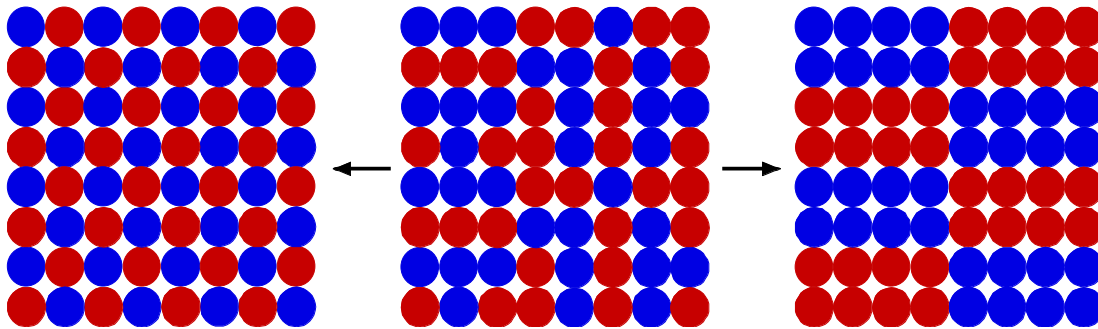


Lecture 25: Ordering Transformation

Today's topics

- Understanding of the concepts of “ideal solution”, “regular solution” and “real solution”, and comparison of the mixing thermodynamics between them regarding the free energy, enthalpy and entropy change.
- Understanding of ordered phase: how to define the short-range order (SRO) and long-range order (LRO).
- Ordering transformation: the way in which the degree of LRO and SRO decreases with temperature is different for different superlattices.



Before going through the Ordering Transformation, we need to understand the following basic thermodynamics about solid solutions

Ideal solution: (refs to the Book, "Phase Transformations in Metals and Alloys", by D. A. Porter, K. E. Easterling and M. Y. Sherif, CRC Press, third edition). Note: the figures below are cited from this Book.

The simplest type of mixing, for which the enthalpy change of the mixing, $\Delta H_{\text{mix}}=0$; the resultant solution is said to be ideal, and the free energy change on mixing is only due to the change in entropy, $\Delta G_{\text{mix}}=\Delta H_{\text{mix}} - T\Delta S_{\text{mix}}= - T\Delta S_{\text{mix}}$.

Since $\Delta S_{\text{mix}} = -R(X_A \ln X_A + X_B \ln X_B)$, we have $\Delta G_{\text{mix}} = RT(X_A \ln X_A + X_B \ln X_B)$

Regular solution: (refs to the same Book above)

The ideal solution as defined above, $\Delta H_{\text{mix}}=0$ is almost impossible in practice, where the mixing is, however, either endothermic (heat absorbed, $\Delta H_{\text{mix}} > 0$) or exothermic (heat evolved, $\Delta H_{\text{mix}} < 0$). For a regular solution, where $\Delta H_{\text{mix}} \neq 0$, the free energy change of the mixing includes the ΔH_{mix} term, which in turn can be described by a so-called “quasichemical model” --- i.e., the heat of the mixing, ΔH_{mix} is only due to the bond energies between adjacent atoms. For this assumption to be valid, it is necessary that *the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are independent of*

composition.

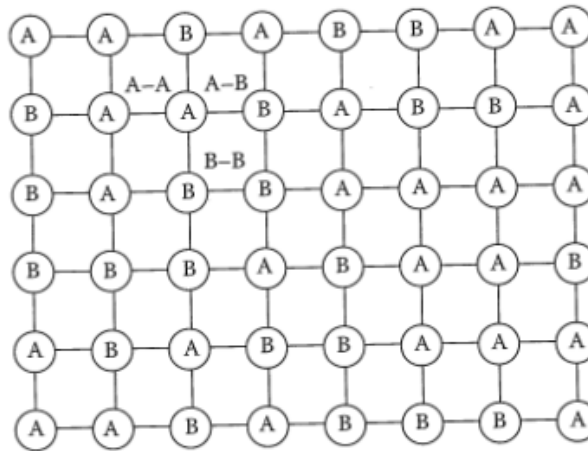


FIGURE 1.13
Different types of interatomic bond in solid solution.

