

Class 11: Structures of intermetallic phases

“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.”

R. Nesper, Bonding patterns, in intermetallic compounds,

Angew. Chem. Intl. Edn.

Engl. 30 (1991) 789.

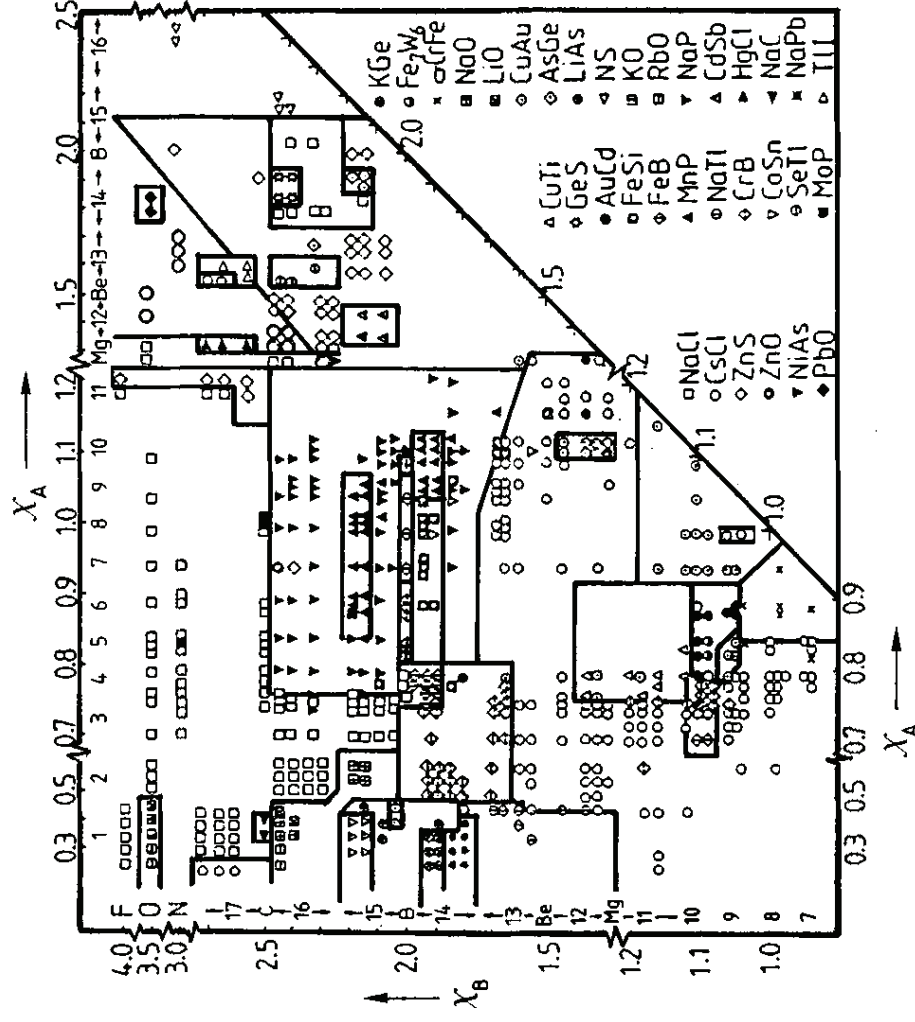
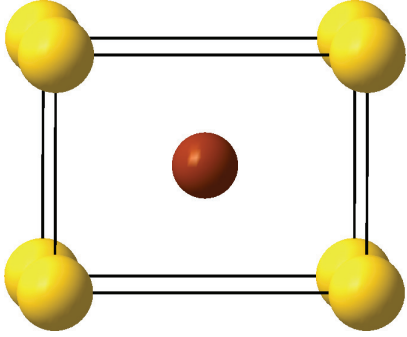


Fig. 2. Structural field after [45] with division of 574 AB compounds by means of a specially adjusted electronegativity.

