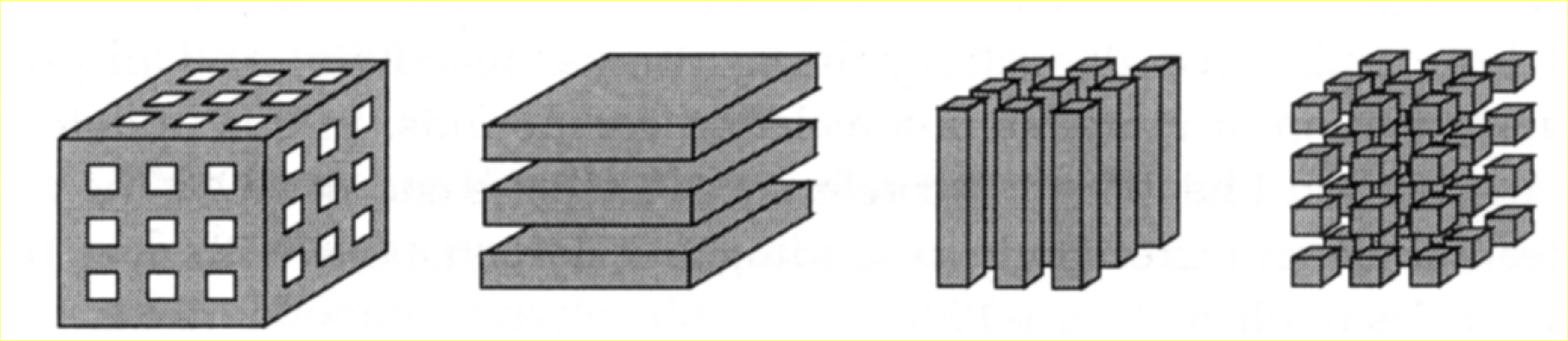
Host-Guest Structures

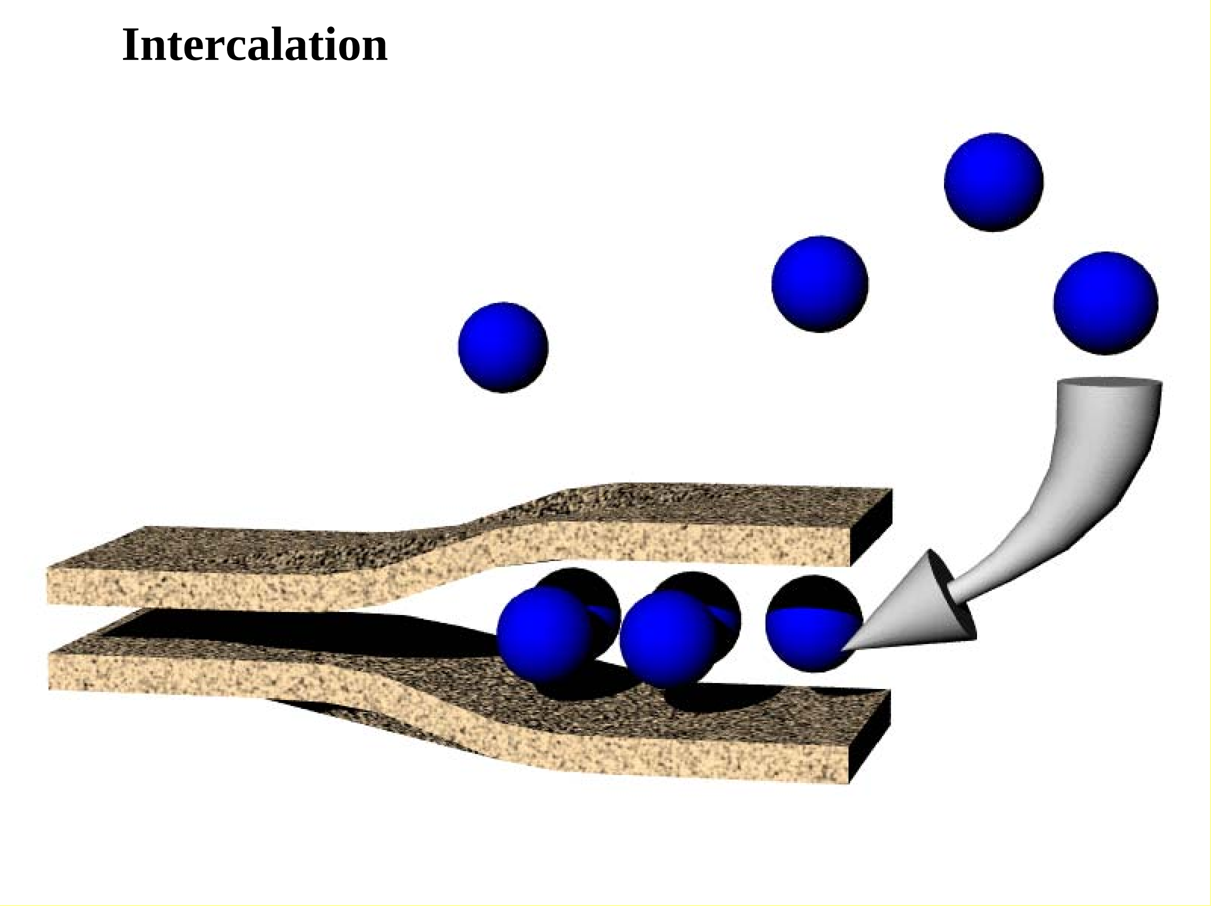
TOPOTACTIC SOLID-STATE REACTIONS = modifying existing solid state structures while maintaining the integrity of the overall structure

