# Order-Disorder

Structure Analysis
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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

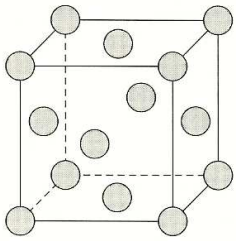
ordered vs. disordered

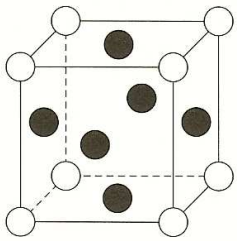
superlattice

long-range order

order-disorder transformation → changes in XRD pattern

## $AuCu_3$





gold atom
copper atom
"average" gold copper atom

T > ~390C

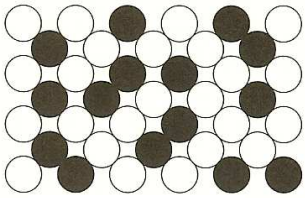
disordered

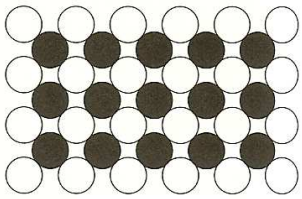
ordered

T < ~390C

fcc

simple cubic





disordered

ordered

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



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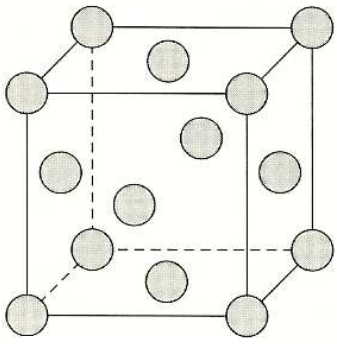
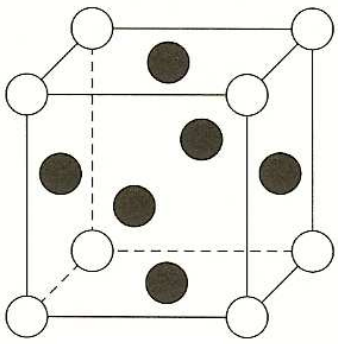
## $AuCu_3$

- 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 @ $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$ → simple cubic





gold atom
copper atom
"average" gold copper atom

disordered

ordered



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## Order-disorder in $AuCu_3$

**Complete disorder** — 4 average atoms @ 000; ½½0; ½0½; 0½½

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

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

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

$F = 0$, for $hkl$ mixed.

fundamental peaks

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

**Complete order** — One Au @ 000 & three Cu @ ½½0; ½0½; 0½½

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

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

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

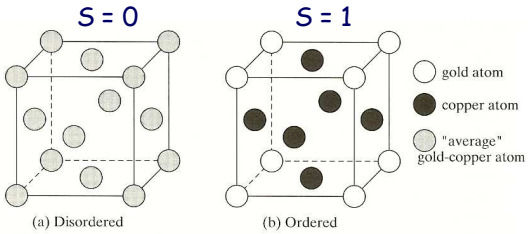
$$S = \frac{r_A - F_A}{1 - F_A}$$

$r_A$ = 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 $AuCu_3$; 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

## Order-disorder in $AuCu_3$

**Complete disorder**

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

fundamental peaks

$F = 0$, for $hkl$ mixed.

**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



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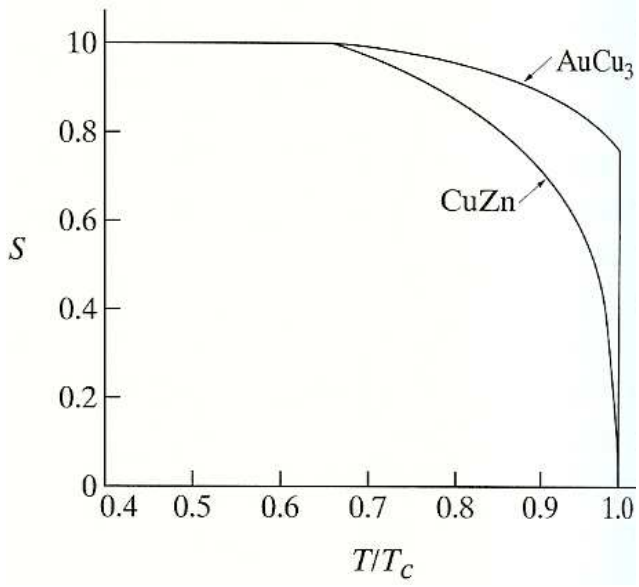
## S vs. Temp

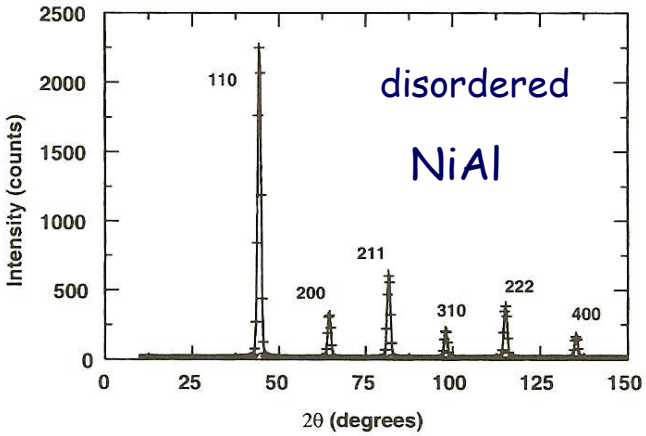


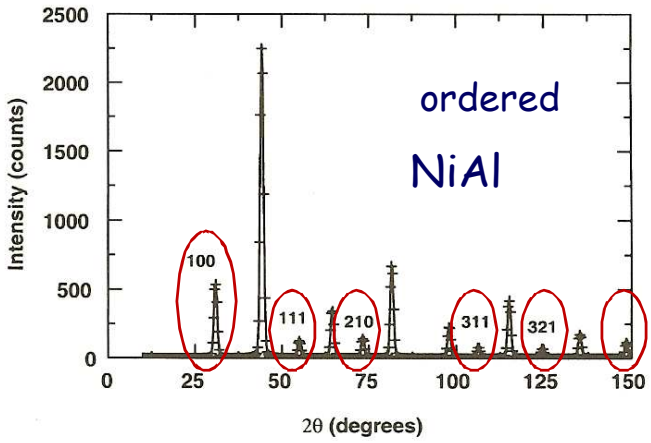

- @ $(T/T_c) > 1$, the energy lost from the supperlattice peaks → diffuse scattering → diffuse BKG due to randomness



Cullity, Figure 10-7

## Order – disorder in NiAl



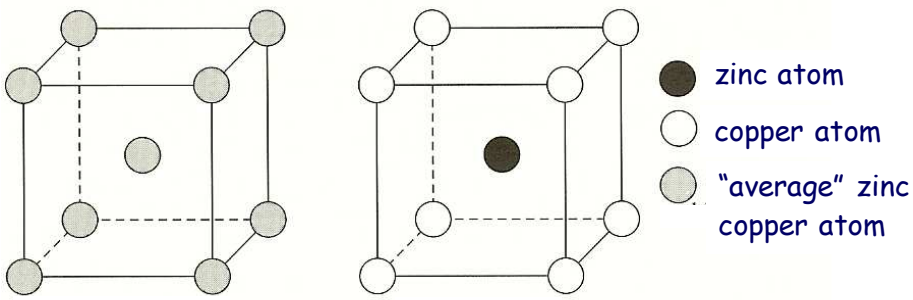




superlattice peaks

Krawitz



## Order-disorder in CuZn




disordered ordered

T > ~460C T < ~460C

bcc 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



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