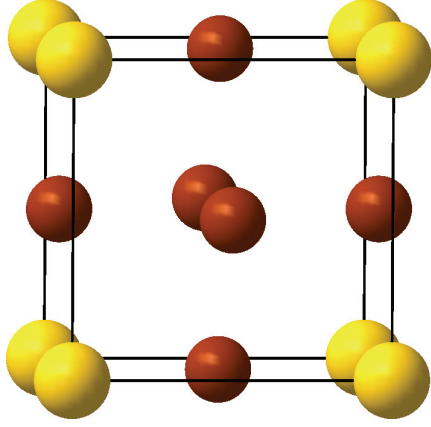
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Au-Cu phase diagram: AuCu and AuCu₃



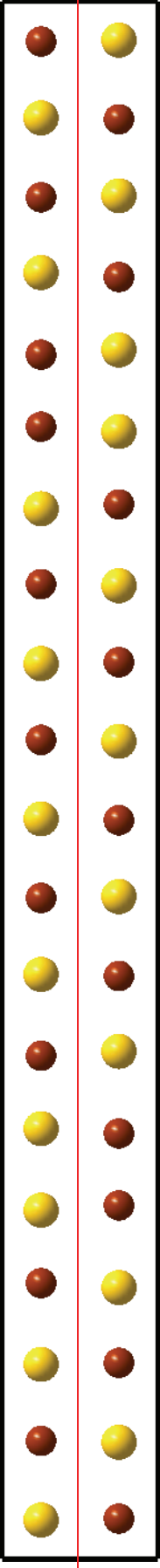
AuCu: $P4/mmm$ $a = 2.802 \text{ \AA}$, $c = 3.671 \text{ \AA}$
Au at $0,0,0$ and Cu at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

Order-disorder phase transitions !



AuCu₃: $Pm-3m$ $a = 3.753 \text{ \AA}$
Au at $0,0,0$ and Cu at $\frac{1}{2} \frac{1}{2} 0$

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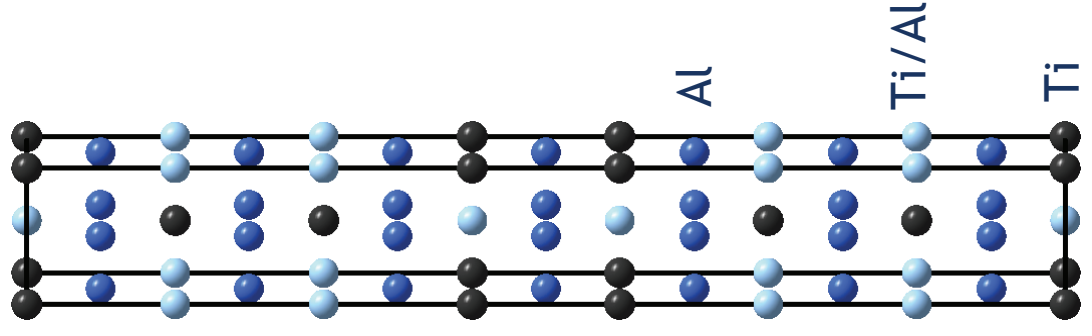


Modulated *Imma* structure of AuCu: 20 atoms per unit cell.

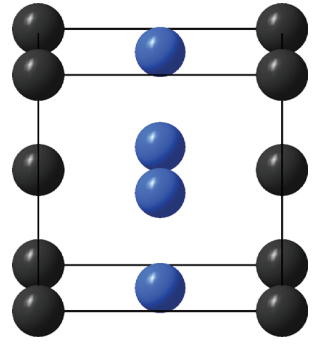
$a = 3.676(2)$; $b = 3.956(3)$; $c = 39.72(2)$

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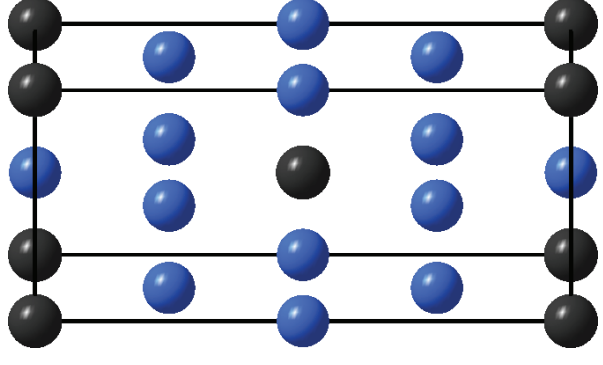
Al rich (Al is fcc)