Host dimensionality

3D **2D** **1D** **0D**



Layered Compounds



Layered Compounds

GRAPHITE INTERCALATION

G (s) + K (melt or vapour) $\rightarrow$ C_8K (bronze)

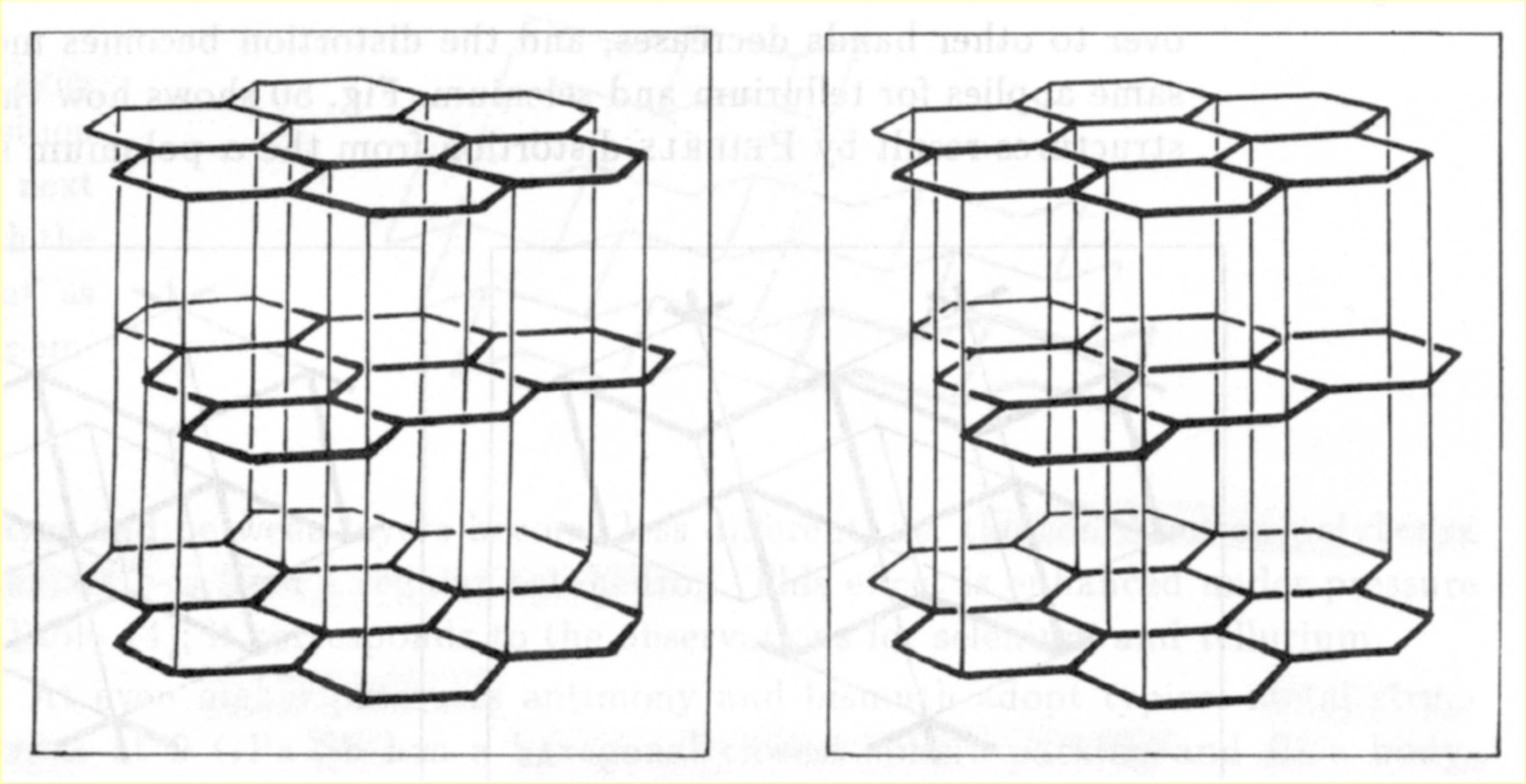
C_8K (vacuum, heat) $\rightarrow$ $C_{24}K$ $\rightarrow$ $C_{36}K$ $\rightarrow$ $C_{48}K$ $\rightarrow$ $C_{60}K$

