Using LAMMPS to Derive Crystal Structure Rule

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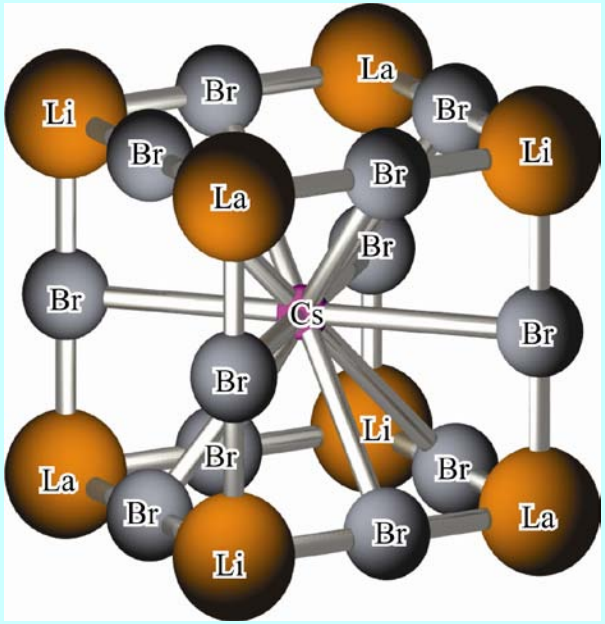
Example: Alkali Halides

To predict alkali halide crystals, our embedded-ion method interatomic potential database

1. **contains all nine alkali halide elements (Li, Na, K, Rb, Cs F, Cl, Br, I),**
2. **incorporates atomic size, electronegativity, and bond energy effects,**
3. **uses elemental properties directly as model parameters without parameterization, and**
4. **gives good trend of charge, energy, and bond length predictions.**

Role of Electronegativity

Double Perovskite $Cs_2LiLaBr_6$



Observations:

1. Lattice constant of $Cs_2LiLaBr_6$ is $a = 2r_{LiLa} = 11.289$ Å[1], i.e., $r_{LaLa} = 7.983$ Å.
2. fcc La has a lattice constant a = 5.307 Å and a cohesive energy $E_c = -4.446$ eV/atom[2]. In fcc La, $r_{LaLa} = 3.753$ Å.
3. It is difficult to for a potential to be transferrable to both $Cs_2LiLaBr_6$ and La.

Solution:

The electronegativity difference-induced ionization can increase the bond length and reduce the bond strength.

[1]. P. Yang, M. A. Rodriguez, F. P. Doty, X. Zhou, M. R. Sanchez, and K. S. Shah, submitted.
[2]. X. W. Zhou, and F. P. Doty, *Phys. Rev. B*, **78**, 224307 (2008).

Embedded Ion Method (EIM)

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\phi_{ij}(r_{ij}) + \sum_{i=1}^{N}E_i(q_i,\sigma_i)$$