Ti-Al phases



TiAl $P4/mmm$



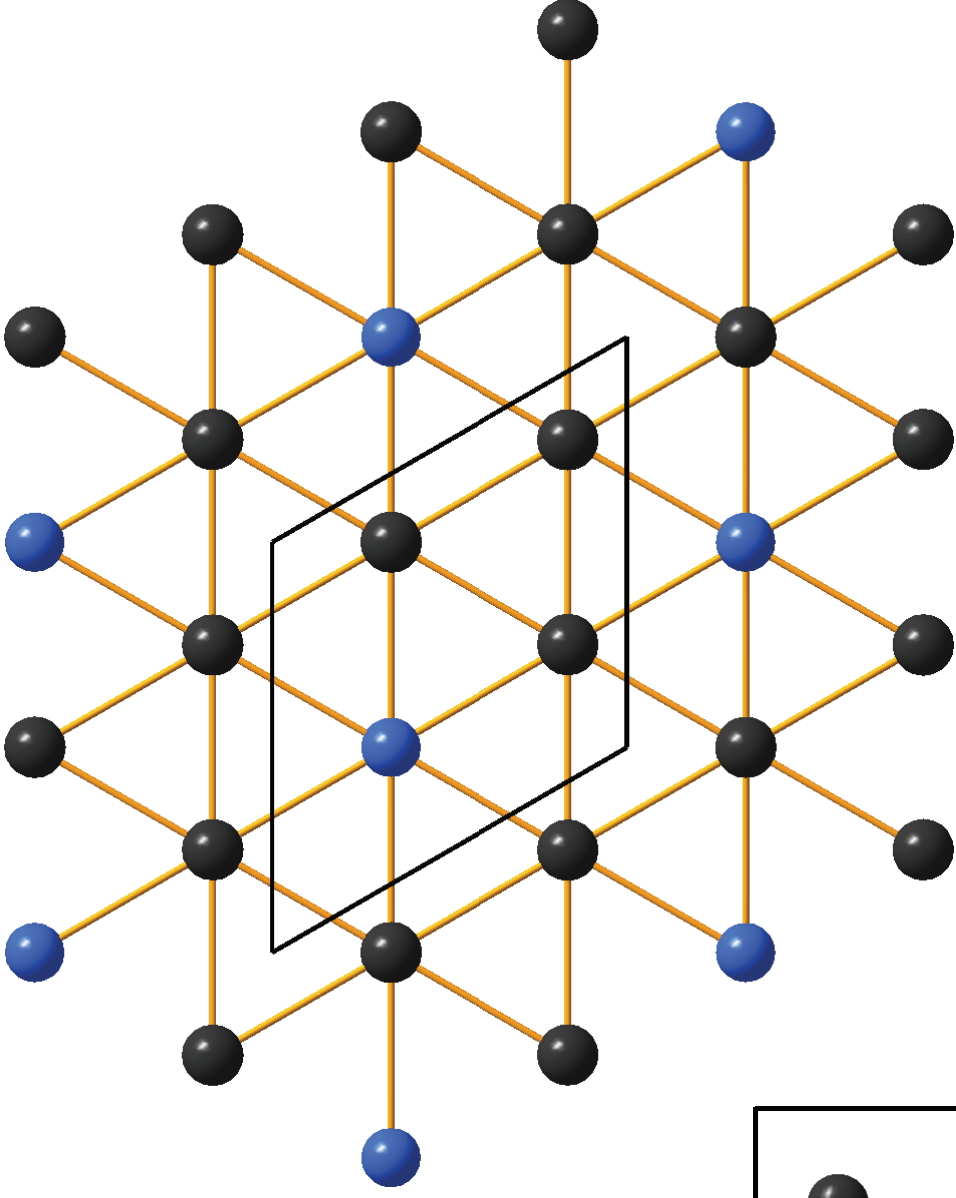
TiAl₃ $I4/mmm$

Ti₂Al₅ $I4/mmm$

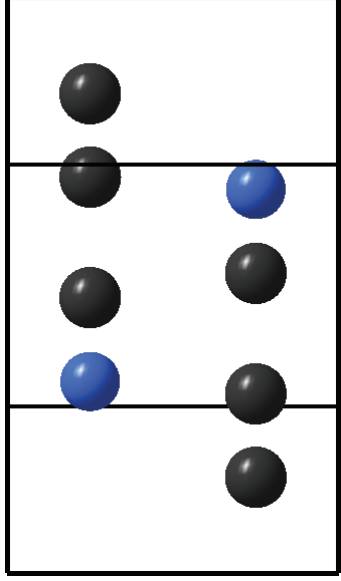
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Ti rich (Ti is hcp)