Graphite sp^2 sigma-bonding in-plane p-π-bonding out of plane
Hexagonal graphite = two-layer ABAB stacking sequence

SALCAOs of the p-π-type create the valence and conduction bands of graphite, very small band gap, metallic conductivity properties in-plane, 104 times that of out-of plane conductivity

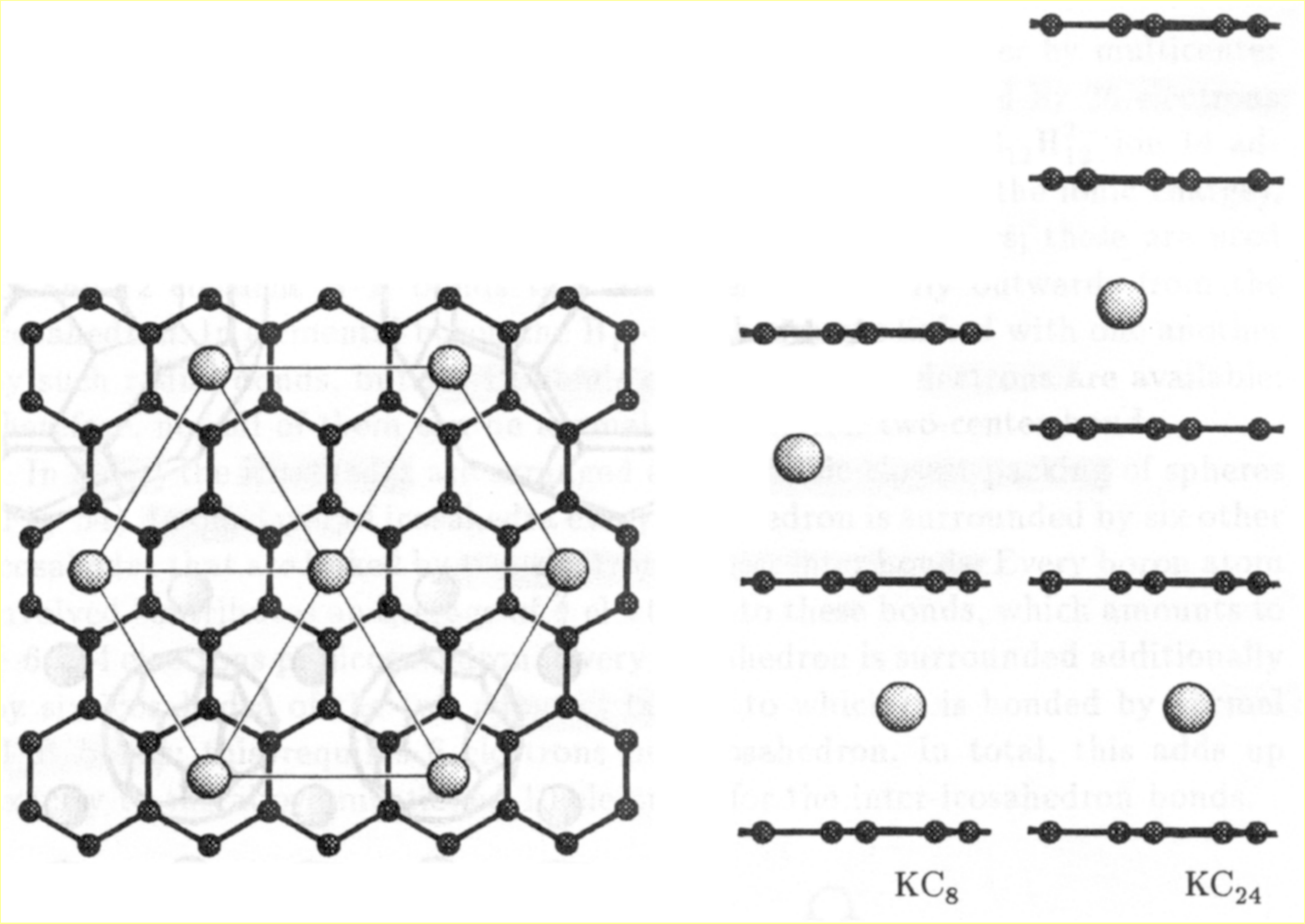
C_8K potassium graphite ordered structure
Ordered K guests between the sheets, K to G charge transfer
AAAA stacking sequence, reduction of graphite sheets, electrons enter CB
K nesting between parallel eclipsed hexagonal planar carbon six-rings

