

Alloys

General Reminder: Alloys are mixtures of metal with other metals or non-metals.

A crystal is composed of two elements A and B that occupy at random the regular lattice sites of the structure, in proportion x and $1-x$ for the structure A_xB_{1-x} alloy.

The translation symmetry is no longer perfect in alloys.

Does it affect: Fermi surface, Band gaps etc.
Will insulator becomes conductor?

Why alloys are important ?

Mixing metals together or with non-metals offers enhanced hardness, lower melting points, and better tensile strength. Since pure metals have a high melting point, they tend to be very soft. Pure gold tends to be very malleable and is easily bent with a small amount of heat applied. This is the reason why most gold jewellery is actually an alloy.

Metals tend to be very reactive and have high melting points. Iron, for example, is very strong but reacts with moisture in the air and can rust very easily. Casting iron as an alloy can help to increase its inertness and prevent this.

The physical properties of metals can be tuned by alloying with the suitable element(s).

Types of alloys

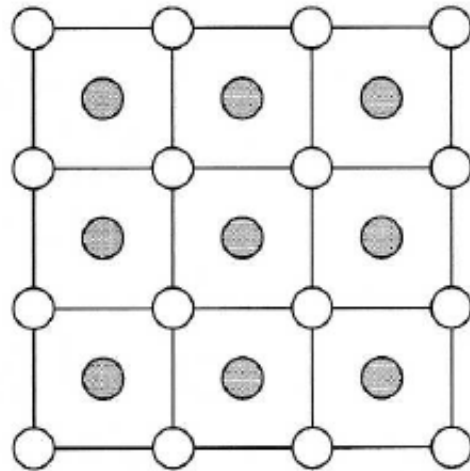
Substitutional solid solutions: Solute substitutes the solvent crystal lattice without structural changes. The atoms of the original metal are literally replaced with atoms that have roughly the same size from another material. Brass, for example, is an example of a substitution alloy of copper and zinc.

(This is of our interest and will be discussed in detail)

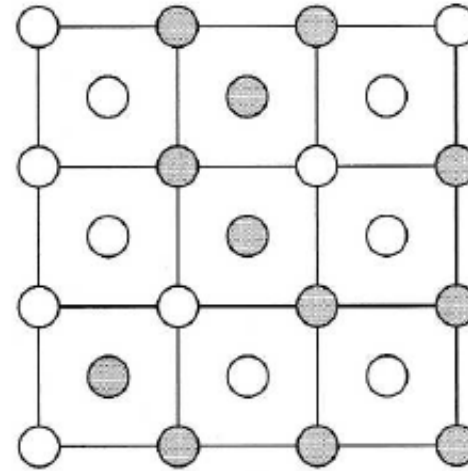
Interstitial: Solute does not occupy the sites in the lattice of the solvent but resides in crystallographic pores. Mix the atoms together with large difference in their atomic radii.

Alloys: ordered and disordered

In substitutional solid solution, the arrangement of the solute atoms may be disordered (random) or ordered.



Ordered



Disordered

Ordered Phase: A and B in $A_{1-x}B_x$ occupy a particular site (either at centre or corner) of the lattice

Disordered Phase: A and B in $A_{1-x}B_x$ alloy occupy the lattice sites of the structure randomly

Alloys: Substitutional solid solutions

Substitution of metal A to metal B: Some alloy systems show complete solid solubility while others exhibits limited solubility.

What factors decide solubility ?

These are expressed as a series of rules often called as **Hume-Rothery Rules**. These are the empirical requirements for the solubility of a solid solutions of A and B as single phase system

Alloys: Substitutional solid solutions

Hume-Rothery Rule 1: Atomic Size compatibility

Extensive substitutional solid solution occurs only if the difference between the atomic diameters (radii) of the two atoms is less than 15%. If the difference $> 15\%$, the solubility is limited. The empirical rule given by Hume-Rothery is given as:

$$\text{Difference (radii)} = \left(\frac{r_{\text{Solute}} - r_{\text{Solvent}}}{r_{\text{Solvent}}} \right) \times 100 < 15\%$$

Example: The diameters are favourable in Cu(2.55Å) – Zn (2.65Å) alloy system, where Zn dissolves in Cu as a FCC solid solution up to 38%. The diameters are less favourable for Cu(2.55Å)-Cd(2.97Å) system, where only 1.7 % of Cd soluble in Cu.

