

Order-Disorder

Cullity Chap 10-9
Krawitz Chap 11.6
Hammond Chap 9.7

Order-Disorder

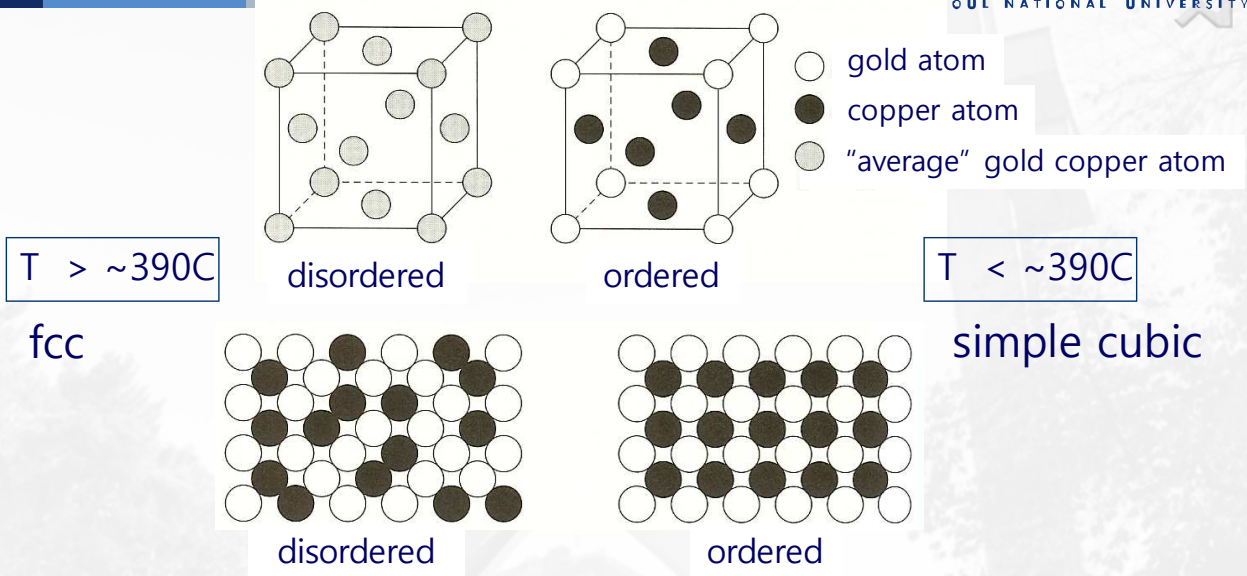
- Distribution of atoms among atomic sites may not be random.
- A preferential pattern of site occupation – order

ordered vs. disordered

superlattice

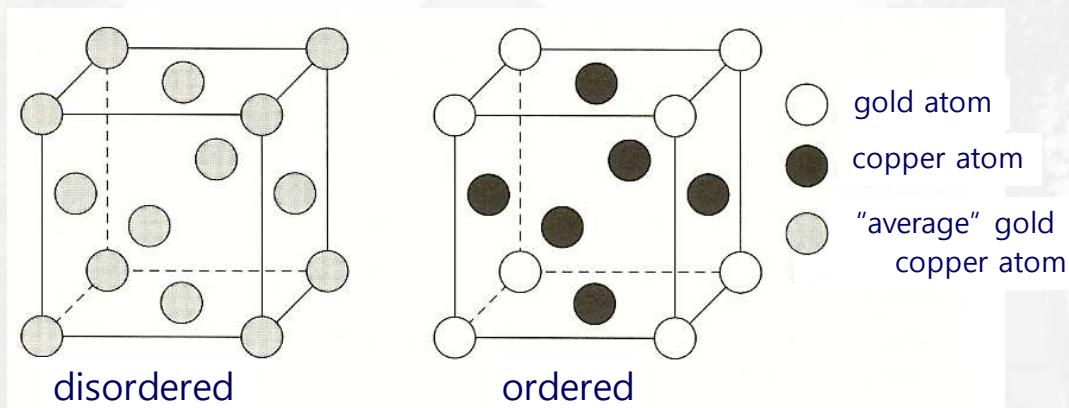
long-range order

order-disorder transformation → changes in XRD pattern



- Little change in lattice parameter, no change in shape → no change in d
- Change in atom positions → change in I

- Body center – 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
- Face center - 000, $0\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$
- Base center - 000, $\frac{1}{2}\frac{1}{2}0$ (or 000, $0\frac{1}{2}\frac{1}{2}$, or 000, $\frac{1}{2}0\frac{1}{2}$)
- AuCu₃ when ordered – Au atom @ 000, Cu atom @ $0\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}0$ → simple cubic



Complete disorder

4 average atoms @ 000; 1/2 1/2 0; 1/2 0 1/2; 0 1/2 1/2

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

$$F = \sum f e^{2\pi i(hv+kv+lw)} = f_{av}[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

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

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

fundamental peaks

FCC

$$F = 4f \text{ for unmixed indices}$$

$$F = 0 \text{ for mixed indices}$$

Complete order

One Au @ 000 & three Cu @ 1/2 1/2 0; 1/2 0 1/2; 0 1/2 1/2

$$F = f_{Au} + f_{Cu}[e^{\pi i(h+k)} + e^{\pi i(h+l)}e^{\pi i(k+l)}]$$

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

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

superlattice peaks

✓ much weaker than f-peaks ("difference peaks")

✓ direct evidence of ordering

Long-range order parameter (S)

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

long-range order parameter (S)