Layered Compounds



ABABAB

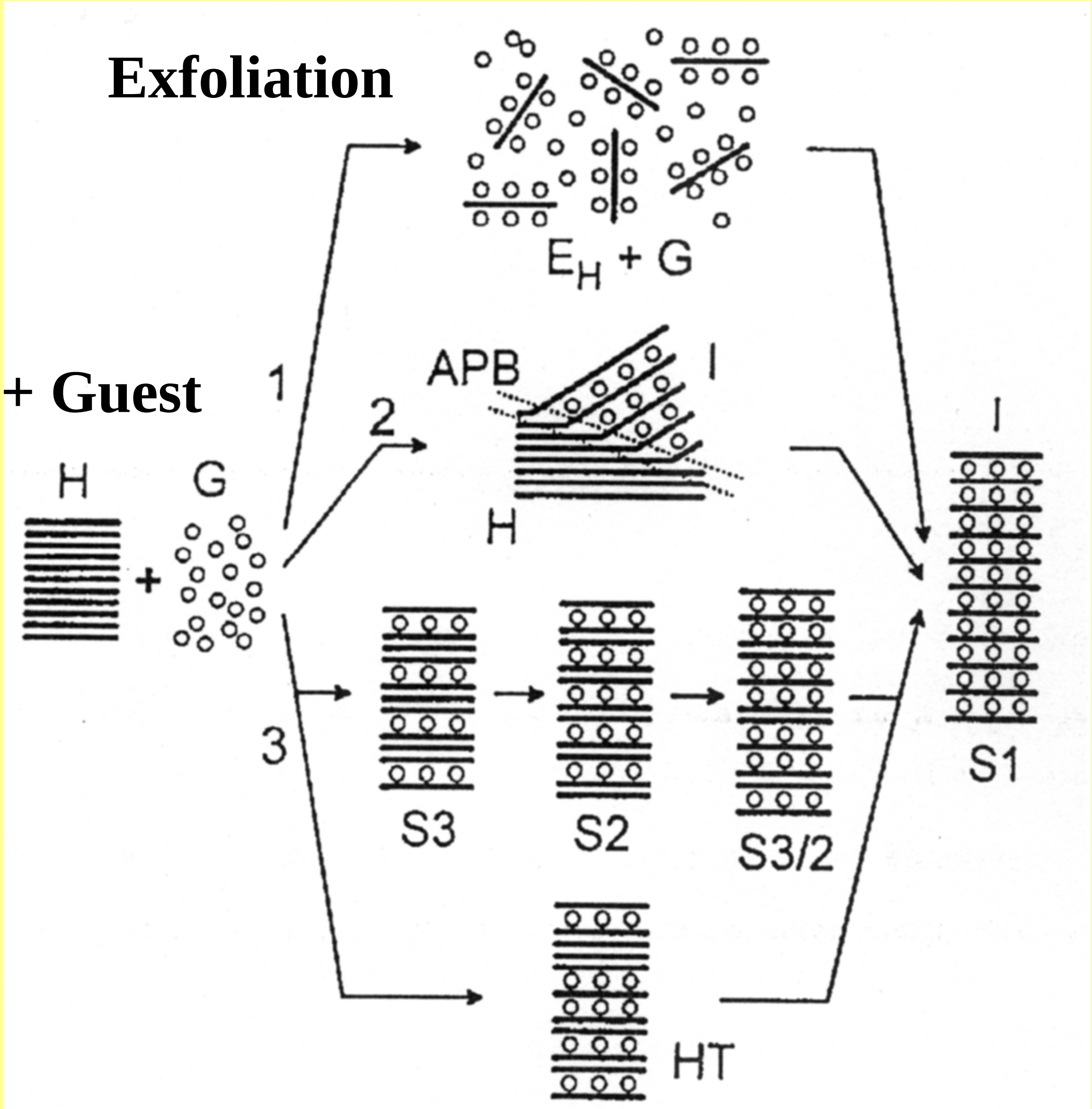
