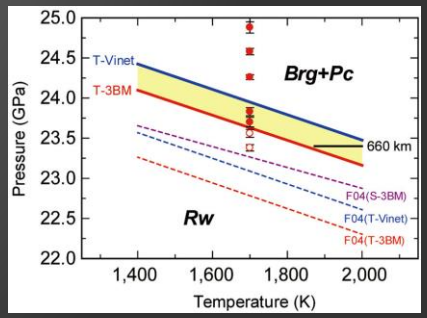
# Conclusions




• The ionic modulus model correctly predicts compression in crystalline ionic solids, and is not just a mathematical trick… it is capturing **real atomic physics at high pressures**

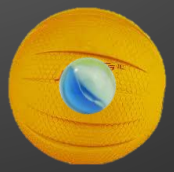


• The model works best for materials with strongly ionic bonding (like **halides** and **oxides**), but deviates from experiment for materials with significant covalent bonding (like **sulfides**)



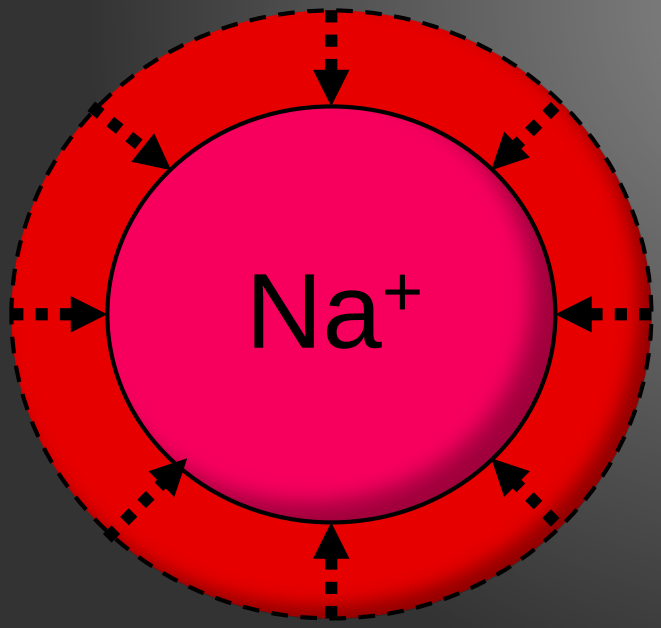

• Together with Pauling's rules, the model can be used to make ***theoretical predictions of entire phase diagrams*** and model interiors of rocky planets

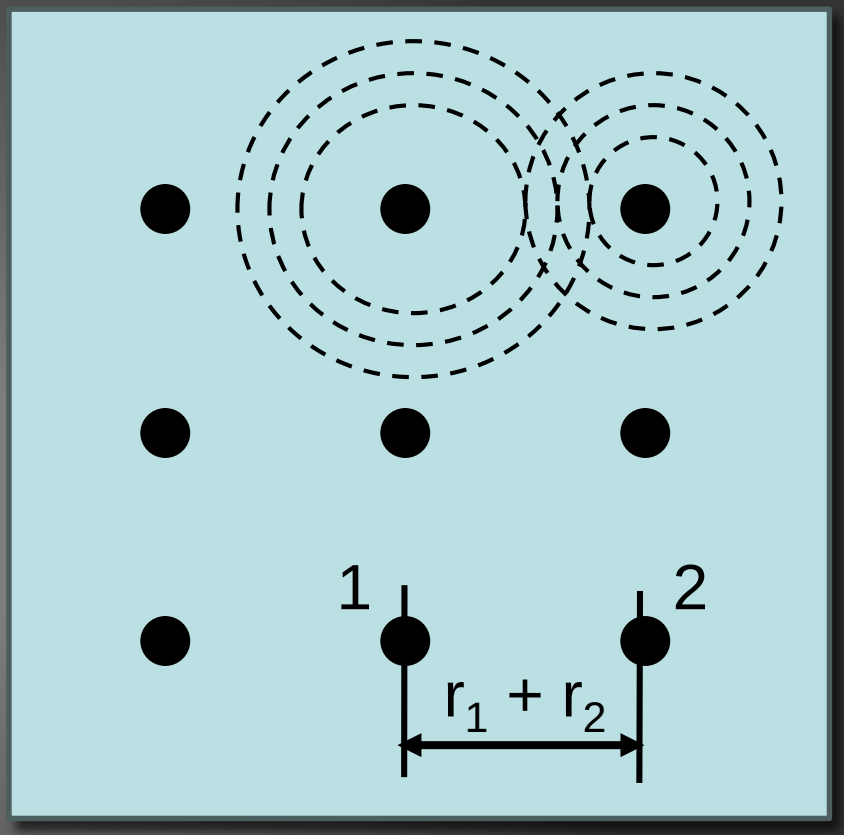
• ***Atoms are Nerf balls with marbles in the middle***