Ti-Al phases

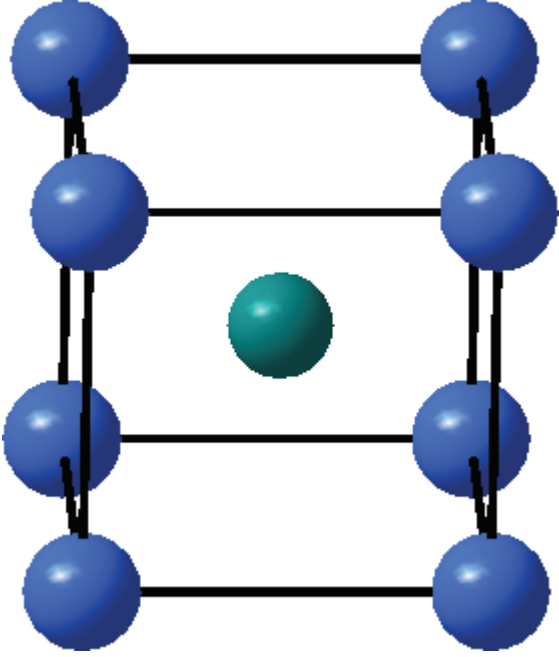


Ti_3Al



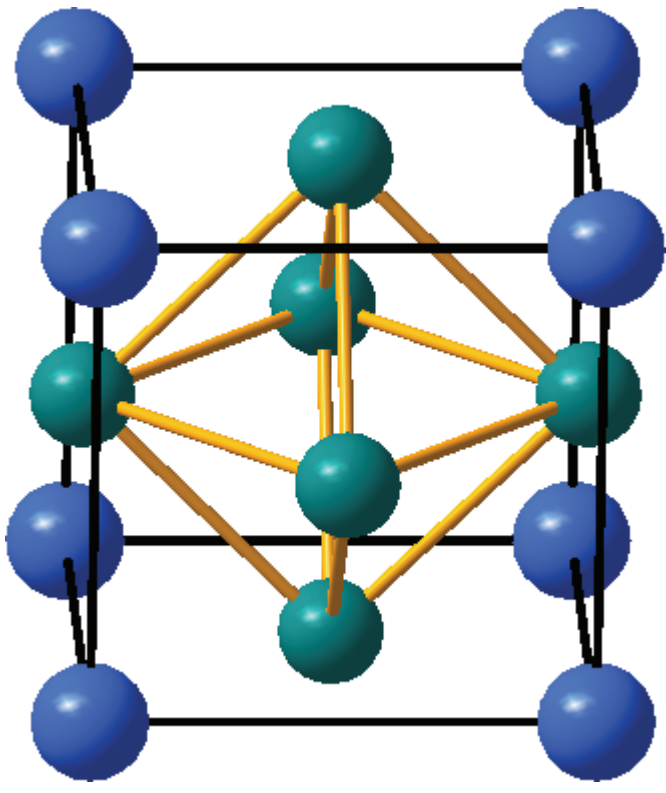
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Ni-Al phases



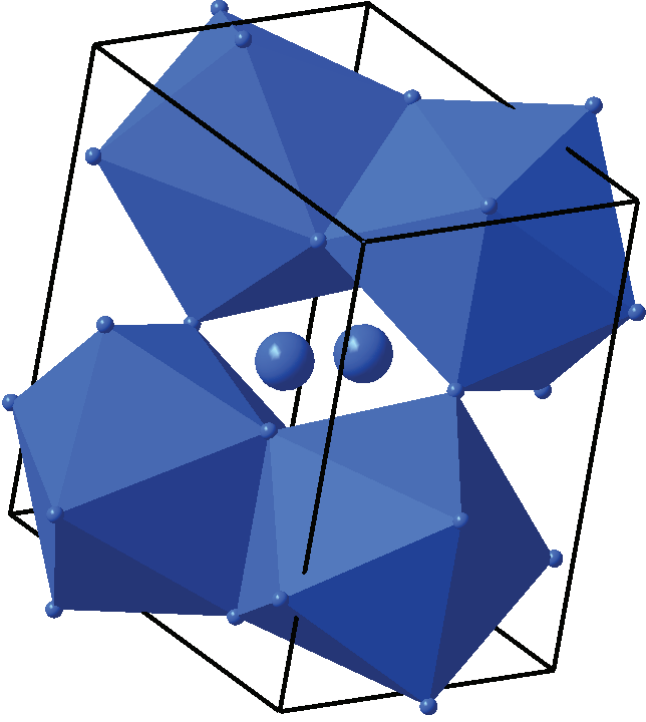
NiAl (CsCl)

