Distortions on the CPS-rim

Pathways connecting hcp, bcc and fcc

The transformation pathways connecting bcc to fcc, and bcc to hcp can be viewed within the two-dimensional strain order parameter space spanned by $e_2$ and $e_3$ shown in fig. 4. The Bain distortion\textsuperscript{1} (fig. 1) describes a strain deformation that can transform the bcc structure into fcc or vice-versa. The conventional bcc cell can be stretched along one of its ⟨100⟩ directions to obtain a body-centered tetragonal cell. The fcc crystal structure is reached when the $\frac{c}{a}$ ratio of this cell is equal to $\sqrt{2}$.

The conventional cell of a body centered cubic crystal structure with lattice parameter $b$ can be represented in matrix form with each column corresponding to one of the lattice vectors as:

$$ P = \begin{bmatrix} b & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & b \end{bmatrix} $$

(S1)
There are three different ways to stretch this cell to generate three equivalent fcc crystals. The distorted lattice for an fcc crystal with lattice parameter $f$ is formed by stretching along the $z$ axis to yield a matrix of fcc lattice vectors:

$$
S = \begin{bmatrix}
\frac{f}{\sqrt{2}} & 0 & 0 \\
0 & \frac{f}{\sqrt{2}} & 0 \\
0 & 0 & f
\end{bmatrix}
$$

(S2)

Using eq. (1), the deformation tensor is then given by:

$$
F = \frac{f}{b} \begin{bmatrix}
\frac{1}{\sqrt{2}} & 0 & 0 \\
0 & \frac{1}{\sqrt{2}} & 0 \\
0 & 0 & 1
\end{bmatrix}
$$

(S3)

Using the order parameters of eqs. (3) to (5), the resulting point in order parameter space that corresponds to this fcc crystal structure is:

$$
\vec{e} = \begin{bmatrix}
3 \log f + \log \sqrt{3} \\
\log 2 \sqrt{6} \\
0 \\
0 \\
0
\end{bmatrix}
$$

(S4)

There are two other equivalent fcc crystal structures that can be obtained from bcc. They are found at points that have the same value of $e_1, e_4, e_5$, and $e_6$, but different $e_2, e_3$ values. These values can be obtained by applying a $120^\circ$ rotation in the two-dimensional space spanned by $e_2$ and $e_3$. The high-symmetry fcc crystal is found at three special points in the $e_2 - e_3$ space.

The Burgers path connects the bcc and hcp crystal structures. Unlike the Bain path, this distortion requires both a strain and a shuffle. The Burgers path also requires a supercell.

S2
of the cubic bcc unit cell with lattice vectors (columns):

$$
P = \begin{bmatrix}
    b & -b & 0 \\
    b & b & 0 \\
    0 & 0 & b
\end{bmatrix}
$$

(S5)

In this supercell, the first and third columns represent two lattice vectors of bcc that define the (110) plane, while the second and third columns represent two lattice vectors that define the (110) plane. This cell is transformed to form the hcp crystal structure with lattice parameters of $a$ and $c$:

$$
S = a \begin{bmatrix}
    \sqrt{\frac{3}{2}} & -\frac{1}{\sqrt{2}} \frac{c}{a} & 0 \\
    \sqrt{\frac{3}{2}} & \frac{1}{\sqrt{2}} \frac{c}{a} & 0 \\
    0 & 0 & 1
\end{bmatrix}
$$

(S6)

The deformation tensor and Hencky strain for the Burgers deformation is given by:

$$
F = \begin{bmatrix}
    \frac{c \sqrt{2} + a \sqrt{6}}{4b} & \frac{\sqrt{6}a - \sqrt{2}c}{4b} & 0 \\
    \frac{\sqrt{6}a - \sqrt{2}c}{4b} & \frac{c \sqrt{2} + a \sqrt{6}}{4b} & 0 \\
    0 & 0 & \frac{a}{b}
\end{bmatrix}
$$