# Quantitative Testing

***How do we directly measure the modulus of an ion under pressure?***

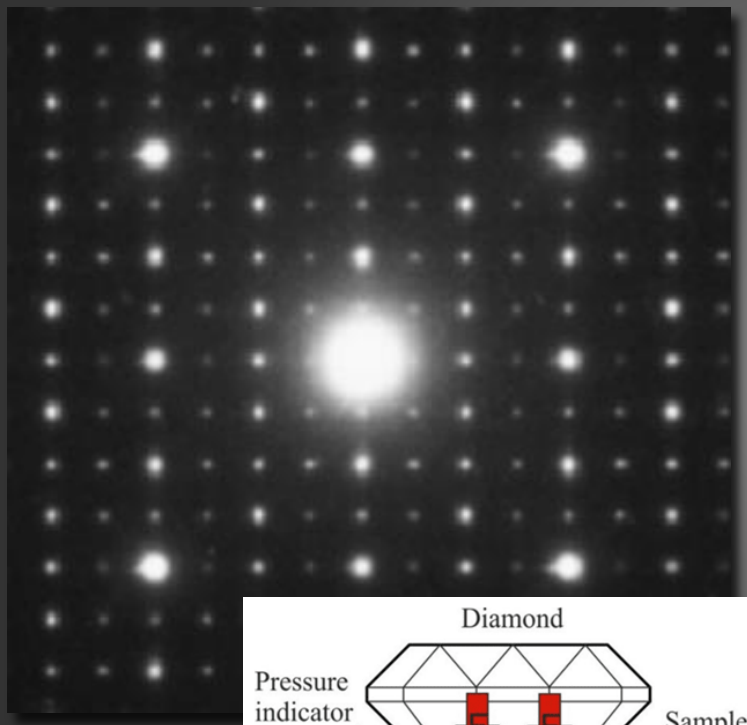


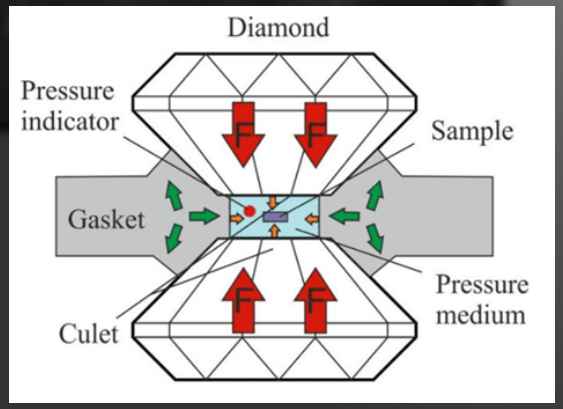




*Traditional diffraction measurements only give us internuclear separation (not invidividual radii)*