Ni₃Al (Cu₃Au)

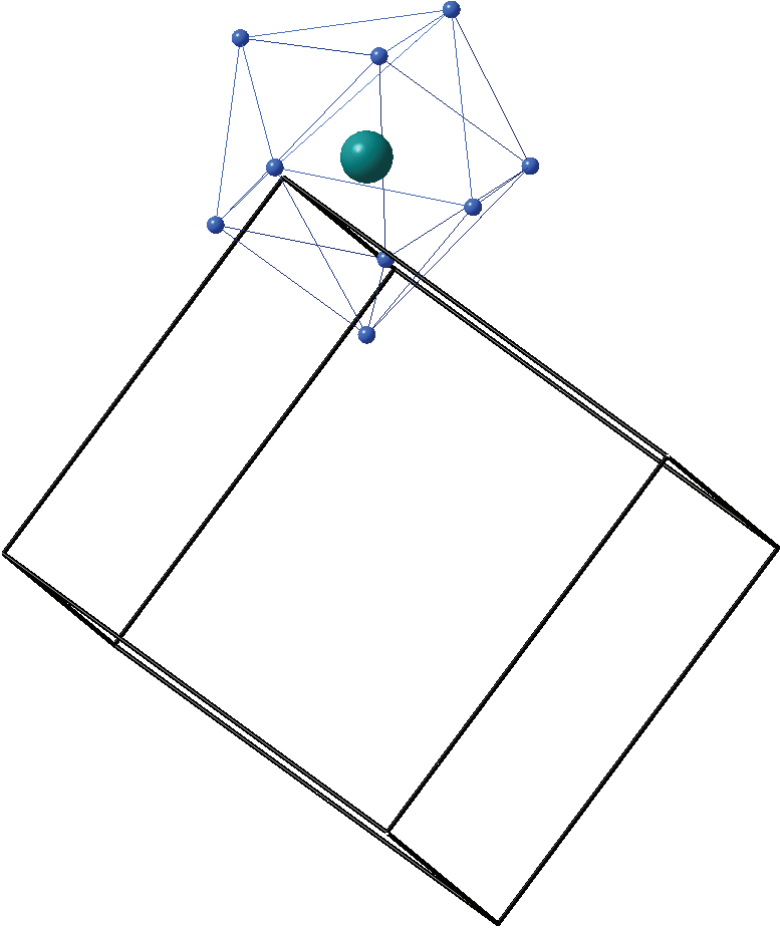


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Ni-Al phases

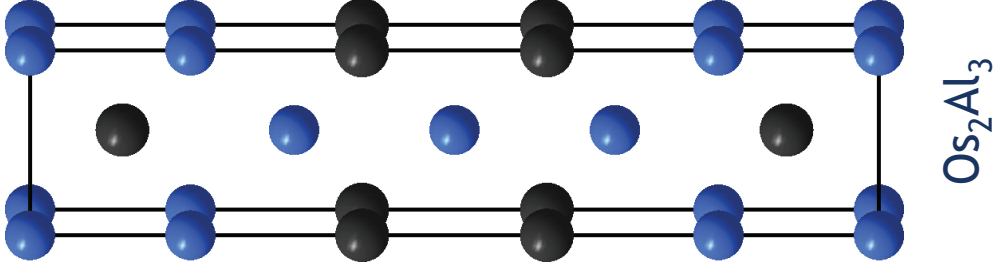
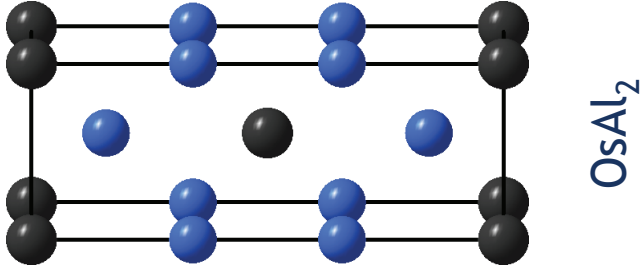
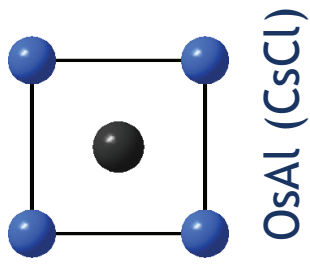