Hume-Rothery Rule 2: Crystal Structure

The crystal structures of the two elements must be same.

Hume-Rothery Rule 3: Valency Rule.

A metal will dissolve a metal of higher valency to a greater extent than one of lower valency. The solute and solvent atoms should typically have the same valence in order to achieve maximum solubility.

Hume-Rothery Rule 4: Electronegativity Rule

The solid solution will not be form if one element is strongly electropositive and other is strongly electronegative. In this case, the greater is the likelihood that they will form an intermetallic compound instead of a substitutional solid solution. Electronegativity difference close to 0 gives maximum solubility.

Cu-Zn Alloy: Phase diagram

Changes in the electron concentration determines the structural changes in alloy systems. Electron concentration means average electrons per atom.

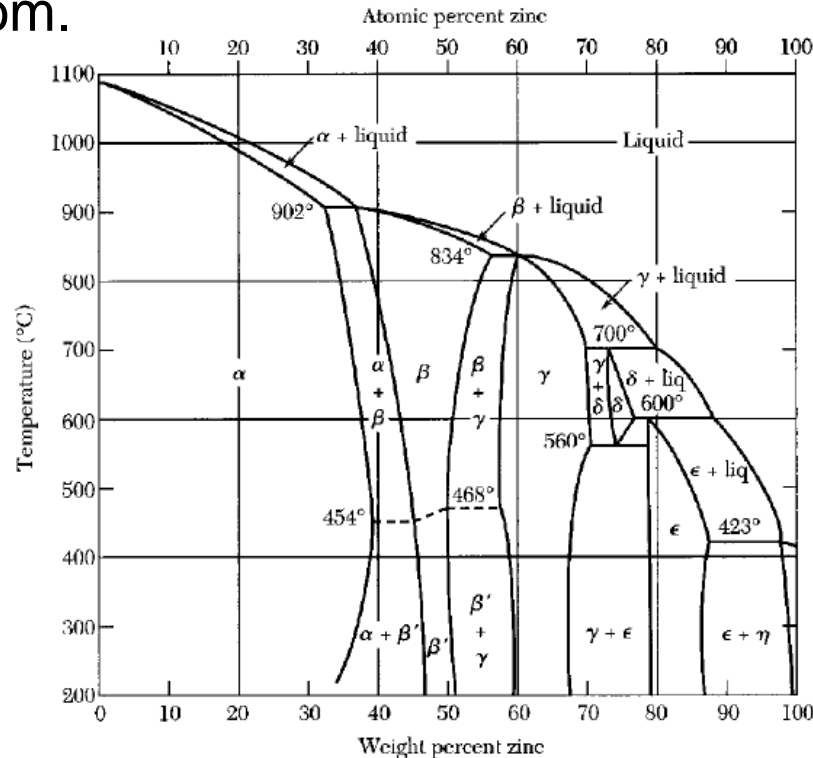


Figure Equilibrium diagram of phases in the copper-zinc alloy system. The α phase is fcc; β and β' are bcc; γ is a complex structure; ϵ and η are both hcp, but ϵ has a c/a ratio near 1.56 and η (for pure Zn) has $c/a = 1.86$. The β' phase is ordered bcc, by which we mean that most of the Cu atoms occupy sites on one sc sublattice and most of the Zn atoms occupy sites on a second sc sublattice that interpenetrates the first sublattice. The β phase is disordered bcc: any site is equally likely to be occupied by a Cu or Zn atom, almost irrespective of what atoms are in the neighboring sites.