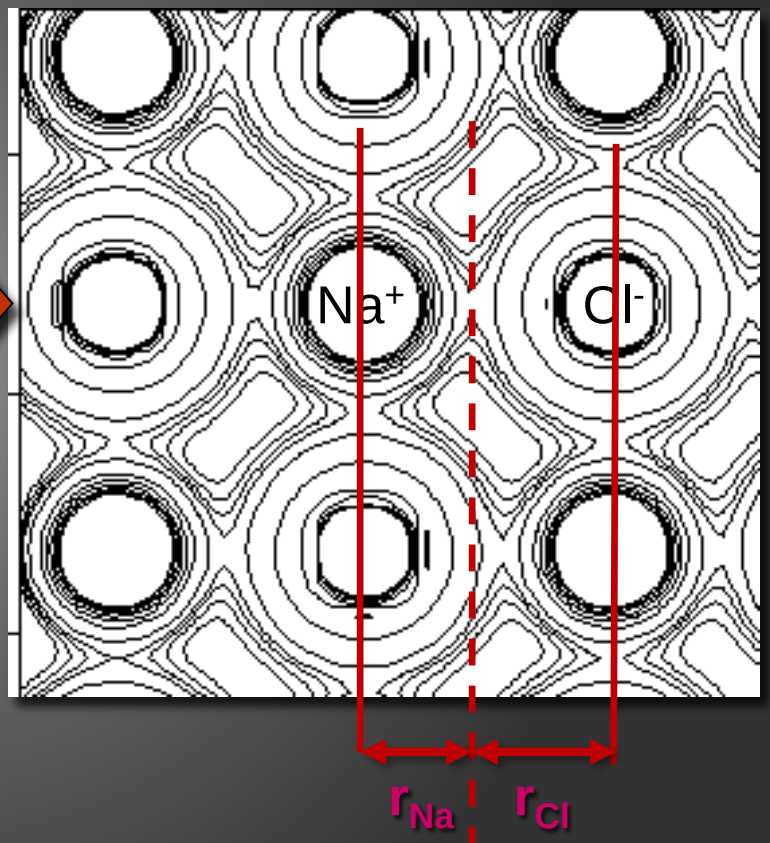
# Quantitative Testing

## Single Crystal Diffraction






## Electron Density Map

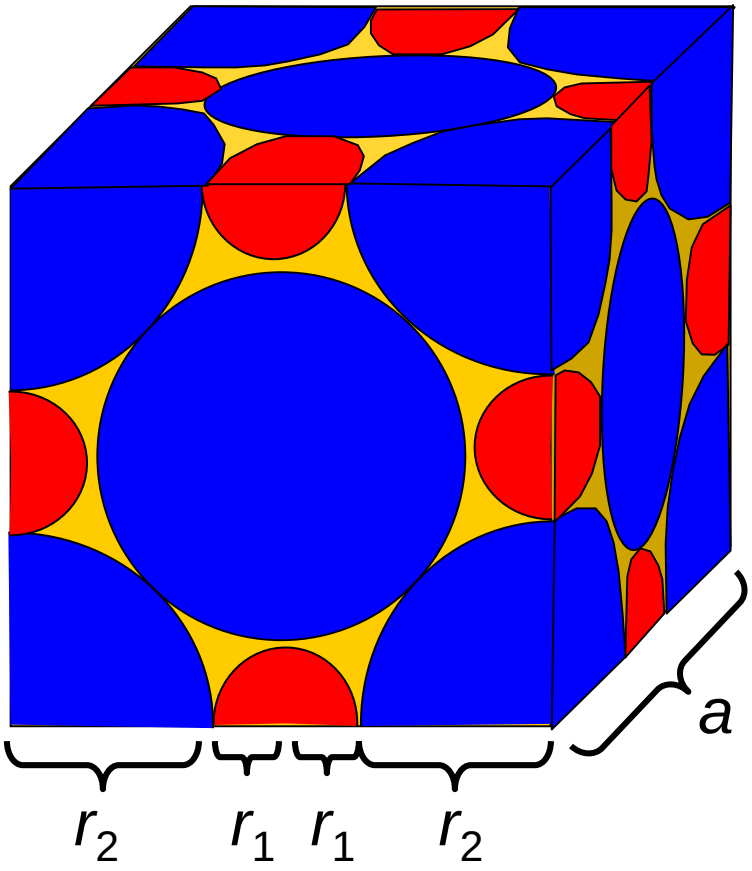



**Electron density minimum**

# B1 Structure

$$V_{ions} = 4\left(\frac{4}{3}\pi \cdot r_1^{\,3} + \frac{4}{3}\pi \cdot r_2^{\,3}\right) = \frac{16\pi}{3}\left(r_1^{\,3} + r_2^{\,3}\right)$$

$$V_{total} = a^3 = \left(2r_1 + 2r_2\right)^3 = 8\left(r_1 + r_2\right)^3$$

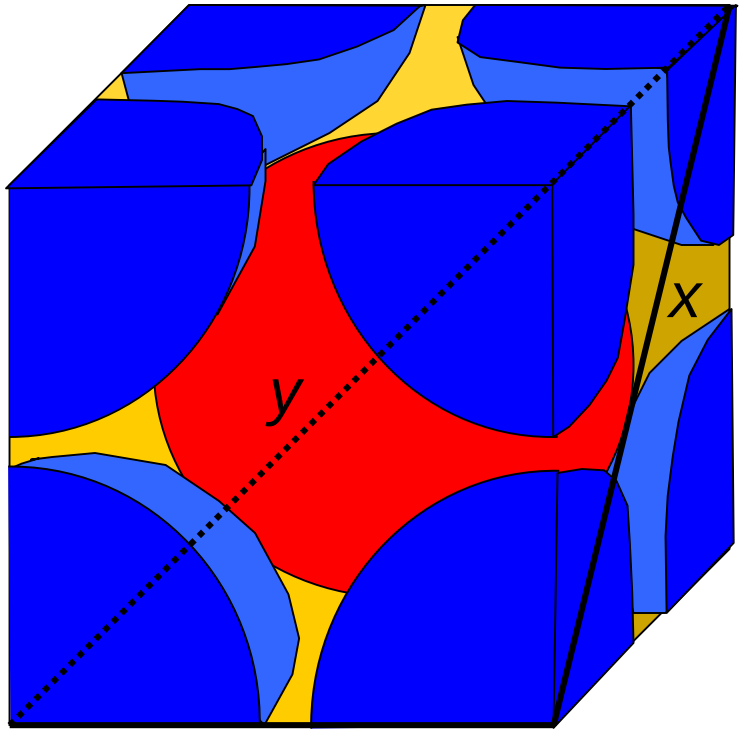



$$C = \frac{V_{ions}}{V_{total}} = \frac{\frac{16\pi}{3}\left(r_1^{\,3} + r_2^{\,3}\right)}{8\left(r_1 + r_2\right)^3} = \frac{2\pi}{3}\frac{\left(r_1^{\,3} + r_2^{\,3}\right)}{\left(r_1 + r_2\right)^3}$$

# B2 Structure

$$V_{ions} = \frac{4}{3}\pi \cdot r_1^{\,3} + \frac{4}{3}\pi \cdot r_2^{\,3} = \frac{4\pi}{3}\left(r_1^{\,3} + r_2^{\,3}\right)$$

$$V_{total} = a^3 = 8 \cdot 3^{-3/2}\left(r_1 + r_2\right)^3$$




$$C = \frac{V_{ions}}{V_{total}} = \frac{\frac{4\pi}{3}\left(r_1^{\,3} + r_2^{\,3}\right)}{8 \cdot 3^{-3/2}\left(r_1 + r_2\right)^3} = \frac{\sqrt{3}}{2}\pi \frac{\left(r_1^{\,3} + r_2^{\,3}\right)}{\left(r_1 + r_2\right)^3}$$