As shown in Figure 1.13 above (cited from the book above): the structure of a regular solid solution, where three types of interatomic bonds are present:

1. A-A bonds each with an energy ϵ_{AA}
2. B-B bonds each with an energy ϵ_{BB}
3. A-B bonds each with an energy ϵ_{AB}

Lets define zero energy to be the state where the atoms are separated to infinity, then ϵ_{AA} , ϵ_{BB} , ϵ_{AB} , are all negative in quantity (forming a bond is an exothermic process), and become increasingly more negative as the bonds become stronger. The internal energy (E) of the solution will be determined by the number of bonds of each type, P_{AA} , P_{BB} , P_{AB} ,

$$E = P_{AA} \epsilon_{AA} + P_{BB} \epsilon_{BB} + P_{AB} \epsilon_{AB}$$

Then, the change of internal energy on mixing (ΔH_{mix}) can be expressed as

$$\Delta H_{\text{mix}} = P_{AB} \epsilon$$

where, $\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2$, is the difference between the A-B bond energy and the average of the A-A and B-B bond energies.

For an ideal solution, $P_{AB} = N_0 z X_A X_B$ (bonds per mole),

where N_0 is the Avogadro constant, z is the number of bonds per atom, X_A and X_B are the molar fraction of A and B atom, respectively.

Assuming ϵ is not too different from zero (quite close to the situation of ideal solution), for a regular solution we can still approximately have: $P_{AB} = N_0 z X_A X_B$ (bonds per mole),

Now, let's define $\Omega = N_0 z \epsilon$; Ω is interaction parameter

$$\text{Then, } \Delta H_{\text{mix}} = P_{AB} \epsilon = \Omega X_A X_B$$

Therefore, for a regular solution, we have the free energy change of mixing:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}} = \Omega X_A X_B + RT(X_A \ln X_A + X_B \ln X_B)$$

Real solution: (refs to the same *Book above*)

Considering the “quasichemical model” described above --- i.e., the heat of the mixing, ΔH_{mix} is only due to the bond energies between adjacent atoms, or in other words, *the volumes of pure A and B are equal and do not change during mixing so that the interatomic distance and bond energies are **independent of composition**,*

However, the model is oversimplified for many systems in practice (i.e., the **real solutions**), and does not provide correct dependence of ΔG_{mix} on **composition** and **temperature**. For the **real solutions**, it is simply not true to assume that a random arrangement of atoms (as shown in Figure 1.13 above) is the equilibrium (or the most stable arrangement); the calculated value of ΔG_{mix} will not give the minimum free energy change.

The actual atomic arrangement for a real solution (as depicted in Figure 1.18) will be a compromise that gives the **lowest internal energy** (i.e., $|\Delta H_{\text{mix}}|$ is maximized) consistent with **sufficient entropy** (or randomness, ΔS_{mix}), so as to achieve the minimum ΔG_{mix} .

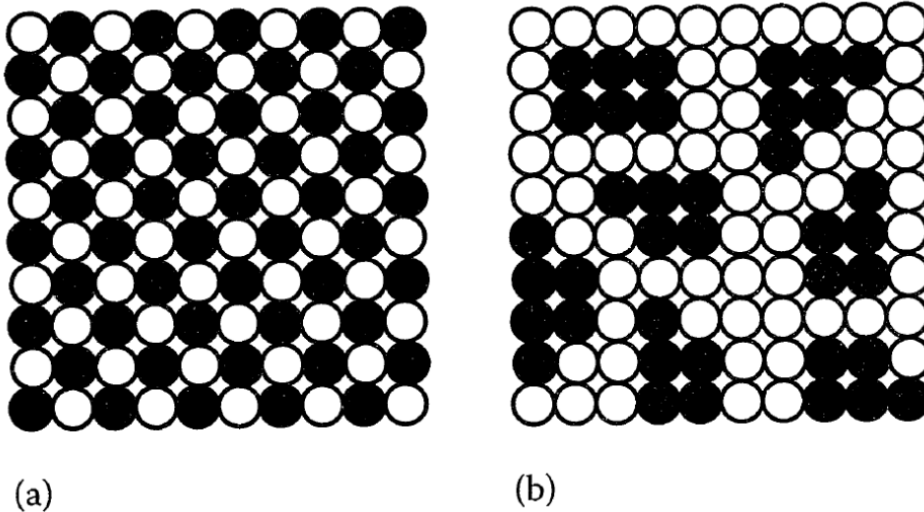


FIGURE 1.18

Schematic representation of solid solutions: (a) ordered substitutional, (b) clustering

