The importance of shear in the \( bcc \rightarrow hcp \) transformation in iron

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Phase transformations in iron

A strong shock wave will induce phase transitions producing complicated microstructure.

Ground state ferromagnetic \textit{bcc} undergoes a \textit{martensitic} phase transformation to non-magnetic \textit{hcp} at \textit{\sim}10 GPa.

\textbf{Goal:} understand scatter and hysteresis in transition pressures

- Large scatter in the measured TP
- Fuzzy phase boundaries
- Mixed states
- Large hysteresis
Phase transformations in iron

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Selected references include:
- After Transition

```
T (K)
5000
4000
3000
2000
1000
0
P (GPa)
100
200
300
```
Martensite in iron – length scales

- Variants of bcc Fe produced by bcc→hcp→bcc transformation induced by shock loading (Bowden and Kelly)
- Micron-length scales require continuum analysis!
Atomistic – continuum connexion

Cauchy-Born Rule

undeformed

\[ y \]

\[ y(x) \]

deformed

\[ e_1 = Fe_1^o \]
\[ e_2 = Fe_2^o \]
\[ e_3 = Fe_3^o \]
\[ F = \nabla y(x) \]
Kinematics of $bcc \rightarrow hcp \rightarrow bcc$ phase transformations

$<100>$ compression
$<110>$ elongation

$U(V) = \begin{pmatrix}
\frac{\alpha(V)}{2} - \frac{3}{4\sqrt{2}} & \frac{\alpha(V)}{2} - \frac{3}{4\sqrt{2}} & 0 \\
\frac{\alpha(V)}{2} - \frac{3}{4\sqrt{2}} & \frac{\alpha(V)}{2} + \frac{3}{4\sqrt{2}} & 0 \\
0 & 0 & \sqrt{3}/2
\end{pmatrix}$

$u = \begin{pmatrix}
1/4\sqrt{2} \\
-1/4\sqrt{2} \\
0
\end{pmatrix}$

- $U$ is an $hcp$ deformation
- $u$ is the shuffle
- $\alpha(V) = \sqrt{3}/2$ ($%$)

View of $<110>$ Plane

initial $bcc$ variant

6 $hcp$ variants

12 $bcc$ variants

$G \in bcc$ point group

$H \in hcp$ point group

19 total variants
Multi-well elastic energy for iron

\[ W(F) = \min_{i=0,...,18} W^i(F) \]

DFT calculations prove to costly for on-the-fly \( W(F) \) or tabulated \( W(F) \)

**Assumption:** each deformation close to deformation of a variant

**Approximation:** Taylor expansion around variant deformation

**Taylor Expansion**

\[ W^i(C) = W_0^i(V) + \frac{1}{2} (C - C^i(V))^T \Gamma^i(V)(C - C^i(V)) \]

\[ \Gamma^i(V) = \left. \frac{\partial^2 W^i}{\partial C^2} \right|_{C^i(V)} \]

\[ C = F^T F \]

**DFT Calculations**

- Variant deformation, \( C^i(V) \) (hcp c/a ratio)
- Equation of State, \( W_0^i(V) = W^i(C^i(V)) \)
- Non-Linear Elastic Constants, \( \Gamma(V) \)
  (Calculated using volume conserving shears)

\[ bcc \text{ and } fcc : \Gamma_{11} \Gamma_{12} \Gamma_{44} \]
\[ hcp : \Gamma_{11} \Gamma_{33} \Gamma_{12} \Gamma_{13} \Gamma_{44} \]

**DFT Details**

- Kohn-Sham DFT within VASP
- GGA and PW-91
- Projector Augmented Wave (PAW) all electron method
- 2 Ions/Cell
- 24×24 ×24 Monkhorst Pack K-Point Grid
- 500 eV Kinetic Energy Cut Off
- Spin-Polarized for \( bcc \)
First-principles input into continuum model

- **bcc** elastic constants compare well with experiment ($C_{11}$ a bit high)
- little experimental data for **hcp**

<table>
<thead>
<tr>
<th>Transition</th>
<th><strong>bcc</strong> to <strong>hcp</strong> transition pressure (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPERIMENT</td>
<td>10-15</td>
</tr>
<tr>
<td>FLAPW*</td>
<td>11.5</td>
</tr>
<tr>
<td>PAW</td>
<td>10</td>
</tr>
</tbody>
</table>

PAW predicts the **bcc** to **hcp** transition pressure within the measured range

Multi-well elastic energy $\rightarrow$ phase mixing!