Hume-Rothery Rules: Predictions through band theory

The H-R rules find a simple expression on the basis of band theory of nearly free electron model. The observed limit of the FCC phase occurs close to the electron concentration of 1.36 at which an inscribed Fermi sphere (FS) makes contact with Brillouin zone (BZ) boundary for FCC lattice. For BCC and γ phase, it is 1.48 and 1.54, respectively. Contact of FS for HCP phase is at the electron concentration 1.69. Here, electron concentration is the average number of electrons per atom

The connection between electron concentration and structural changes:

It may be energetically favourable for a crystal structure to change to one which can contain Fermi surface of larger volume (accommodate more number of electrons) before touching the zone boundary of the Brillouin Zone.

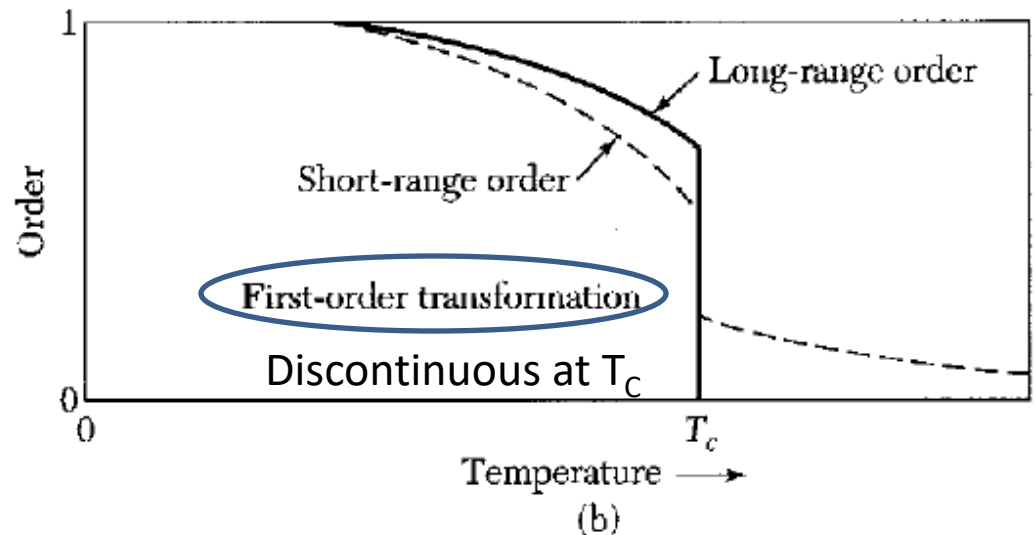
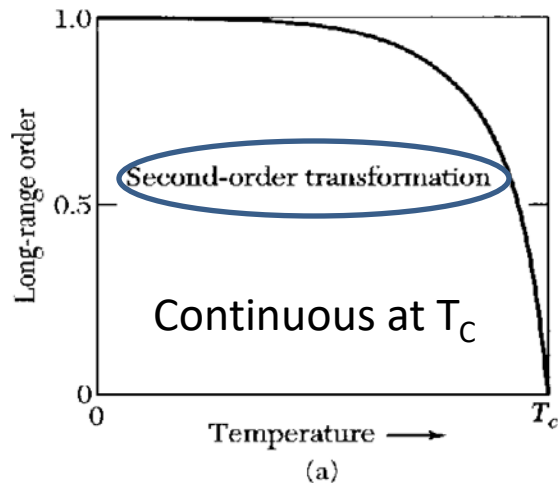
Representative experimental value for various alloys

Table 1 Electron/atom ratios of electron compounds

Alloy	fcc phase boundary	Minimum bcc phase boundary	γ -phase boundaries	hcp phase boundaries
Cu-Zn	1.38	1.48	1.58–1.66	1.78–1.87
Cu-Al	1.41	1.48	1.63–1.77	
Cu-Ga	1.41			
Cu-Si	1.42	1.49		
Cu-Ge	1.36			
Cu-Sn	1.27	1.49	1.60–1.63	1.73–1.75
Ag-Zn	1.38		1.58–1.63	1.67–1.90
Ag-Cd	1.42	1.50	1.59–1.63	1.65–1.82
Ag-Al	1.41			1.55–1.80

Ordered – Disordered Transitions

Any alloy system is completely ordered at absolute zero. As the temperature goes up, it becomes less ordered, until a transition temperature is reached above which it becomes disordered. The transition temperature represents the disappearance of **long-range order (LRO)**. In some cases, **short range order (SRO)** which is correlation between nearest neighbours, persists above the transition temperature.