NiAl₃



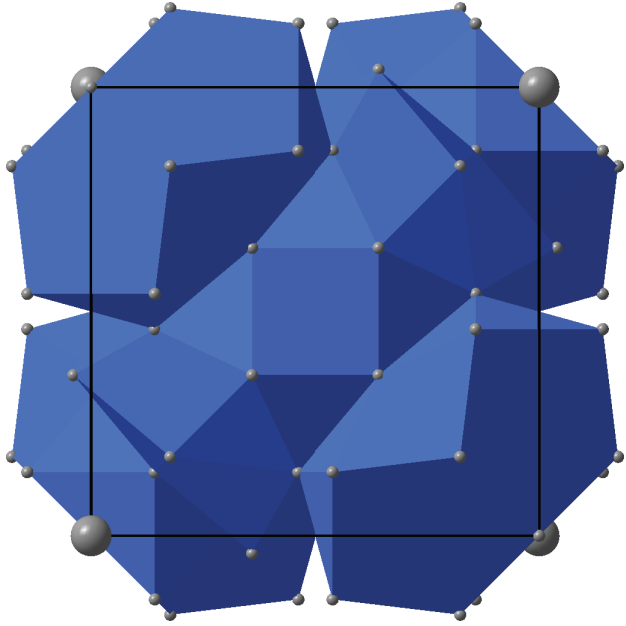
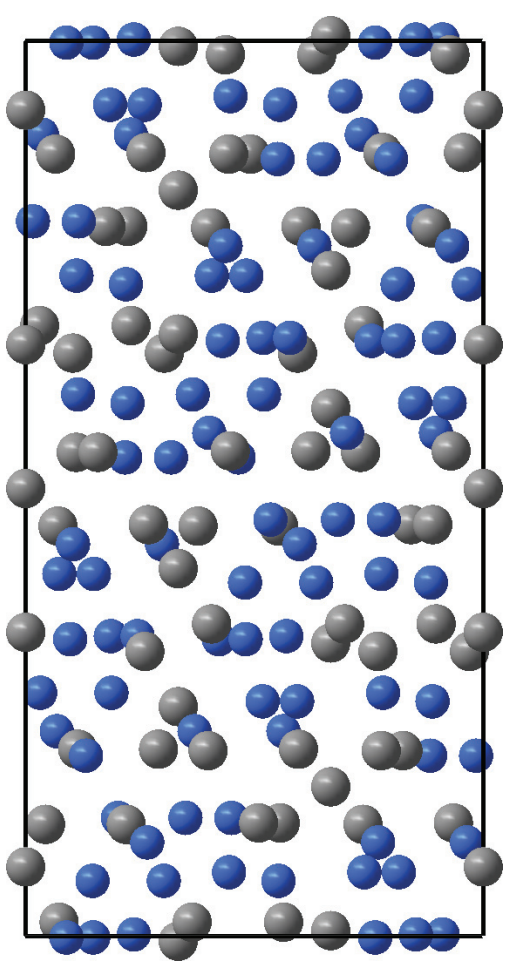
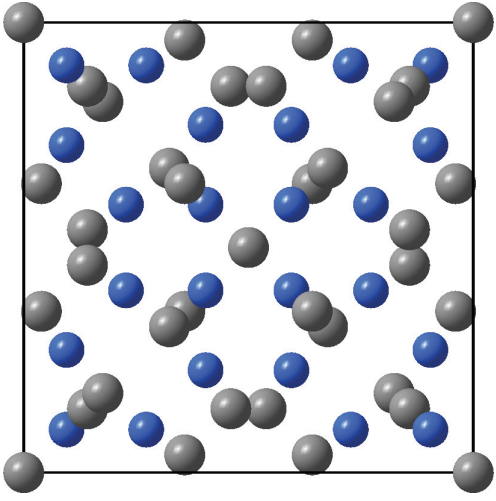
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Os-Al phases