system total energy

$$E_i(q_i,\sigma_i) = \frac{1}{2}q_i\cdot\sigma_i\ *$$

embedding energy at i

$$q_i = \sum_{j=i_1}^{i_N}\eta_{ji}(r_{ij})$$

charge on atom i

$$\sigma_i = \sum_{j=i_1}^{i_N} q_j\cdot\varphi_{ij}(r_{ij})$$

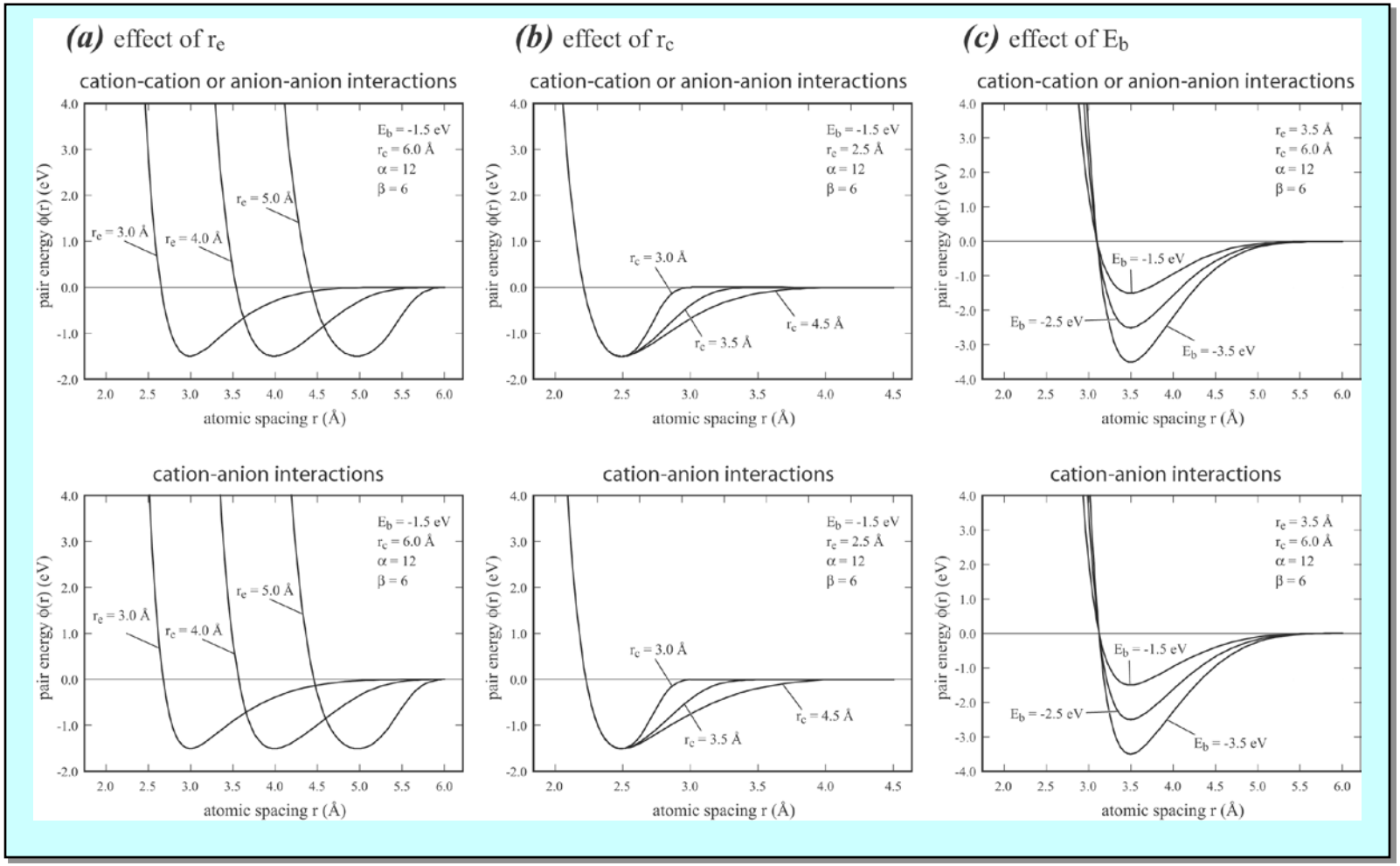
electrical potential (in voltage) at i

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\phi_{ij}(r_{ij}) + \sum_{i=1}^{N}\left\{\left(\sum_{j=i_1}^{i_N}\eta_{ji}(r_{ij})\right)\cdot\sum_{j=i_1}^{i_N}\left[\left(\sum_{k=j_1}^{j_N}\eta_{kj}(r_{jk})\right)\cdot\varphi(r_{ij})\right]\right\}$$

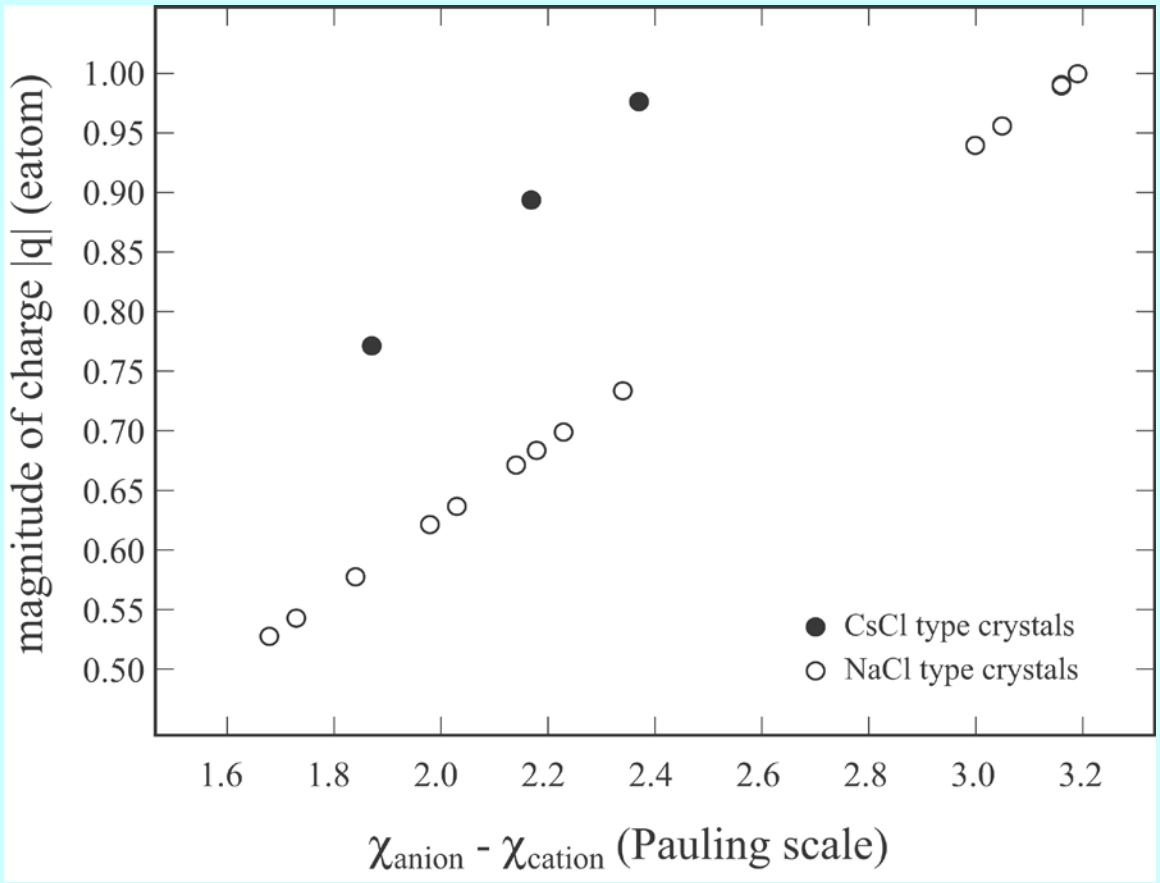
*when $\varphi_{ij}(r) \sim r^{-1}$, the embedding energy reduces to Coulomb interactions between i and its neighbors:

$$E_i(q_i,\sigma_i) = \frac{1}{2}\sum_{j=i_1}^{i_N}\frac{q_i\cdot q_j}{r_{ij}}$$

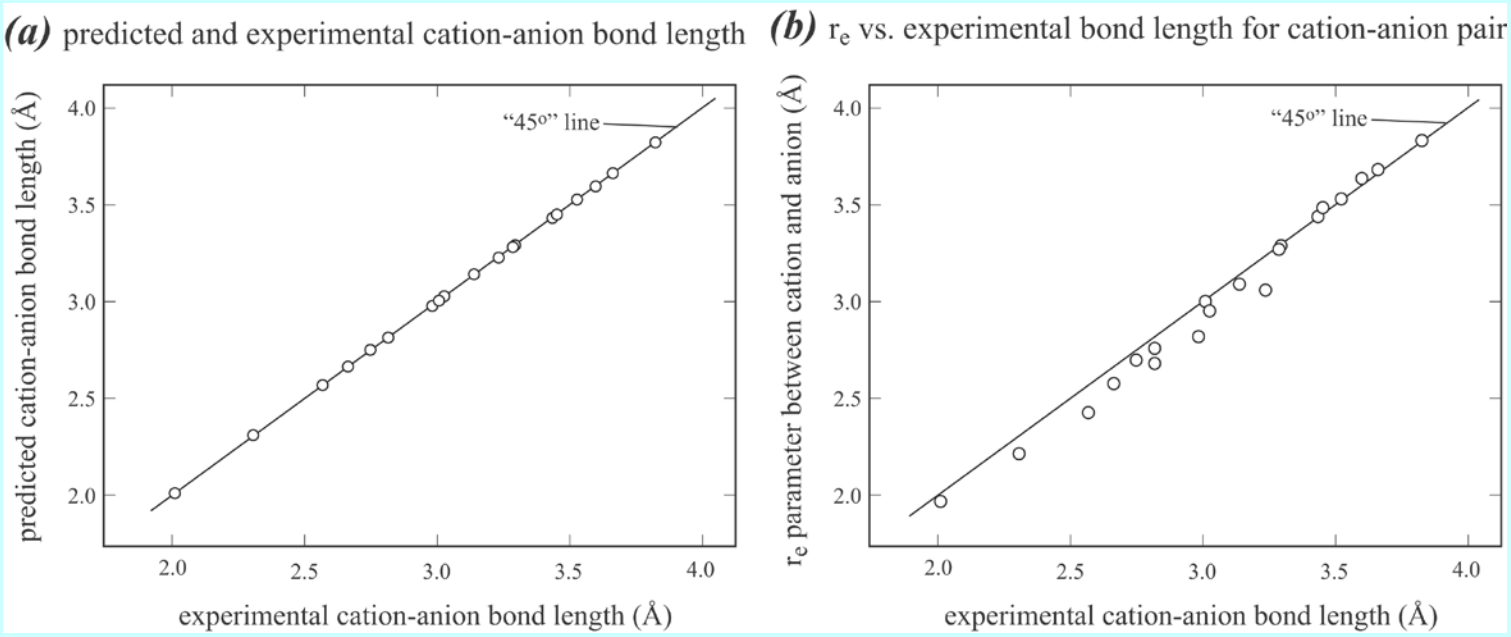
Fitting-Free Parameters



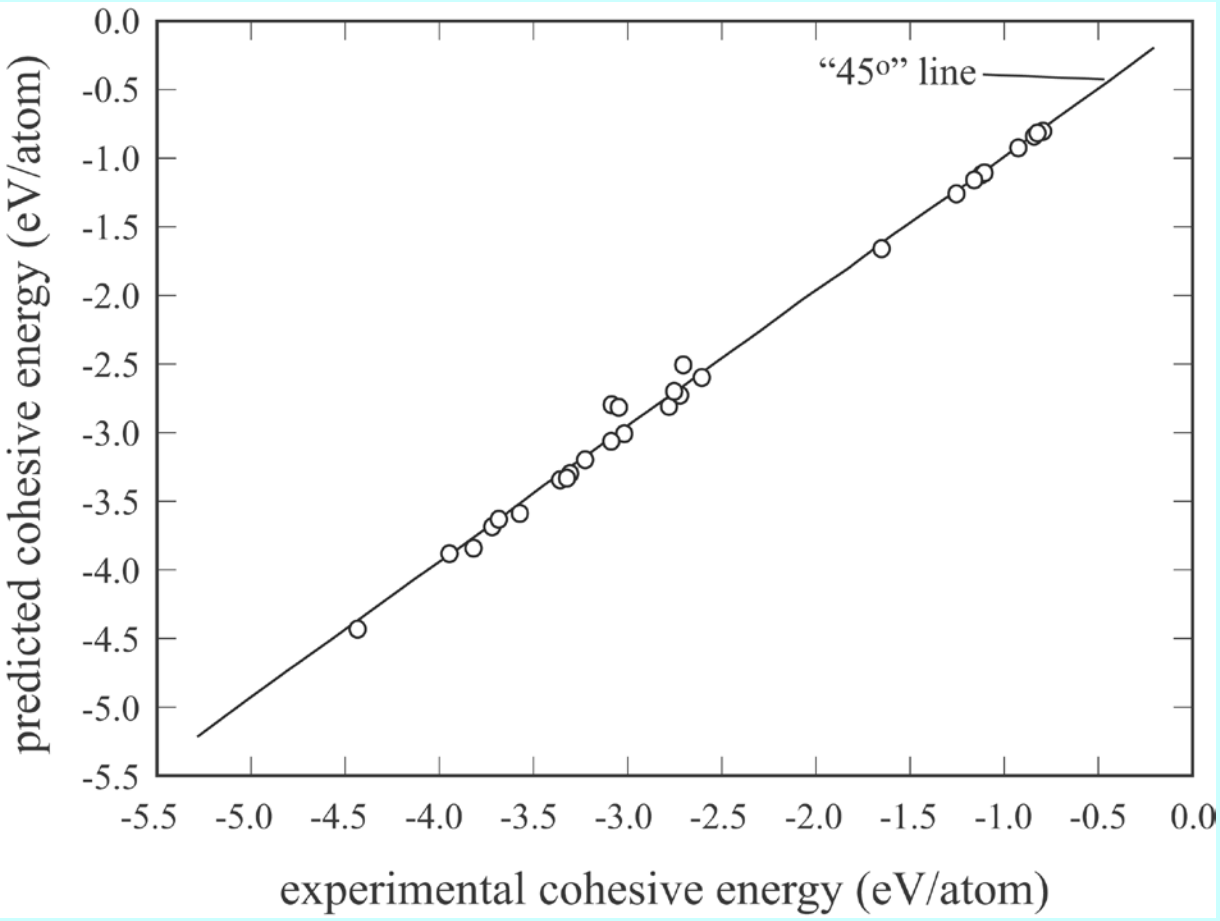
Predicted Charge vs. Electronegativity