Layered Compounds



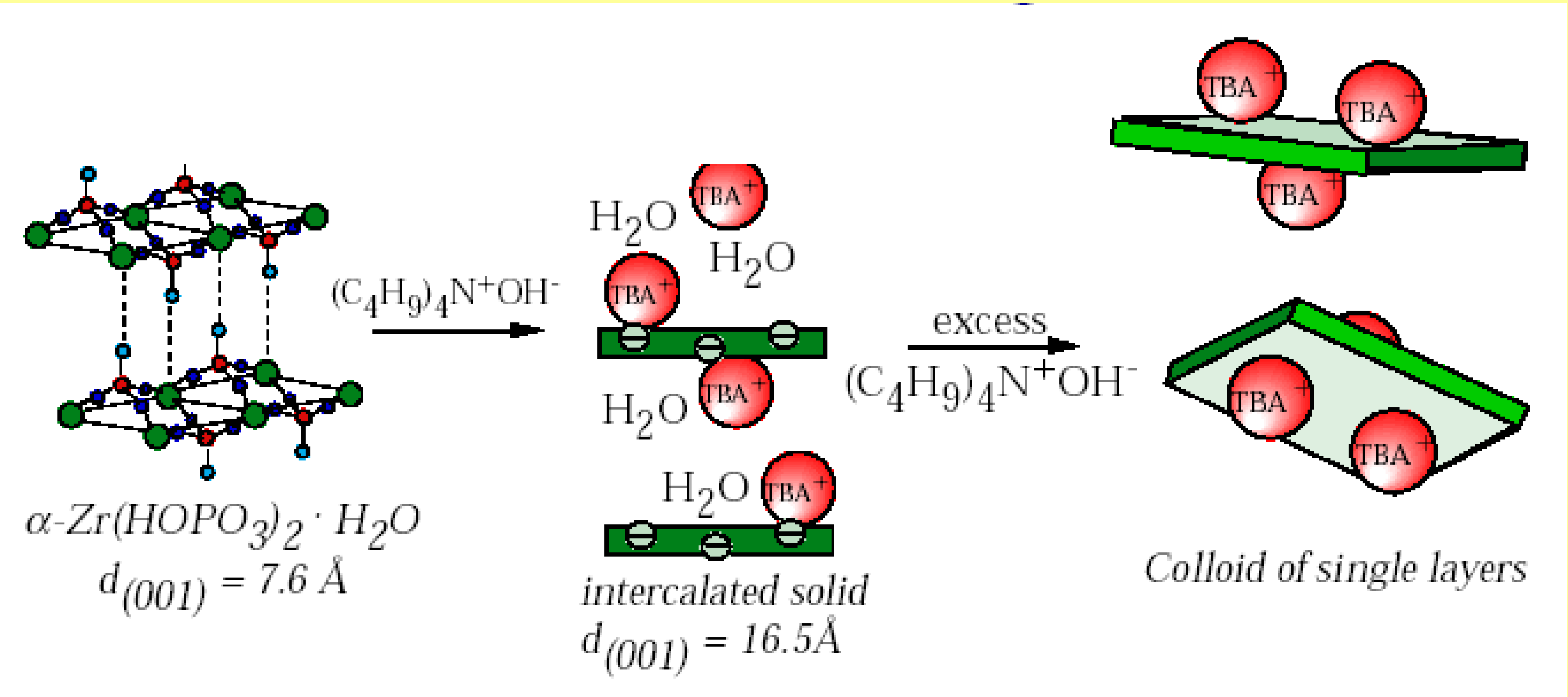
Layered Compounds

Exfoliation