(S7)

$$
E = \begin{bmatrix}
    \frac{1}{4} \log \left(\frac{3a^2 c^2}{4b^4}\right) & \frac{1}{4} \log \left(\frac{3a^2 c^2}{c^4}\right) & 0 \\
    \frac{1}{4} \log \left(\frac{3a^2 c^2}{c^4}\right) & \frac{1}{4} \log \left(\frac{3a^2 c^2}{4b^4}\right) & 0 \\
    0 & 0 & \frac{1}{2} \log \left(\frac{a^2}{b^2}\right)
\end{bmatrix}
$$

(S8)

The strain order parameters then become:

$$
\vec{e} = \begin{bmatrix}
    \log \left(\frac{3a^4 c^2}{4b^6}\right) & 0 & \log \left(\frac{4b^4}{3a^2 c^2}\right) + 2 \log \left(\frac{a^2}{b^2}\right) & 0 \\
    0 & 0 & \log \left(\frac{3a^2 c^2}{4b^4}\right) & 0
\end{bmatrix}
$$

(S9)

While the exact location of hcp in the strain order parameter space spanned by $e_2$ and $e_3$ depend on the $\frac{c}{a}$ ratio, we set it equal to the ideal hard-sphere packing ratio of hcp, i.e.
\[
\frac{c}{a} = \sqrt{\frac{8}{3}}. \text{ For this ratio, } e_3 \text{ evaluates to } -\frac{\log 2}{2\sqrt{6}}.
\]

Each bcc crystal has six (110) type planes that can be deformed to triangular planes. After the deformation, there are two possible shuffles that can be applied to generate an hcp structure. Thus, each bcc crystal structure is connected to a total of twelve hcp structures through the Burgers path.

**Shear transformations across stacking sequences**

All stacking sequences of close-packed planes that differ from fcc and hcp can be generated from bcc by combining Bain and Burgers type distortions. We start with the following supercell of the bcc cubic unit cell:

\[
\mathbf{B} = \begin{bmatrix}
b & -mb & 0 \\
b & nb & 0 \\
0 & 0 & b
\end{bmatrix}
\]

(S10)

where \(b\) is the lattice constant of the bcc crystal structure and \(m\) and \(n\) are positive integers. The first and third columns of \(\mathbf{B}\), denoted \(\mathbf{b}_1\) and \(\mathbf{b}_3\), define the (110) planes of the bcc lattice that will be converted into triangular lattices. The second column, \(\mathbf{b}_2\), is a vector out of the (110) plane that defines the repeat unit of the close-packed structure to be generated upon application of a combination of Bain and Burgers type deformations. For example, to generate hcp along the Burgers path \(n=m=1\).

The (110) planes of bcc can be converted to a triangular lattice with a combination of \(e_2\) and \(e_3\) strains as described in Section 2. This is achieved once the ratio of lengths of the strained vectors \(\mathbf{b}_1'\) and \(\mathbf{b}_3'\) becomes equal to \(\sqrt{3}\). Enforcing this constraint leads to the following relationship between \(e_2\) and \(e_3\):

\[
\frac{\exp (\sqrt{2}e_2 + \sqrt{6}e_3)}{\exp (2\sqrt{2}e_2) + 1} = \frac{1}{3}
\]

(S11)
Equation (S11) corresponds to the locii of points of the bottom branch of the Reuleaux circle of fig. S1.

Figure S1: Locii of points in $e_2$-$e_3$ space that correspond to a triangular lattice. High-symmetry points corresponding to the fcc, bcc and hcp variants are marked.