Cation-Anion Spacing

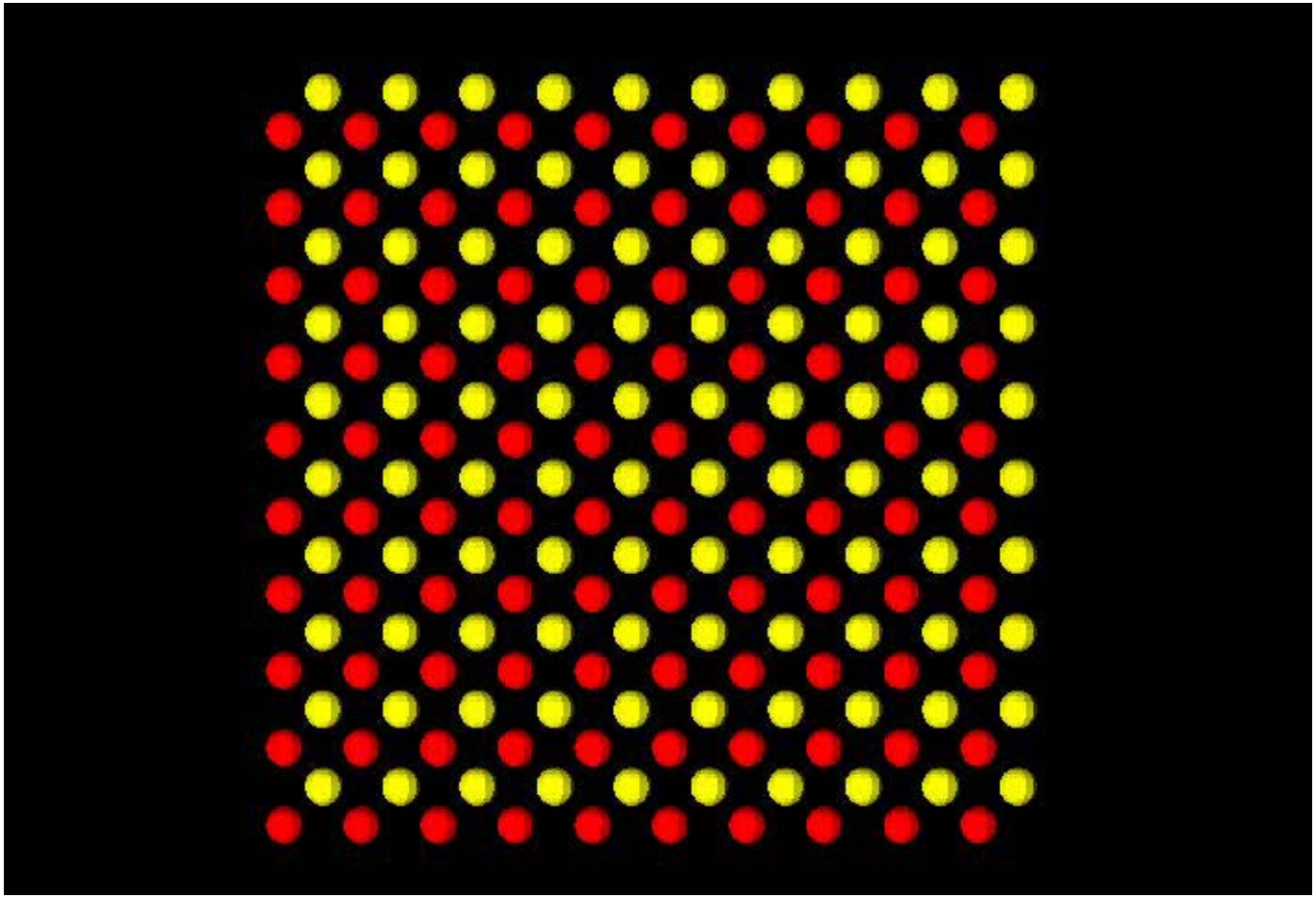


Cohesive Energy Prediction

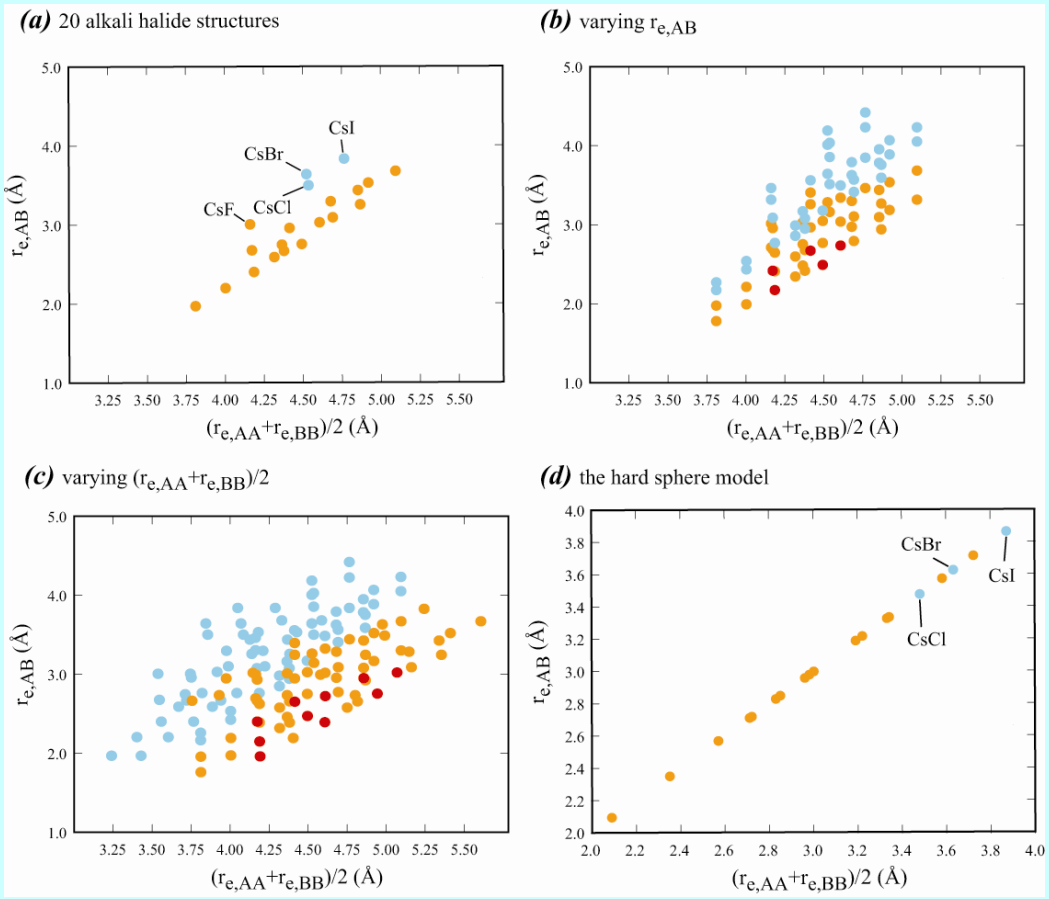


Simulated Annealing: NaCl at 300 K

Over a 25 ps period

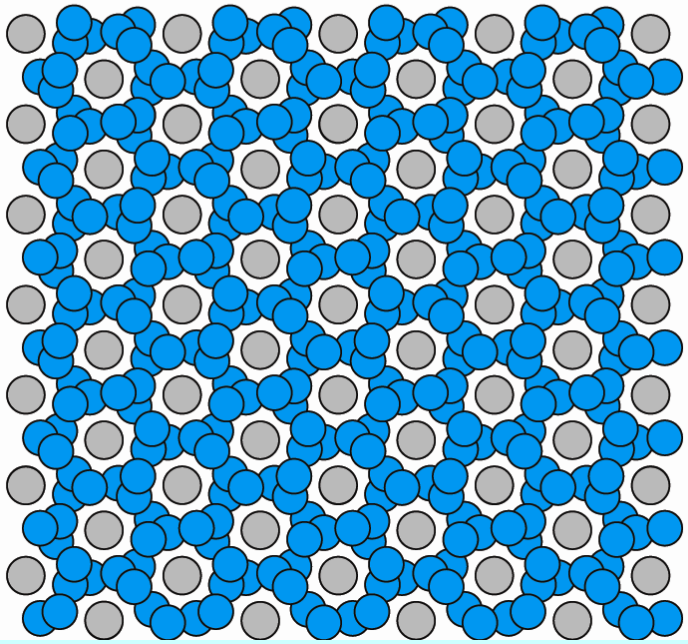