- When $\epsilon < 0$, A-B bonding is thermodynamically favorable (or atoms in solution prefer to be surrounded by atoms of the opposite type), the internal energy of the system is reduced (or ΔH_{mix} becomes more negative) by increasing the number of A-B bonds, i.e., by **ordering** the two atoms as shown in Figure 1.18a.
- When $\epsilon > 0$, A-B bonding is not thermodynamically favorable (or atoms in solution prefer to cluster by themselves), the internal energy of the system can be reduced (or ΔH_{mix} becomes more negative) by increasing the number of A-A and B-B bonds, i.e., by **clustering** the atoms into A-rich and B-rich domains, as shown in Figure 1.18b.
- Both the two situation above describe **substitutional** solid solution, for which the degree of **ordering** and **clustering** will decrease when temperature increases due to the increasing importance of **entropy**.

Ordered phase: (refs to the same *Book above*)

If the atoms in a substitutional solid solution are completely randomly arranged, each atom position is equivalent and the probability that any given site in the lattice will be occupied by an A atom will be equal to the fraction of A atoms in the solution X_A , in the same way X_B for the B atoms. In such a case, the number of

A-B bonds, now marked as P_{AB} (random), can be given following the same equation above:

$$P_{AB}(\text{random}) = N_0 z X_A X_B \text{ (bonds per mole)}$$

If the real number of A-B bonds, P_{AB} , $>$ $P_{AB}(\text{random})$, the solution is said to contain **short-range order (SRO)**.

The degree of ordering can be quantified by defining a SRO parameter, “S”, as such

$$S = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$

Where $P_{AB}(\text{max})$ and $P_{AB}(\text{random})$ refer to the maximum number of A-B bonds possible and the number of A-B bonds for a random solution, respectively.

Figure 1.19 shows the difference between random and short-range ordered solutions with total of 100 atoms ($X_A = X_B = 0.5$):

- Figure 1.19a, for a random solution, $P_{AB} = P_{AB}(\text{random}) = 100$, then, $s = 0$.
- Figure 1.19b, for a short-range ordered solution, $P_{AB} = 132$, with $P_{AB}(\text{max}) \sim 200$, we have $s = 0.32$.

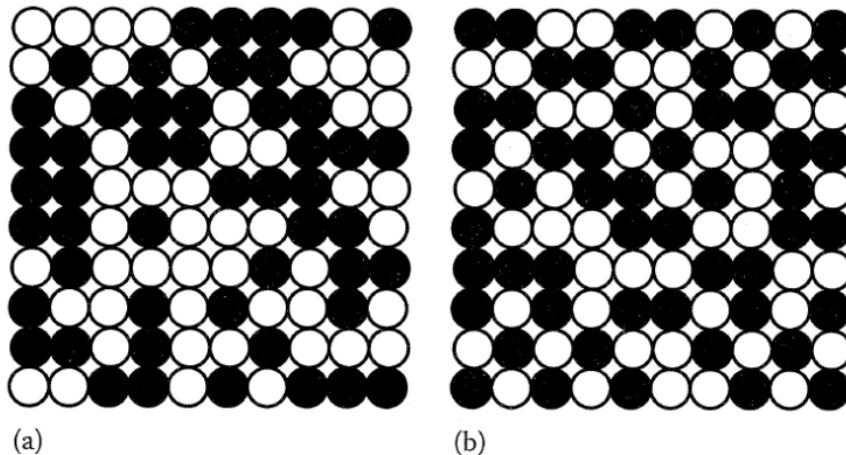


FIGURE 1.19

(a) Random A–B solution with total of 100 atoms and $X_A = X_B = 0.5$. $P_{AB} \sim 100$, $S = 0$. (b) Same alloy with SRO $P_{AB} = 132$. $P_{AB(\text{max})} \sim 200$, $S = (132 - 100)/(200 - 100) = 0.32$.