The integers $m$ and $n$ that define the vector $\vec{b}_2$ (second column of eq. (S10)) determine the number of triangular layers, $l$, in the repeat unit of the close-packed phase. In order to generate a close-packed stacking sequence, the deformed vector $\vec{b}_2'$ must have a projection on the basal plane of the deformed supercell, eq. (S10), spanned by $\vec{b}_1'$ and $\vec{b}_3'$, according to;

$$\frac{\vec{b}_1' \cdot \vec{b}_2'}{||\vec{b}_1'||^2} = -m + \frac{m + n}{1 + \exp \left(\frac{2}{2\sqrt{2}}e_2\right)} = 0, \frac{1}{3}, -\frac{1}{3}.$$

(S12)

This ensures that the triangular layer $l$ layers above the first layer (having sequence A) of the repeat unit has either an A, B or C stacking sequence. For a given $m$ and $n$, the above equation specifies a value of $e_2$ that is compatible with a close-packed stacking sequence. Subsequent shuffles within the repeat unit can then be applied (similar to the Burgers path) to generate different stacking sequences among the $l$ layers of the repeat unit. The results
can be summarized with macroscopic strains given by:

\[
 e_2 = \begin{cases} 
 0, & l = \text{even} \\
 \frac{1}{\sqrt{2}} \tanh^{-1} \left( \frac{-2}{3l} \right), & l = \text{even} \\
 \frac{1}{2\sqrt{2}} \log \left( \frac{3l-5}{3l+5} \right), & l = \text{odd} \\
 \frac{1}{2\sqrt{2}} \log \left( \frac{3l-1}{3l+1} \right), & l = \text{odd}
\end{cases} 
\]  
(S13)

The corresponding values of \( e_3 \) may be calculated from eq. \((S11)\). The points in strain space for each of these cases are shown in fig. S2.

![Graph showing discretized points for different supercells](image)

**Figure S2:** Discretized points for different supercells showing distortions that give rise to triangular stackings.

**Algorithmic generation of the stacking-ordered phases**

Each close-packed stacking sequence of triangular lattices will have a particular repeat unit \( n \). For example, fcc is made of a periodically repeating block of \( n = 3 \) close-packed planes having stacking sequence ABC. A more complex stacking such as 9\( R \) has a repeat unit consisting of \( n = 9 \) planes with stacking sequence ABCBCACAB. An algorithm to generate a particular repeat unit \( n \) starting with bcc can proceed as follows. The first task is to identify a supercell within the original bcc lattice that upon a suitable combination of \( e_2 \) and \( e_3 \) strains forms a cell consisting of \( n \) triangular layers. We illustrate the algorithm for \( n = 5 \) in fig. S3. The first supercell vector, \( \mathbf{A} \), aligns with the shortest vector along the [110] direction. The second supercell vector, \( \mathbf{B} \), connects a site in the \((n + 1)^{th}\) (1\( \bar{1} \)0)
plane and forms an angle with the first supercell vector \( \mathbf{A} \) that is as close as possible to 90°. The third supercell vector, \( \mathbf{C} \), is the shortest vector along the [001] direction and points out of the plane in fig. S3. The next step is then to apply a combination of \( e_2 \) and \( e_3 \) that will simultaneously convert the (1\overline{1}0) planes into triangular lattices and shear the unit cell until \( \mathbf{B} \) adopts an angle to \( \mathbf{A} \) that is compatible to one of the three possible stacking sequences. Figure S3 illustrates an example where a combination of \( e_2 \) and \( e_3 \) are applied until \( \mathbf{B} \) is perpendicular to \( \mathbf{A} \) (in this case, the \((n+1)^{th}\) layer is identical to the first layer of the repeated block). The last step involves internal shuffles of the deformed (1\overline{1}0) planes to realize a particular stacking sequence within the \( n \)-layer repeat unit. Each repeat unit \( n \) corresponds to a particular point on the dashed curves of fig. 4.

Figure S3: The formation of a 5 period long stacking ordered phase from bcc by first forming triangular layers through a deformation along \( e_3 \) followed by a distortion along \( e_2 \)

Convergence data for lithium, sodium and magnesium

The energy difference between bcc and fcc for all three elements is shown as a function of plane-wave cutoff and k-point density in figs. S4 and S5. The energies are well-converged to within less than 1 meV/atom at a density of 71 k-points per Å\(^{-1}\) and a cutoff of 500 eV
Figure S4: Convergence of energy difference with respect to the k-grid

Figure S5: Convergence of energy difference with respect to the planewave cutoff
References