Investigation of degree of ordered phase

Experimental technique: X-ray Diffraction

The ordered structure has extra diffraction lines not present in the disordered structure. These extra lines are called superstructure lines.

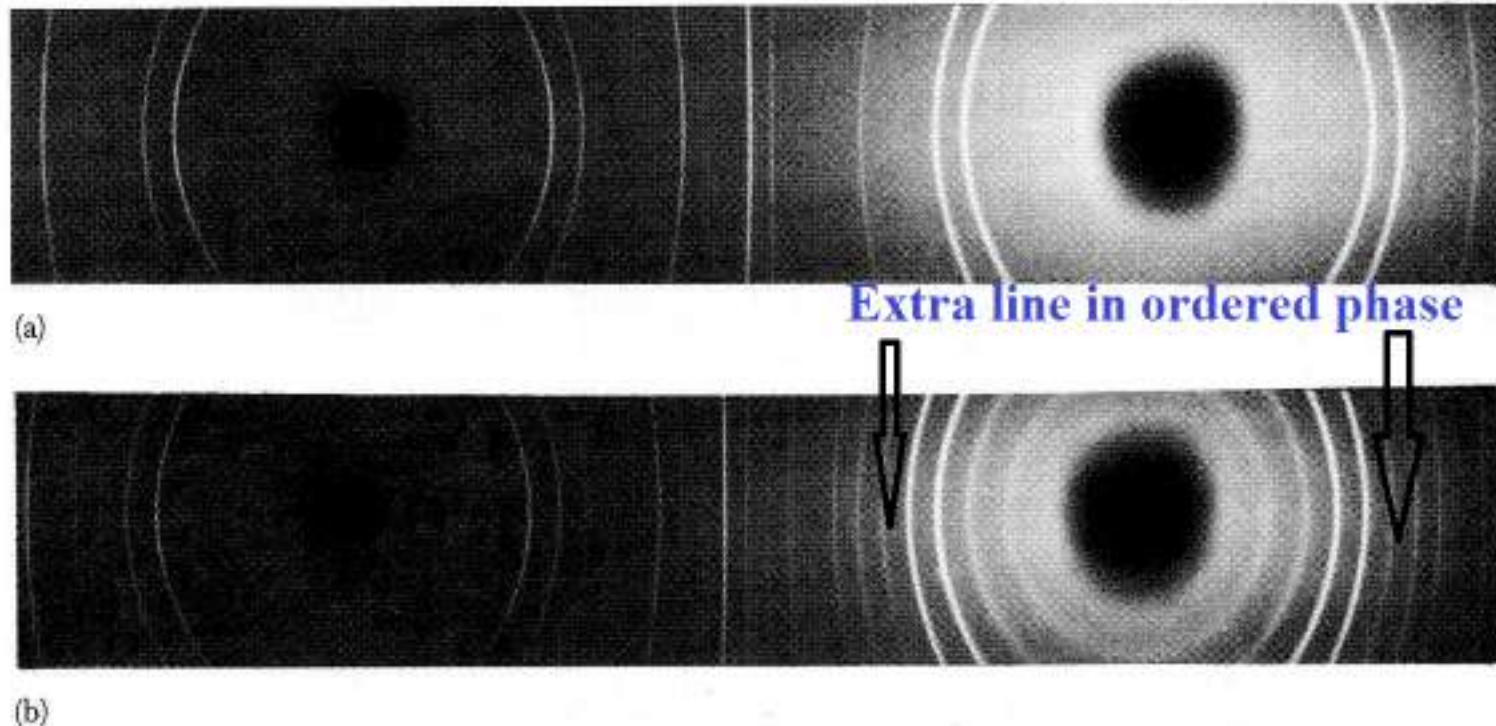


Figure X-ray powder photographs in AuCu₃ alloy. (a) Disordered by quenching from $T > T_c$; (b) ordered by annealing at $T < T_c$. (Courtesy of G. M. Gordon.)