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Mg-Al phases:



Topologically close packed phases

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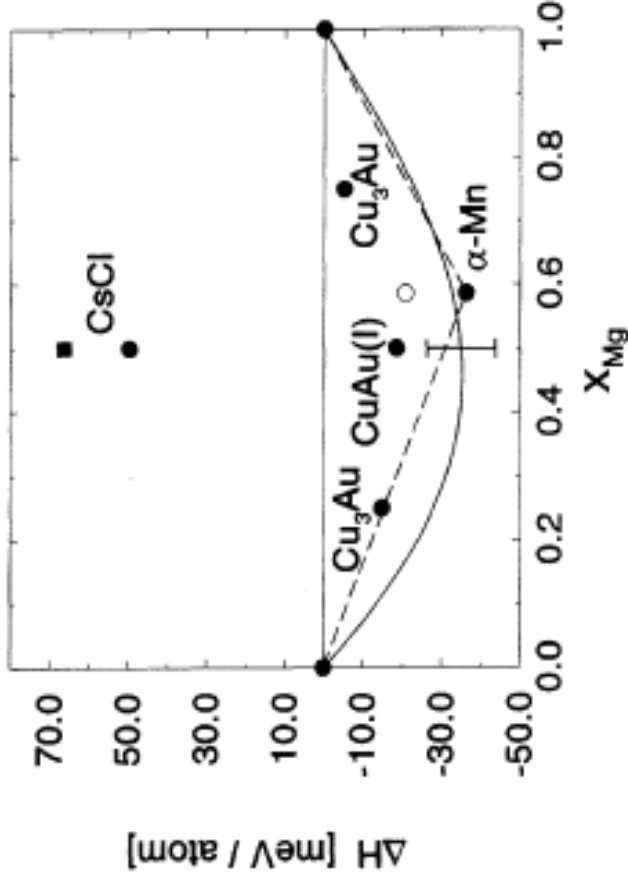


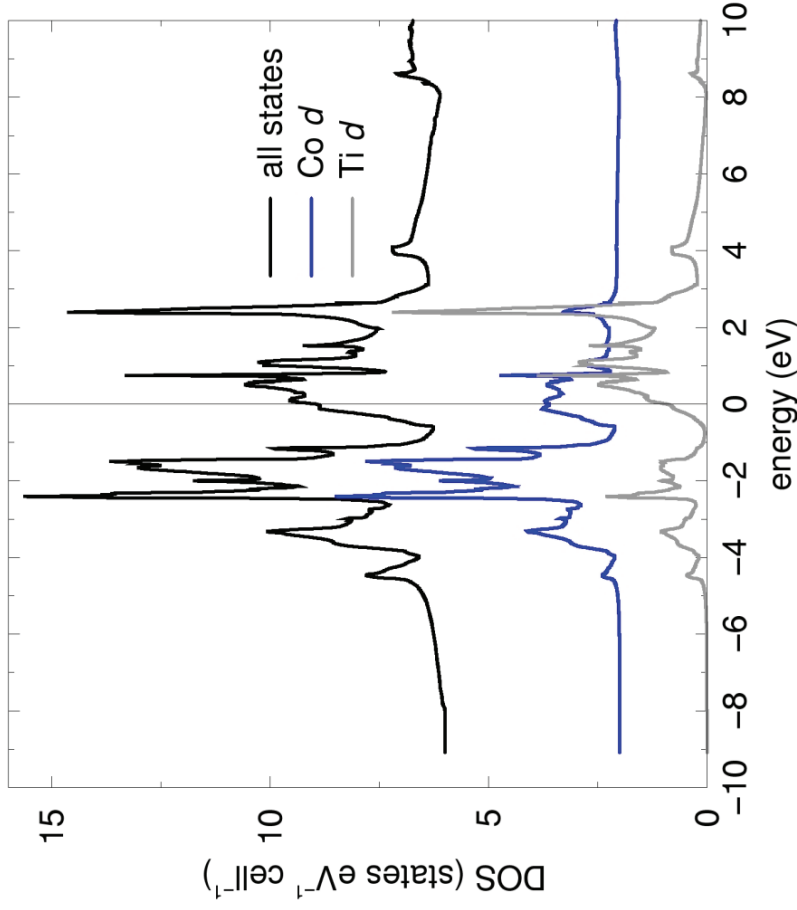
FIG. 1. Heats of formation for $Al_{1-x}Mg_x$ compounds, as a function of Mg concentration x . Labels indicate the structure considered. Filled circles are theoretical values from our calculations, the square is the result from the calculation of Pettifor and Gelatt (Ref. 16), and the solid line is the experimental data (with error bar) for the liquid state. The empty circle shows the theoretical value we obtain for $Al_{12}Mg_{17}$ when internal structural parameters are not relaxed but are set equal to the experimental values. The dashed lines are tie lines for $Al_{12}Mg_{17}$ (as a guide to the eye).