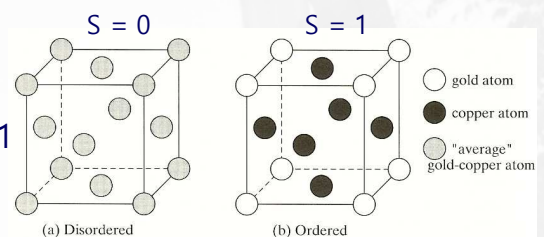
$$S = \frac{r_A - F_A}{1 - F_A}$$

r_A = fraction of A sites occupied by A atoms

F_A = 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 AuCu₃; 25 Au, 75 Cu → $F_{Au} = 25/100 = 0.25$, $F_{Cu} = 0.75$

25 Au in Au site, 0 Au in Cu site → $r_{Au} = 25/25 = 1$, $S = (1-0.25)/(1-0.25) = 1$

22 Au in Au site, 3 Au in Cu site → $r_{Au} = 22/25 = 0.88$,

$$S = (0.88-0.25)/(1-0.25) = 0.84$$

72 Cu in Cu site, 3 Cu in Au site → $r_{Cu} = 72/75 = 0.96$,

$$S = (0.96-0.75)/(1-0.75) = 0.84$$

Complete disorder $F = 4f_{av} = (f_{Au} + 3f_{Cu})$, for hkl unmixed
 $F = 0$, for hkl mixed. fundamental peaks

Complete order $F = (f_{Au} + 3f_{Cu})$, for hkl unmixed,
 $F = (f_{Au} - f_{Cu})$, for hkl mixed.
superlattice peaks

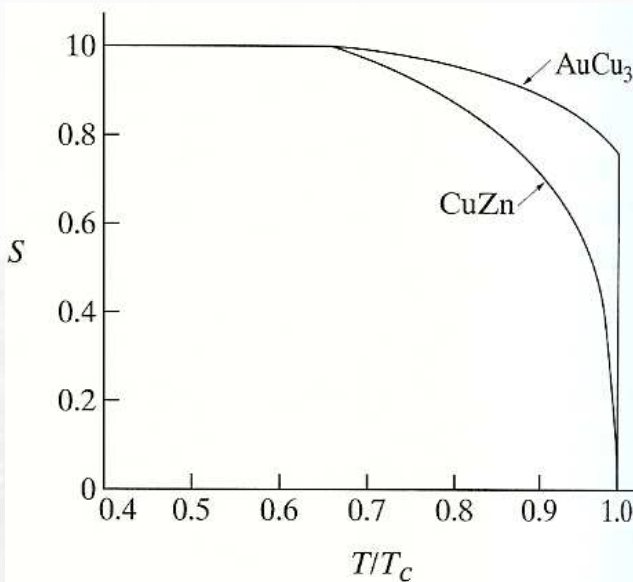
Partially ordered

$F = (f_{Au} + 3f_{Cu})$, for hkl unmixed.

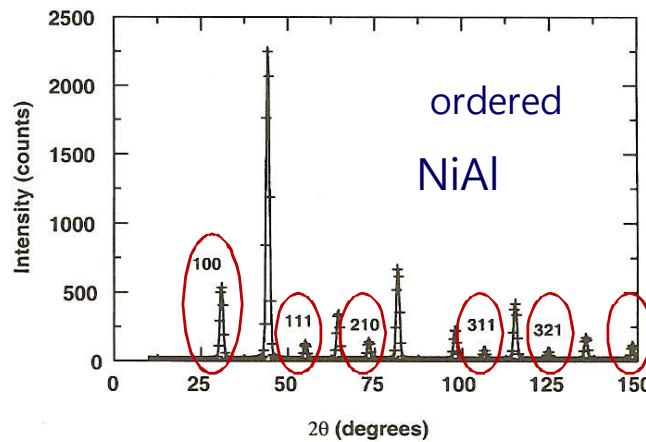
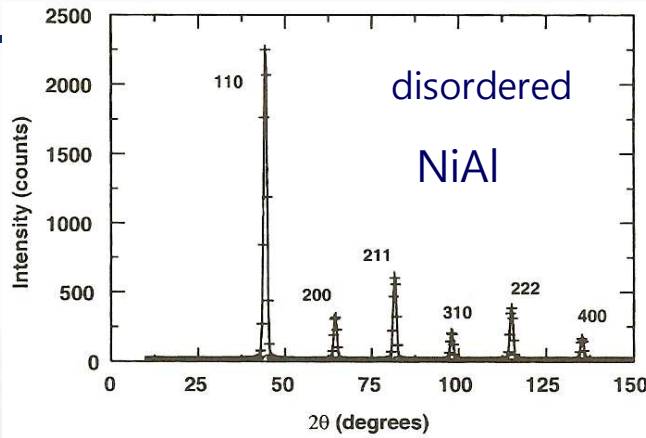
$F = S(f_{Au} - f_{Cu})$, for hkl mixed.

- 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.

S vs. Temp

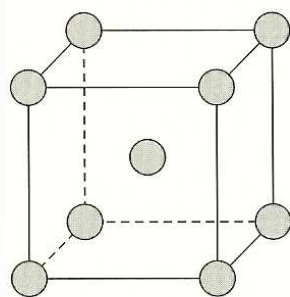


- @ $(T/T_c) > 1$, the energy lost from the superlattice peaks → diffuse scattering → diffuse BKG due to randomness



superlattice peaks

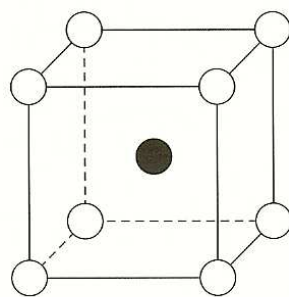
Order-disorder in CuZn



disordered

$$T > \sim 460C$$

bcc



ordered

$$T < \sim 460C$$

simple cubic

- zinc atom
- copper atom
- "average" zinc copper atom

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

fundamental peaks

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

superlattice peaks