Crystal Phase Diagram

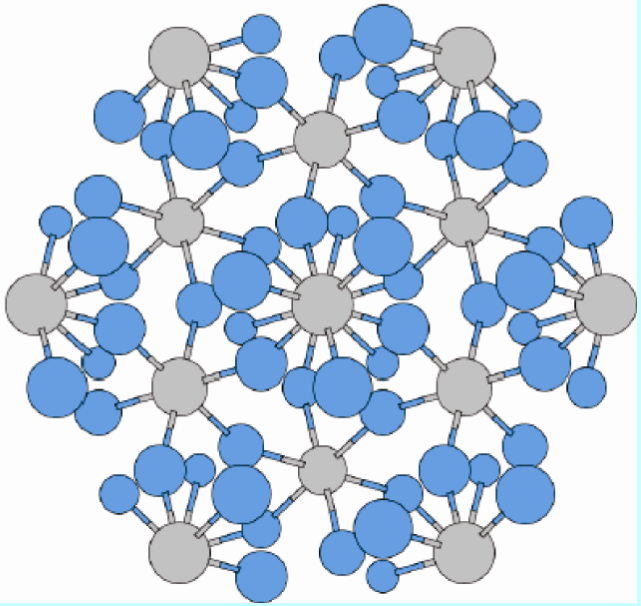


Working on Lanthanide

Predicted structure when r_{AB} becomes small



(0001) image of R32 structure
(componds with small atoms, e.g., ScF_3)