Ab initio study of polytetrahedral packing: The Al-Mg system, S. Narasimhan and J. W. Davenport, *Phys. Rev. B* 51 (1995) 659.

Unusual topologies are justified by the Fermi energies lying in pseudogaps and dips. This is associated with unusual stoichiometries and very large unit cells.

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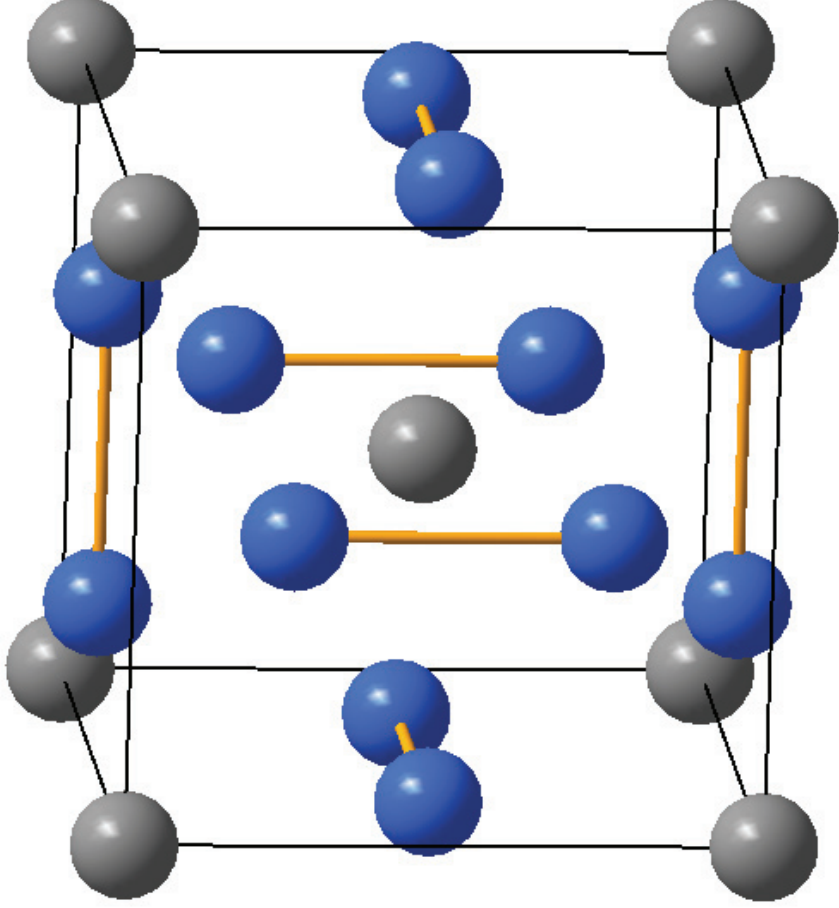
Polar intermetallic compounds: Compounds of early and late transition elements. *Transition metal alloys of extraordinary stability - example of generalized Lewis-acid-base interactions in metallic systems*, L. Brewer and P. R. Wengert, *Metal. Trans.* **4** (1973) 83.



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)



Nb₃Sn:
Pm-3n (223)
 $a = 5.290 \text{ \AA}$
Sn at 0 0 0
Nb at $\frac{1}{4} 0 \frac{1}{2}$

(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 β Wolfram (A15) and sodium chloride (B1) structures, with $e/a \simeq 4.7$. The σ phase (D8_b), α Mn (A12) and Laves phases are crystal classes which produce compounds with $e/a \simeq 6.5$, and critical temperatures up to ~ 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:

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