In solutions with compositions that are close to a simple ratio of A:B atoms another type of order can be found as shown schematically in Figure 1.18a. This is known as **long-range order (LRO)**. Now the atom sites are no longer equivalent, but can be labeled as A-sites and B-sites. Such a solution can be considered to be a different (ordered) phase separate from the random or nearly random solution.

An example of LRO is for Cu-Au alloy, as shown in Figure 1.20, where Cu and Au are both fcc and totally miscible:

- At high temperatures Cu and Au atoms can occupy any site and the lattice can be considered as fcc with a “random” atom at each lattice point as shown in Figure 1.20a.

- At low temperatures, however, solutions with $X_A = X_B = 0.5$, form an ordered structure in which the Cu and Au atoms are arranged in alternate layers as shown in figure 1.20b. Now, each atom position is no longer equivalent and the lattice is described as a CuAu **superlattice**.
- For alloys with the composition Cu_3Au , another superlattice is found as shown in Figure 1.20c.

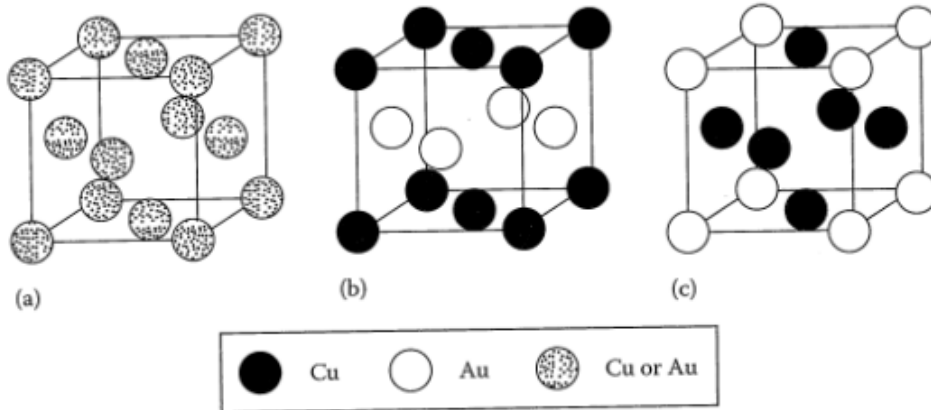


FIGURE 1.20
 Ordered substitutional structures in the Cu–Au system: (a) high-temperature disordered structure, (b) CuAu superlattice, and (c) Cu_3Au superlattice.

Including the ordered lattice shown in Figure 1.20, there are five most common ordered lattices as summarized in Figure 1.22 along with their Strukturbericht notation and examples of alloys in which they are found.