Conclusions

- LAMMPS can now be used to explore crystal rule in the atomic size-electronegativity-bond energy space.
- Preliminary application of LAMMPS in the atomic size space already results in a new crystal rule beyond the hard sphere model.
- The new rule is mathematically very robust in that in AB binary compounds, larger A-B spacing with respect to A-A or B-B spacings favors the CsCl type of crystals and smaller A-B spacing with respect to A-A or B-B spacings favors the NaCl type of crystals.

Derivative Calculation

$$\sum_{i=1}^{N}\frac{\partial E_i(q_i,\sigma_i)}{\partial X} = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\left[\frac{\partial q_i}{\partial X}\cdot q_j\cdot\varphi(r_{ij})+q_i\cdot\frac{\partial q_j}{\partial X}\cdot\varphi(r_{ij})+q_i\cdot q_j\cdot\frac{\partial\varphi(r_{ij})}{\partial X}\right]$$

$$= \frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial q_i}{\partial X}\cdot\sigma_i\right)+\frac{1}{2}\sum_{j=1}^{N}\left(\frac{\partial q_j}{\partial X}\cdot\sigma_j\right)+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\left[q_i\cdot q_j\cdot\frac{\partial\varphi(r_{ij})}{\partial X}\right]$$

$$= \sum_{i=1}^{N}\left(\frac{\partial q_i}{\partial X}\cdot\sigma_i\right)+\frac{1}{2}\sum_{i=1}^{N}\sum_{j=i_1}^{i_N}\left[q_i\cdot q_j\cdot\frac{\partial\varphi(r_{ij})}{\partial X}\right]$$

Pair Functions

$$f_c(r, r_p, r_c) = \left[0.510204 \cdot erfc\left(\frac{1.64498(2r - r_p - r_c)}{r_c - r_p} \right) - 0.010204 \right]$$

cutoff function (r_c: cutoff distance)

$$\phi_{ij}(r) = \left[\frac{E_{b,ij} \cdot \beta_{ij}}{\beta_{ij} - \alpha_{ij}} \cdot \left(\frac{r_{e,ij}}{r} \right)^{\alpha_{ij}} - \frac{E_{b,ij} \cdot \alpha_{ij}}{\beta_{ij} - \alpha_{ij}} \cdot \left(\frac{r_{e,ij}}{r} \right)^{\beta_{ij}} \right] \cdot f_c(r, r_{e,ij}, r_{c\phi,ij})$$

pair energy function between cation and anion

$$\phi_{ij}(r) = \left[\frac{E_{b,ij} \cdot \beta_{ij}}{\beta_{ij} - \alpha_{ij}} \cdot \exp\left(-\alpha_{ij} \cdot \frac{r - r_{e,ij}}{r_{e,ij}} \right) - \frac{E_{b,ij} \cdot \alpha_{ij}}{\beta_{ij} - \alpha_{ij}} \cdot \exp\left(-\beta_{ij} \cdot \frac{r - r_{e,ij}}{r_{e,ij}} \right) \right] \cdot f_c(r, r_{e,ij}, r_{c\phi,ij})$$

