Order-Disorder

Structure Analysis
Materials Science & Engineering
Seoul National University
CHAN PARK

Cullity Chap 10-9
Krawitz Chap 11.6
Hammond Chap 9.7

Order-Disorder

- Distribution of atoms among atomic sites may not be random
- A preferential pattern of site occupation - order

ordered vs. disordered
superlattice
long-range order
order-disorder transformation → changes in XRD pattern
AuCu$_3$

- Little change in lattice parameter, no change in shape $\rightarrow$ no change in $d$
- Change in atom positions $\rightarrow$ change in $I$

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> Body center - 000, $\frac{1}{2} \frac{1}{2} \frac{1}{2}$
> Face center - 000, $0 \frac{1}{2} \frac{1}{2}$, $\frac{1}{2} 0 \frac{1}{2}$, $\frac{1}{2} \frac{1}{2} 0$
> Base center - 000, $\frac{1}{2} \frac{1}{2} 0$ (or 000, $0 \frac{1}{2} \frac{1}{2}$, or 000, $\frac{1}{2} 0 \frac{1}{2}$)

> AuCu$_3$ when ordered - Au atom @ 000, Cu atom @ $0 \frac{1}{2} \frac{1}{2}$, $\frac{1}{2} 0 \frac{1}{2}$, $0 \frac{1}{2} \frac{1}{2}$ $\rightarrow$ simple cubic

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Order-disorder in AuCu$_3$

**Complete disorder**

4 average atoms @ 000; $\frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}$

\[
f_{av} = (\text{atomic fraction Au})f_{Au} + (\text{atomic fraction Cu})f_{Cu} = \frac{1}{4}f_{Au} + \frac{3}{4}f_{Cu}
\]

\[
F = \sum f_{av}e^{2\pi(ih+k)e} + e^{2\pi(ih+l)} = f_{av}[1 + e^{2\pi(ih+k)} + e^{2\pi(ih+l)}]
\]

\[
F = 4f_{av} = (f_{Au} + 3f_{Cu}), \text{ for } hkl \text{ unmixed}
\]

\[
F = 0, \text{ for } hkl \text{ mixed.}
\]

**Complete order**

One Au @ 000 & three Cu @ $\frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$

\[
F = f_{Au} + f_{Cu}[e^{2\pi(ih+k)} + e^{2\pi(ih+l)}]
\]

\[
F = (f_{Au} + 3f_{Cu}), \text{ for } hkl \text{ unmixed.}
\]

\[
F = (f_{Au} - f_{Cu}), \text{ for } hkl \text{ mixed.}
\]

**Fundamental peaks**

- much weaker than f-peaks ("difference peaks")
- direct evidence of ordering

**Superlattice peaks**

FCC

- $F = 4f$ for unmixed indices
- $F = 0$ for mixed indices

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**Long-range order parameter (S)**

- Degree of long-range order (departure from perfect order)

\[
S = \frac{r_A - F_A}{1 - F_A}
\]

- $r_A = \text{fraction of A sites occupied by A atoms}$
- $F_A = \text{fraction of A atoms in alloy}$

When long-range order is perfect, $r_A = 1 \rightarrow S = 1$

When completely random, $r_A = F_A \rightarrow S = 0$

100 atoms of AuCu$_3$; 25 Au, 75 Cu $\rightarrow$ $F_{Au} = 25/100 = 0.25$, $F_{Cu} = 0.75$

- 25 Au in Au site, 0 Au in Cu site $\rightarrow$ $r_{Au} = 25/25 = 1$, $S = (1-0.25)/(1-0.25) = 1$
- 22 Au in Au site, 3 Au in Cu site $\rightarrow$ $r_{Au} = 22/25 = 0.88$
  \[
  S = (0.88-0.25)/(1-0.25) = 0.84
  \]
- 72 Cu in Cu site, 3 Cu in Au site $\rightarrow$ $r_{Cu} = 72/75 = 0.96$
  \[
  S = (0.96-0.75)/(1-0.75) = 0.84
  \]
Order-disorder in AuCu$_3$

**Complete disorder**

\[ F = 4f_{av} = (f_{Au} + 3f_{Cu}), \text{ for } hkl \text{ unmixed.} \]

\[ F = 0, \text{ for } hkl \text{ mixed.} \]

**Complete order**

\[ F = (f_{Au} + 3f_{Cu}), \text{ for } hkl \text{ unmixed.} \]

\[ F = (f_{Au} - f_{Cu}), \text{ for } hkl \text{ mixed.} \]

**Partially ordered**

\[ F = (f_{Au} + 3f_{Cu}), \text{ for } hkl \text{ unmixed.} \]

\[ F = S(f_{Au} - f_{Cu}), \text{ for } hkl \text{ mixed.} \]

- Only the superlattice peaks are affected by disorder
- \( I \propto F^2 \rightarrow I \propto S^2 \)
- \( S \) can be determined experimentally by comparing the \( I \)'s of \( f \)-peaks and \( s \)-peaks

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**S vs. Temp**

- @ \((T/T_c) > 1\), the energy lost from the superlattice peaks \(\rightarrow\)
  diffuse scattering \(\rightarrow\) diffuse BKG due to randomness

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Cullity, Figure 10-7
Order-disorder in NiAl

NiAl

disordered

NiAl

ordered

superlattice peaks

Order-disorder in CuZn

CuZn

disordered

T > ~460°C

bcc

ordered

T < ~460°C

simple cubic

F = (f_{Cu} + f_{Zn}), (h+k+l) even

fundamental peaks

F = S(f_{Cu} - f_{Zn}), (h+k+l) odd

superlattice peaks