Why extra diffraction lines in ordered structure?

The structure of the ordered CuZn alloy is the cesium chloride structure of Chapter 1. The space lattice is simple cubic, and the basis has one Cu atom at 000 and one Zn atom at $\frac{111}{222}$. The diffraction structure factor

$$S(hkl) = f_{\text{Cu}} + f_{\text{Zn}} e^{-i\pi(h+k+l)} . \quad (1)$$

This cannot vanish because $f_{\text{Cu}} \neq f_{\text{Zn}}$; therefore all reflections of the simple cubic space lattice will occur. In the disordered structure the situation is different: the basis is equally likely to have either Zn or Cu at 000 and either Zn or Cu at $\frac{111}{222}$. Then the average structure factor is

$$\langle S(hkl) \rangle = \langle f \rangle + \langle f \rangle e^{-i\pi(h+k+l)} , \quad (2)$$

where $\langle f \rangle = \frac{1}{2}(f_{\text{Cu}} + f_{\text{Zn}})$. Equation (2) is exactly the form of the result for the bcc lattice; the reflections vanish when $h + k + l$ is odd. We see that the ordered lattice has reflections (the superstructure lines) not present in the disordered lattice.

Elementary theory of order: Statistical treatment

Consider two simple cubic lattices, one of side a and other b . The BCC lattice is composed of two interpenetrating SC lattices, and the nearest neighbours of an atom on one lattice, lie on the other lattice. If there are N atom A and N atoms B in the alloy. The **long range order parameter P** is defined so that the numbers of A's on the lattice a is equal to $\frac{1}{2}(1+P)N$. The Number of A's on lattice b is equal to $\frac{1}{2}(1-P)N$.

Verification of this assumption:

$P = \pm 1$. In this case all A atoms occupy lattice a and B atoms occupy lattice b . This means the structure is perfectly ordered

$P = 0$, A and B atoms are distributed in equal number on both the lattices. This means there is no long range ordering

Structure is perfectly ordered when order parameter (P) is equals to one and is disordered when P equals to zero.

Elementary theory of order: Statistical treatment

We consider that part of the internal energy associated with the bond energies of AA , AB , and BB nearest-neighbor pairs. The total bond energy is

$$E = N_{AA}U_{AA} + N_{BB}U_{BB} + N_{AB}U_{AB} , \quad (3)$$

where N_{ij} is the number of nearest-neighbor ij bonds and U_{ij} is the energy of an ij bond.

The probability that an atom A on lattice a will have an AA bond is equal to the probability that an A occupies a particular nearest-neighbor site on b , times the number of nearest-neighbor sites, which is 8 for the bcc structure. We assume that the probabilities are independent. Thus, by the preceding expressions for the number of A 's on a and b ,

$$\begin{aligned} N_{AA} &= 8\left[\frac{1}{2}(1+P)N\right]\left[\frac{1}{2}(1-P)\right] = 2(1-P^2)N ; \\ N_{BB} &= 8\left[\frac{1}{2}(1+P)N\right]\left[\frac{1}{2}(1-P)\right] = 2(1-P^2)N ; \\ N_{AB} &= 8N\left[\frac{1}{2}(1+P)\right]^2 + 8N\left[\frac{1}{2}(1-P)\right]^2 = 4(1+P^2)N . \end{aligned} \quad (4)$$

Elementary theory of order: Statistical treatment

The energy (3) becomes

$$E = E_0 + 2NP^2U , \quad (5)$$

where

$$E_0 = 2N(U_{AA} + U_{BB} + 2U_{AB}) ; \quad U = 2U_{AB} - U_{AA} - U_{BB} . \quad (6)$$

