“Intermetallic phases have long been among the black sheep in the family of chemical compounds. Their chemical bonding has eluded description by the valence rules, which otherwise are extremely effective. As a result, understanding of the structure-bonding relationships in these phases to date has remained nebulous, even though they form the largest group of inorganic compounds.”

Au-Cu phase diagram: AuCu and AuCu$_3$

**AuCu:** $P4/mmm$ $a = 2.802$ Å, $c = 3.671$ Å
Au at 0,0,0 and Cu at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

**AuCu$_3$:** $Pm-3m$ $a = 3.753$ Å
Au at 0,0,0 and Cu at $\frac{1}{2} \frac{1}{2} 0$

*Order-disorder phase transitions!*
Class 11: Structures of intermetallic phases

Modulated *Imma* structure of AuCu: 20 atoms per unit cell.

$a = 3.676(2); 
   b = 3.956(3); 
   c = 39.72(2)$
Class 11: Structures of intermetallic phases

Ti-Al phases

TiAl \( P4/mmm \)

Ti\(_2\)Al\(_5\) \( I4/mmm \)

TiAl\(_3\) \( I4/mmm \)

Al rich (Al is fcc)
Class 11: Structures of intermetallic phases

Ti-Al phases

Ti$_3$Al

Ti rich (Ti is hcp)
Class 11: Structures of intermetallic phases

Ni-Al phases

Ni$_3$Al ($\text{Cu}_3\text{Au}$)

NiAl ($\text{CsCl}$)
Class 11: Structures of intermetallic phases

Ni-Al phases

NiAl₃
Class 11: Structures of intermetallic phases

Os-Al phases

OsAl (CsCl)  OsAl₂  Os₂Al₃
Class 11: Structures of intermetallic phases

Mg-Al phases:

Mg$_{12}$Al$_{17}$

Mg$_{23}$Al$_{30}$

Topologically close packed phases

Unusual topologies are justified by the Fermi energies lying in pseudogaps and dips. This is associated with unusual stoichiometries and very large unit cells.
Class 11: Structures of intermetallic phases


DOS of CoTi in the CsCl structure. Note that Co $d$ is almost full and Ti $d$ is almost empty.
Class 11: Structures of intermetallic phases

A15 compounds (superconductors)

\( \text{Nb}_3\text{Sn}: \)

- \( Pm-3n \) (223)
- \( a = 5.290 \text{ Å} \)
- \( \text{Sn at } 0 \ 0 \ 0 \)
- \( \text{Nb at } \tfrac{1}{4} \ 0 \ \tfrac{1}{2} \)
Class 11: Structures of intermetallic phases

Mathias’ Rules:

(i) Superconductivity occurs only in metallic systems, and never if the system exhibits ferro- or antiferromagnetism.

(ii) Superconductivity occurs when the electron to atom ratio \( e/a \) lies between 2 and 8. \( T_c \) depends upon \( e/a \) for metals, and alloys between metals, in the same period of the periodic table. Nontransition metals show \( T_c \) increasing as \( e/a \) increases from 2 to 6 (beyond 6 the nontransition elements are nonmetallic). The transition metals show a much more complicated behaviour, with peaks at \( e/a = 4.7 \) and 6.5, and a sharp minimum in between. A peak was originally thought also to exist at \( e/a = 3 \). This is due to the element lanthanum, whose behaviour is now regarded as atypical (Hamilton and Jensen 1963, Kondo 1963), and this peak is spurious.

(iii) Certain crystal structures are particularly favourable for superconductivity. The highest critical temperatures are found in the \( \beta \) Wolfram (A15) and sodium chloride (B1) structures, with \( e/a \approx 4.7 \). The \( \sigma \) phase (D8\(_b\)), \( \alpha \) Mn (A12) and Laves phases are crystal classes which produce compounds with \( e/a \approx 6.5 \), and critical temperatures up to \( \sim 10 \) K. Superconducting compounds have been reviewed by Roberts (1968).

(iv) \( T_c \) is dependent upon atomic mass \( M \) and atomic volume \( v \). For elements with the same \( e/a \), the critical temperature depends upon \( M \) and \( v \) in the following way:

\[
T_c \propto \frac{v^x}{M} \quad \text{where} \quad 4 < x < 5.
\]

D. Dew-Hughes,