Multi-well free-energy density with 19 variants:

$W(F)$

Ground State $hcp$

$V, T$

Ground State $bcc$

Approximation: Taylor expansion around variant deformation

Goal: understand energy-minimizing deformation patterns (microstructures)

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Prescribed average deformation

- Free-energy minimizers need not be uniform deformations (pure phases)
- Free energy can be reduced by mixing different phases (deformation patterning)
Microstructure of martensite

Cu-Al-Ni, Chunhua Chu and Richard D. James
Microstructure of martensite

Cu-Al-Ni, Chunhua Chu and Richard D. James
Sequential laminates

**Ansatz:** Free-energy minimizing microstructures are sequential laminates

- **Rank-2 laminate**
- **Simple laminate**
- **Coherent interfaces**

Must optimize:
- Interfacial orientations
- Volume fractions
- Nesting of laminates
- Variant sizes

Constraints:
- Equilibrium at interfaces
- Coherent interfaces

(Aubry, Fago and Ortiz, *CMAME*, 2003)
Shear Compression

\[ F(\delta) = (1-\delta) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \delta \begin{pmatrix} \lambda & \varepsilon_f & 0 \\ \varepsilon_f & \lambda & 0 \\ 0 & 0 & \lambda \end{pmatrix} \]

\( \lambda \) is set such that \( V = V_f \)

(Note: \( \text{det}[F] = V \))

\( \varepsilon_f = 0.03 \)

\( \varepsilon_f = 0.04 \)

Note: mapped deformed volume onto reference volume
Role of Shear

- shear is required to activate this transformation
- increasing shear lowers the TP and increases the TV
- variability in measured TPs may be due to shear states
**What are the average bulk properties of the bcc → hcp transformation?**

To explore the transformation, we apply a series of volume-conserving deformations (F) along the transformation path.

\[
F(V, \delta) = \omega_\delta [(1 - \delta) F_{\text{bcc}}(V) + \delta F_{\text{hcp}}(V)]
\]

\[\omega = \text{volume-conserving scale factor}\]

\[0 \leq \delta \leq 1\]

The \(F(V,\delta)\) that minimizes \(W\) determines the transformation properties.
**bcc → hcp Phase Transformation**

- **full conversion to hcp**
- **transition pressure of 10 GPa**
- **hallmarks of Gibbs construction**
  - the lowering of the energy
  - the lag to full conversion to hcp
- **deviation from Gibbs construction**
  - no perfect tangent matching
  - energy is increased
  - caused by the two imposed constraints
    - Hadamard compatibility condition
      \[ F_1 - F_2 = a \otimes n \]
    - dependence on the transformation path
    - constraints introduce frustration
- **hysteresis width of ≈5.2 GPa observed**
  - loading TP = 10.2 GPa
  - unloading TP = 5.0 GPa
  - experimental width 6.2 GPa (Taylor et al.)
Directional Deformation of bcc Fe

- Propagating shock waves apply load in specific directions.

- What effect does the direction of applied load have on the transformation?

vestigate directional loading we applied directional deformation $F_{\theta,\phi}(\delta)$ spanning reaction space (angle space).

$F_{\theta,\phi}(\delta) = \delta(a' \otimes a') + (b' \otimes b') + (c' \otimes c')$

\[
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-sin \theta & 0 & \cos \theta
\end{pmatrix}
\]

\[
(a', b', c') = \left(\begin{array}{ccc}
\cos \phi & \sin \phi & 0 \\
-sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{array}\right)
\left(\begin{array}{ccc}
\cos \theta & 0 & \sin \theta \\
0 & 1 & 0 \\
-sin \theta & 0 & \cos \theta
\end{array}\right)
\]
Directional Deformation of bcc Fe: TP and TV

Transition Pressure

Transition Volume

TP for all angles is high, >20 GPa
- never optimal combination of contraction and shear
region of high pressure for moderate angles
- perhaps no hcp variant along path
loading parallel to simple facets facilitates the transformation
- notably the \(\langle 110\rangle\) planes
loading along the simple axes recovers smallest TP in that region of angle space
- \(\langle 111\rangle < \langle 101\rangle < \langle 100\rangle\)
First-principles input at finite temperature

(Sha, Cohen, Steinle-Neumann)
The pressure/volume properties of Fe subject to external strain at room temperature

Preliminary results show that the temperature effects are not very significant, but still the phase transformation tends to occur at lower pressures at room temperature than at zero temperature.

Plasticity also generates lamintes:

Shocked Ta (Meyers et al., 1995)
Conclusions

Shear Compression
- shear is required for transformation to occur
- increasing shear lowers the TP and increases the TV
- sensitivity to shear may be responsible for the variability in the measured TPs

bcc-to-hcp Transformation
- full conversion to hcp at ≈10 GPa, consistent with the experimentally observed values
- hallmarks of the Gibbs construction
- deviation from “perfect” mixing due to imposed constraints
- shows hysteresis in the TP simply due to the crystalline kinematics

Directional Deformation
- transformation pressure is > 20GPa
- region of very high transformation pressure
- loading || to simple facets facilitates the transformation, in particular along simple axes

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