We now calculate the entropy of this distribution of atoms. There are $\frac{1}{2}(1 + P)N$ atoms A and $\frac{1}{2}(1 - P)N$ atoms B on lattice a ; there are $\frac{1}{2}(1 - P)N$ atoms A and $\frac{1}{2}(1 + P)N$ atoms B on lattice b . The number of arrangements G of these atoms is

$$G = \left[\frac{N!}{[\frac{1}{2}(1 + P)N]![\frac{1}{2}(1 - P)N]!} \right]^2 . \quad (7)$$

From the definition of the entropy as $S = k_B \ln G$, we have, using Stirling's approximation,

$$S = 2Nk_B \ln 2 - Nk_B[(1 + P)\ln(1 + P) + (1 - P)\ln(1 - P)] . \quad (8)$$

This defines the **entropy of mixing**. For $P = \pm 1$, $S = 0$; for $P = 0$, $S = 2Nk_B \ln 2$.

Elementary theory of order: Statistical treatment

The equilibrium order is determined by the requirement that the free energy $F = E - TS$ be a minimum with respect to the order parameter P . On differentiating F with respect to P , we have as the condition for the minimum

$$4NPU + Nk_B T \ln \frac{1+P}{1-P} = 0 . \quad (9)$$

The transcendental equation for P may be solved graphically; we find the smoothly decreasing curve shown in Fig a slide 11 Near the transition we may expand (9) to find $4NPU + 2Nk_B TP = 0$. At the transition temperature $P = 0$, so that

$$T_c = -2U/k_B . \quad (10)$$

For a transition to occur, the effective interaction U must be negative.

Elementary theory of order: Statistical treatment

The **short-range order parameter** r is a measure of the fraction of the average number q of nearest-neighbor bonds that are AB bonds. When completely disordered, an AB alloy has an average of four AB bonds about each atom A . The total possible is eight. We may define

$$r = \frac{1}{4}(q - 4) \quad , \quad (11)$$

so that $r = 1$ in complete order and $r = 0$ in complete disorder. Observe that r is a measure only of the local order about an atom, whereas the long-range order parameter P refers to the purity of the entire population on a given sublattice. Above the transition temperature T_c the long-range order is rigorously zero, but the short-range order is not.

Phase diagram

Many alloy systems exist in more than one phase depending upon the condition of temperature, pressure and compositions. Each phase will have different structure/microstructure and which is related to the physical properties. The phase diagram (as a function of composition and temperature, which is also termed as x-T curve) of Cu-Zn alloy system was shown in slide 8.

In an alloy system, when a small fraction of a homogenous liquid freezes, the composition of the solid that forms is almost always different from that of liquid. If we consider a horizontal section of Cu-Zn phase diagram (x-T curve) near the composition $\text{Cu}_{0.80}\text{Zn}_{0.20}$, there are **three regions** at a given temperature:

$x > x_L$, the equilibrium system is homogeneous liquid

$x_S < x < x_L$, there is a solid phase of composition x_S and a liquid phase of composition x_L

$x < x_S$, equilibrium system is homogenous solid

The point x_L traces a curve called **liquidus** curve, and the point x_S traces the **solidus** curve

Phase diagram: Eutectics

Mixture with two liquidus branches in the phase diagram of Au-Si alloy is shown below. The minimum solidification temperature is called the eutectic temperature; here the composition is the eutectic composition. The solid at this composition consist of two separate phases, as shown in Fig. There are many binary systems in which the liquid phase persists to temperatures below the lower melting temperature of the constituents. Thus $\text{Au}_{0.69}\text{Si}_{0.31}$ solidifies at 370°C as a two-phase heterogeneous mixture, although Au and Si solidify at 1063°C and 1404°C , respectively. One phase of the eutectic is nearly pure gold; the other is nearly pure silicon.