pair energy function between cations or between anions

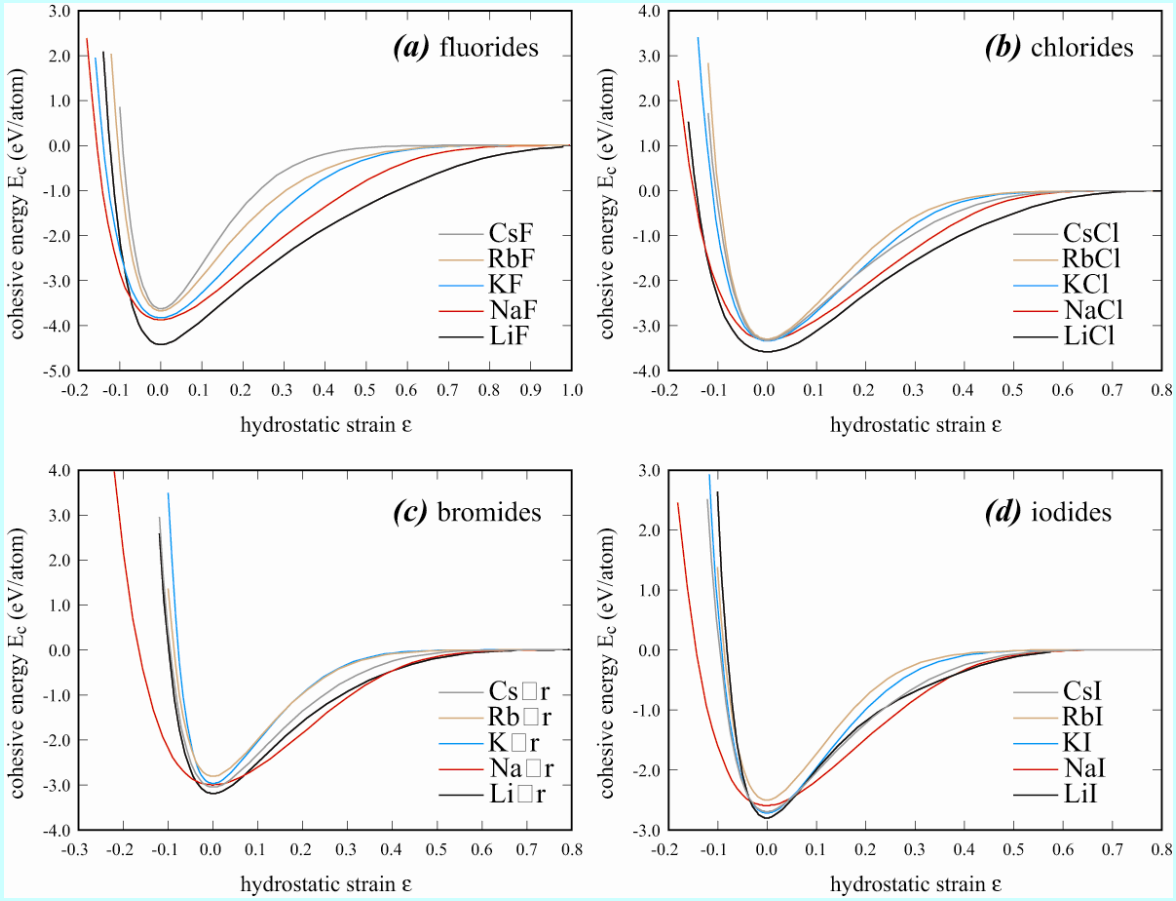
$$\eta_{ji}(r) = A_{\eta_{ij}} (\chi_j - \chi_i) \cdot f_c(r, r_{s\eta,ij}, r_{c\eta,ij})$$

charge transfer function (χ: electronegativity)

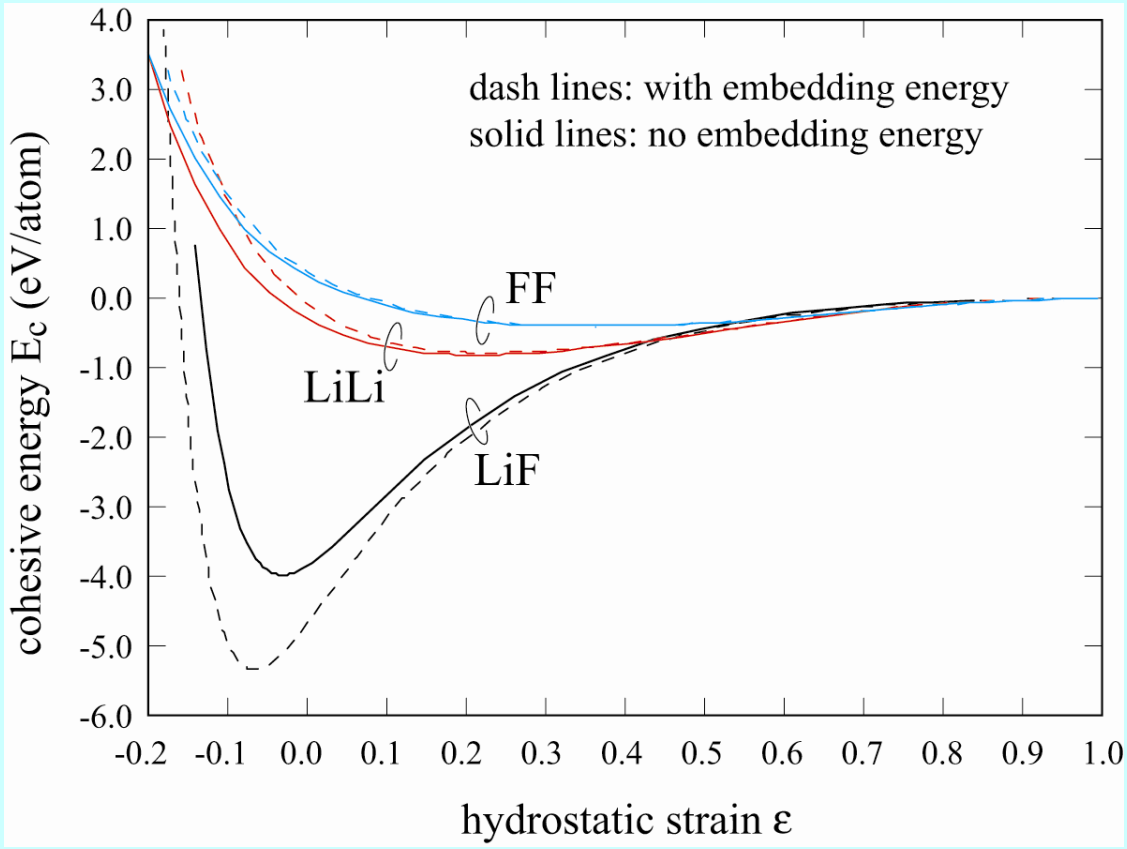
$$\varphi_{ij}(r) = A_{\varphi_{ij}} \cdot \exp(-\zeta_{ij} \cdot r) \cdot f_c(r, r_{s\varphi,ij}, r_{c\varphi,ij})$$