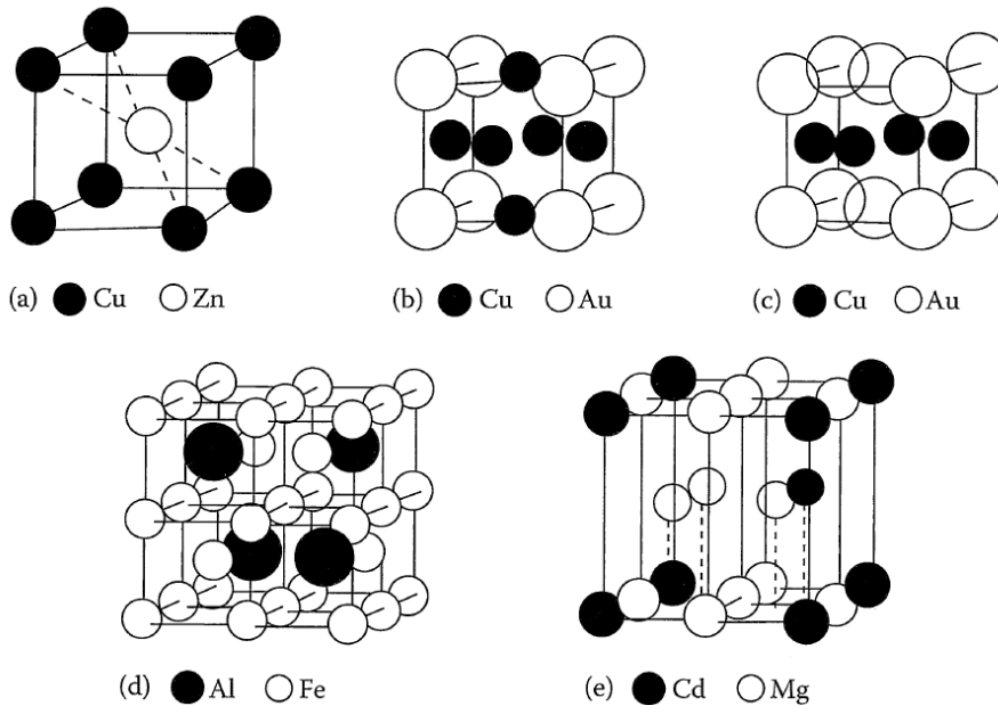


FIGURE 1.22

The five common ordered lattices, examples of which are (a) L2₀: CuZn, FeCo, NiAl, FeAl, AgMg; (b) L1₂: Cu₃Au, Au₃Cu, Ni₃Mn, Ni₃Fe, Ni₃Al, Pt₃Fe; (c) L1₀: CuAu, CoPt, FePt; (d) D0₃: Fe₃Al, Fe₃Si, Fe₃Be, Cu₃Al; (e) D0₁₉: Mg₃Cd, Cd₃Mg, Ti₃Al, Ni₃Sn. (After Smallman, R.E., *Modern Physical Metallurgy*, 3rd edn., Butterworths, London, 1970.)

Ordering Transformation:

It occurs when solution has a negative enthalpy of mixing, $\Delta H_{\text{mix}} < 0$.

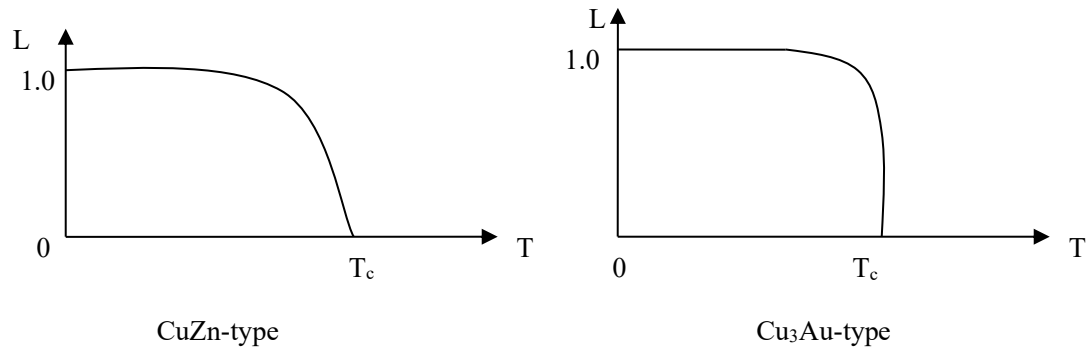
Define long-range order parameter:

$$L = \frac{r_A - X_A}{1 - X_A} = \frac{r_B - X_B}{1 - X_B}$$

Where X_A is molar fraction of A atoms; r_A are probability of A lattice sites occupied by “right” A atoms; X_B and r_B , similarly for B atoms.

- At $T=0$, $L=1$, complete order ($\Delta S = 0$), corresponding to the lowest internal energy, ΔG_{mix} minimized.
- As $T \uparrow$, $L \downarrow$, due to entropy contribution --- some atoms interchange positions by diffusion so that they are located on “wrong” sites. Entropy effects becomes increasingly more important.
- As $T > T_c$, $L = 0$, complete disorder.

Using the quasichemical model as described above for the “regular solution”, it is possible to calculate how L changes with temperature for different superlattices as shown in Figure 1.20 for an example.



Schematic diagram showing the variation of **long-range order parameter (L)** with temperature for (a) CuZn-type and (b) Cu₃Au-type alloy transformation.

From the Figure above we can see: *the way in which L decreases to zero is different for different lattices.*

- For the equiatomic CuZn alloy, L decreases continuously with temperature up to T_c
- For the Cu₃Au alloy, L decreases only slightly up to T_c , and then abruptly drops to zero.