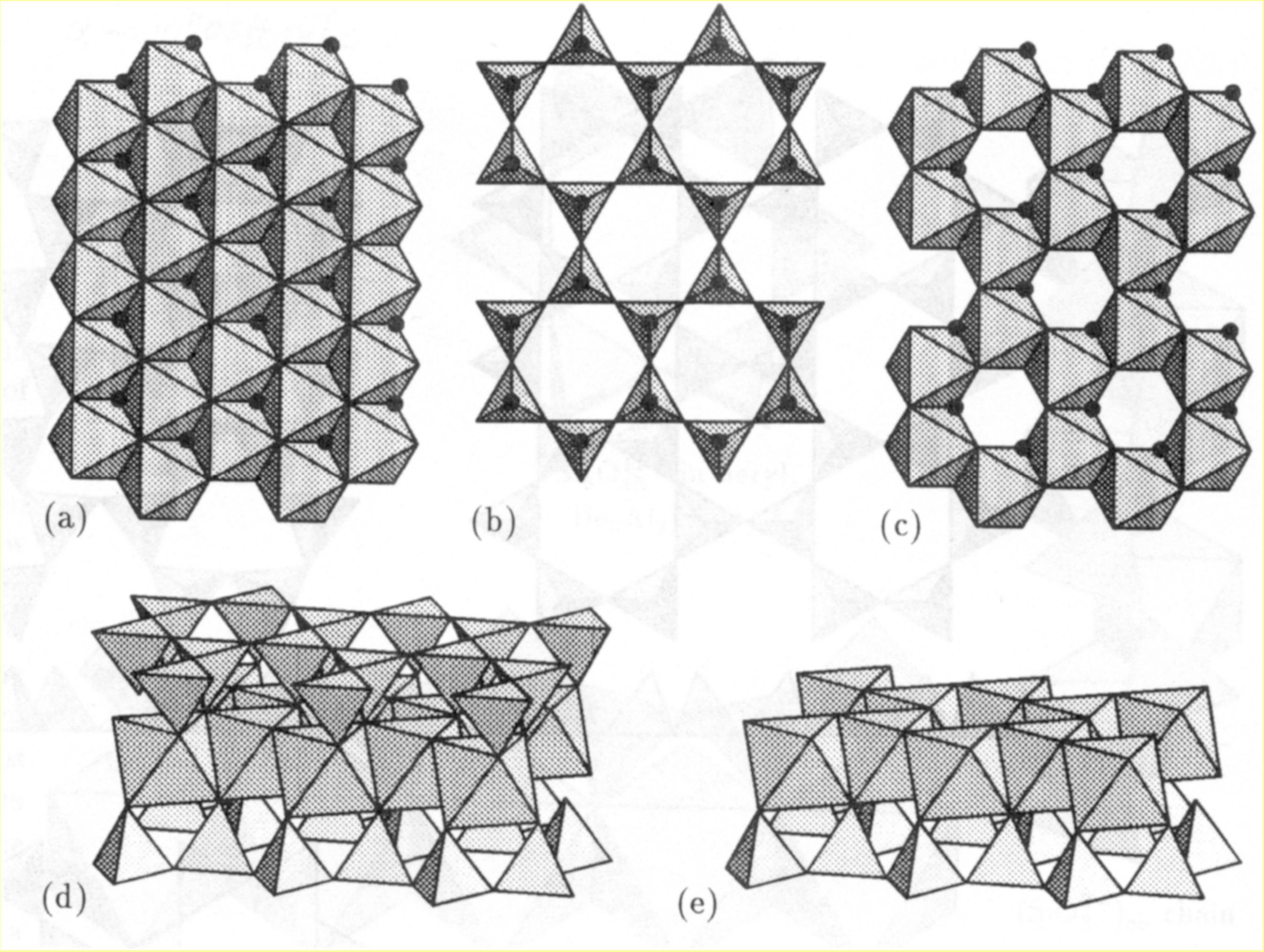
Host + Guest