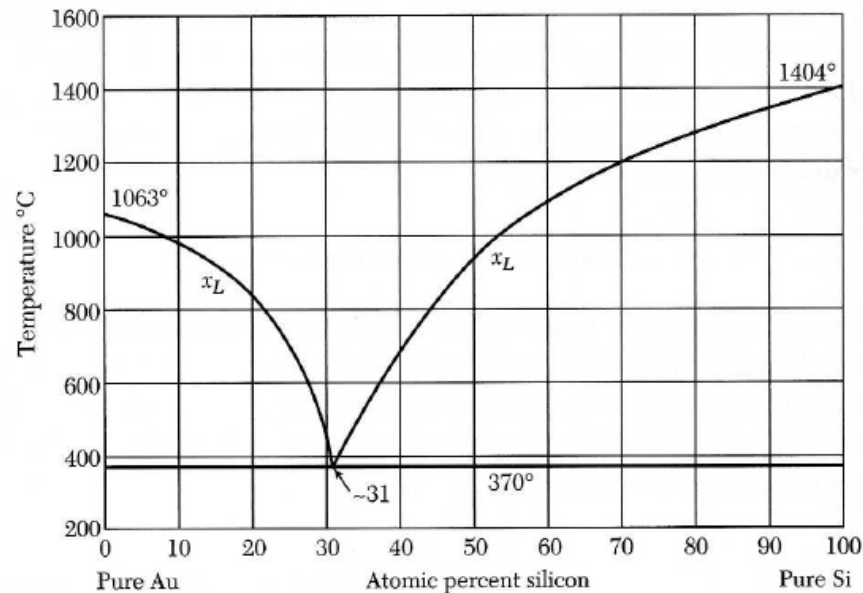
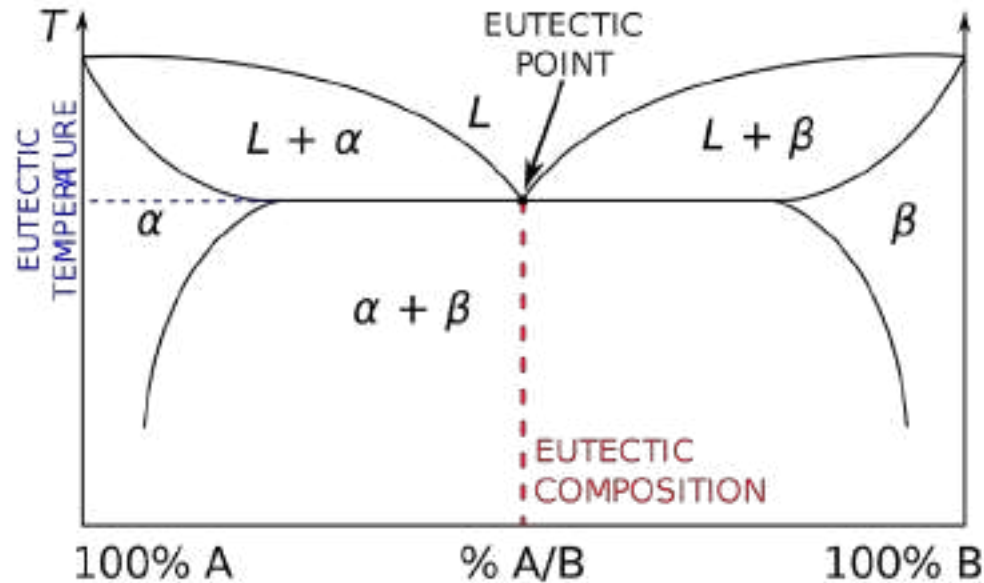


Figure Eutectic phase diagram of gold-silicon alloys. The eutectic consists of two branches that come together at $T_c = 370^\circ\text{C}$ and $x_g = 0.31$ atomic percent Si. (After Kittel and Kroemer, *TP.*)

Reference: Introduction to solid state physics by Kittel Charles

Eutectics: Binary system

A phase diagram for a fictitious binary chemical mixture (with the two components denoted by A and B) used to depict the eutectic composition, temperature, and point. (L denotes the liquid state.)



The Au-Si eutectic is important in semiconductor technology because the eutectic permits low temperature welding of gold contract wires to silicon devices. Lead-tin alloys have similar eutectic of $\text{Pb}_{0.26}\text{Sn}_{0.74}$ and 183°C . This or nearby compositions are used in solder: nearby if a range of melting temperature is desired for ease in handling