Charge interaction function

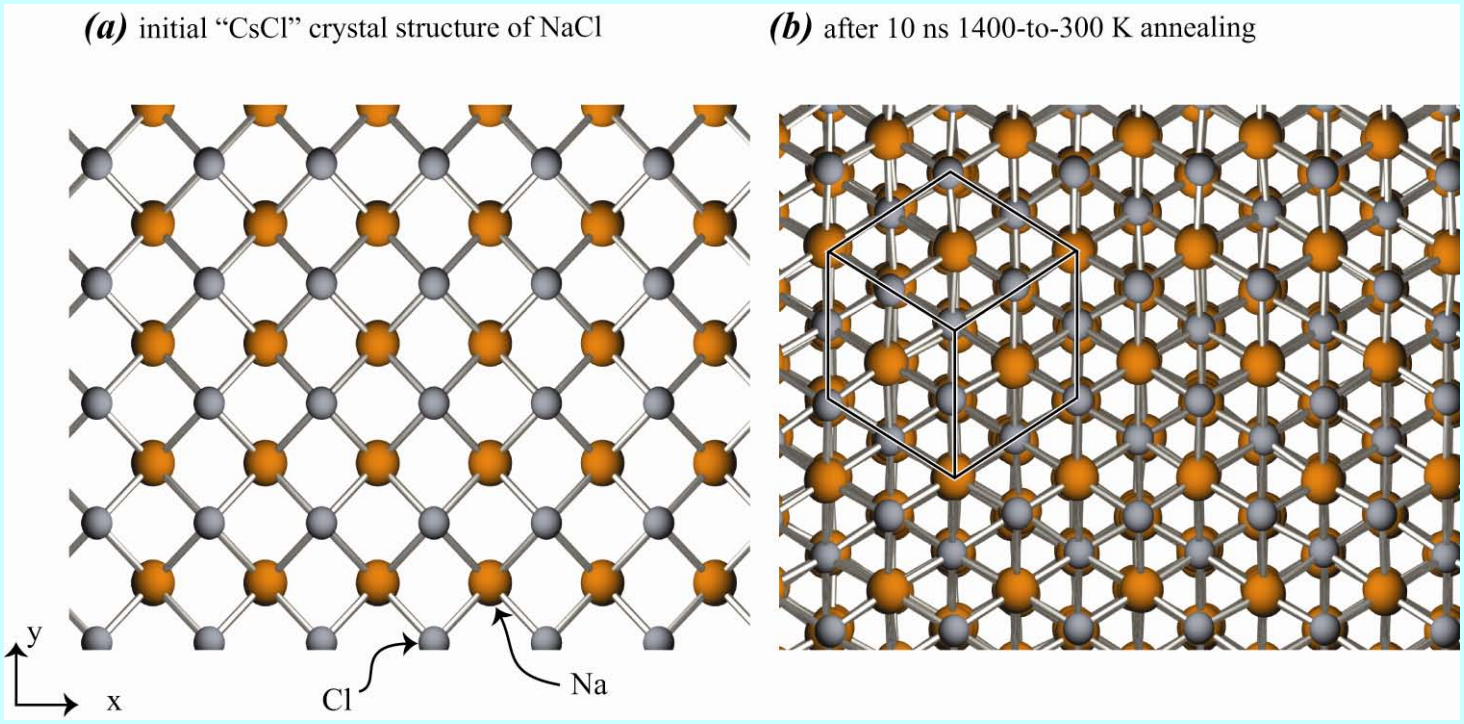
Cohesive Energy Profiles



Reactivity of EIM

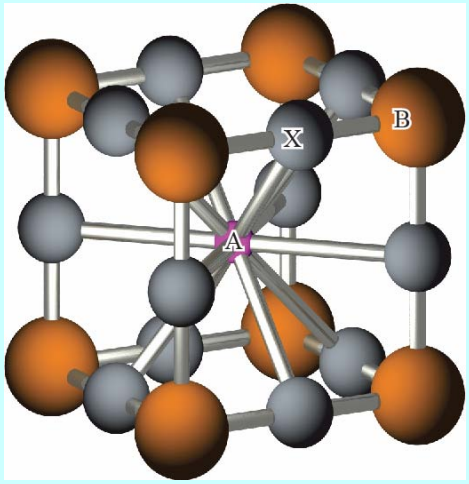


Simulated Annealing



Goldschmidt Criteria[1,2]

Perovskite



$$r_{AX} \Big/ \sqrt{2} \cdot r_{BX} = 1$$

Hard sphere mode: $r_{AX} = R_A + R_X$; $r_{BX} = R_B + R_X$.

Basic criterion: $$0.77 < \frac{R_A + R_X}{\sqrt{2}\left(R_B + R_X\right)} < 1.00$$

Problems:

1. **Hard sphere model not true.**
2. **Environment-independent atomic size not true.**
3. **Electronegativity effects not incorporated.**
4. **Bond energy effects not incorporated.**

Limitations: Goldschmidt criterion has only been successful for perovskite crystals. Even so, a large number of non-perovskite crystals were found to satisfy the criterion, and a large number of perovskite crystals were found to not satisfy the criterion.

[1]. V. M. Goldschmidt, Geochemisce Verterlungsgesetze der Elemente. Norske Videnskap, Oslo, 1927;
[2]. L. Liang, L. Wencong, and C. Nianyi, *J. Phys. Chem. Sol.*, **65**, 855 (2004).