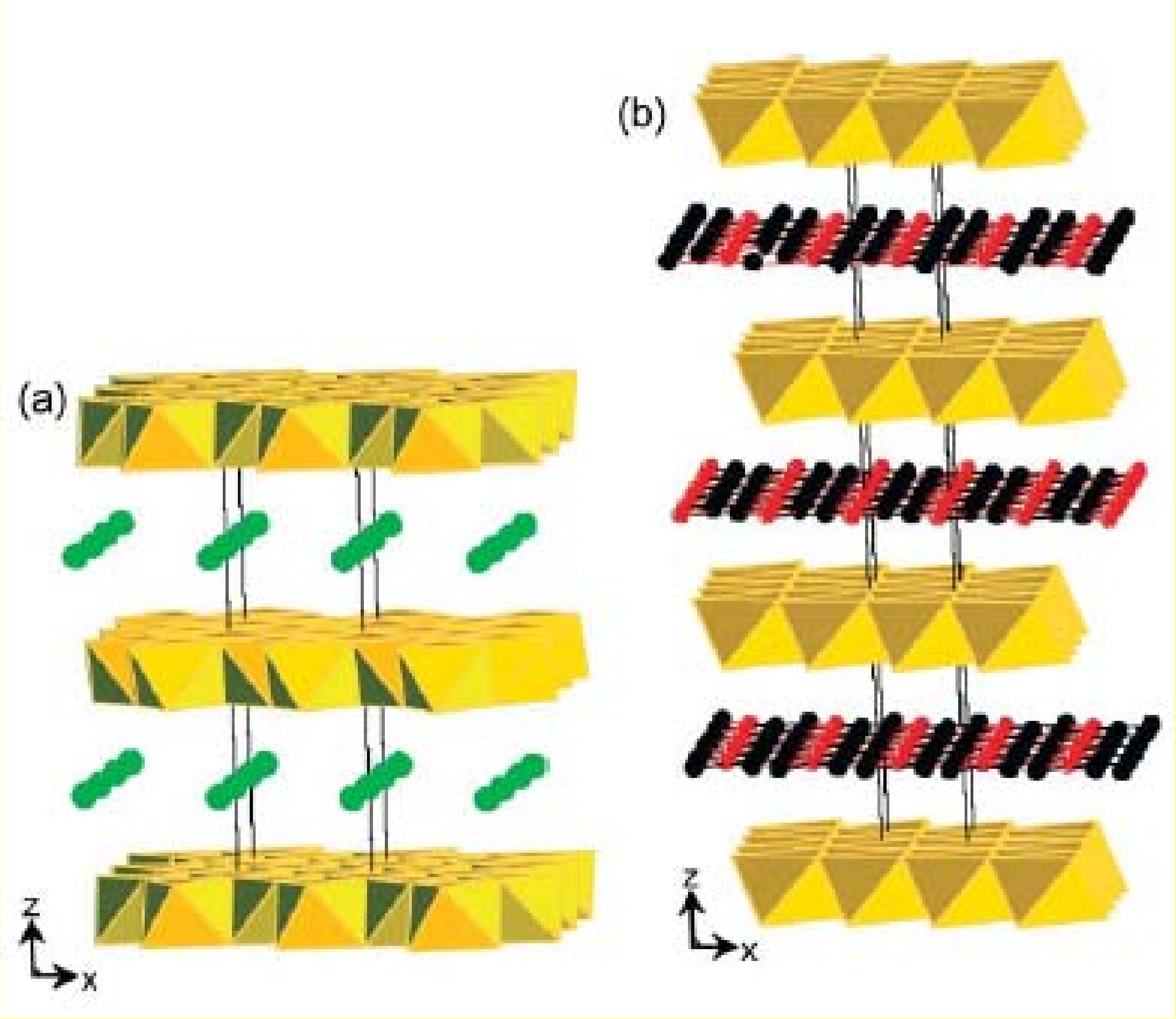
Exfoliation



Layered Compounds



Layered Compounds

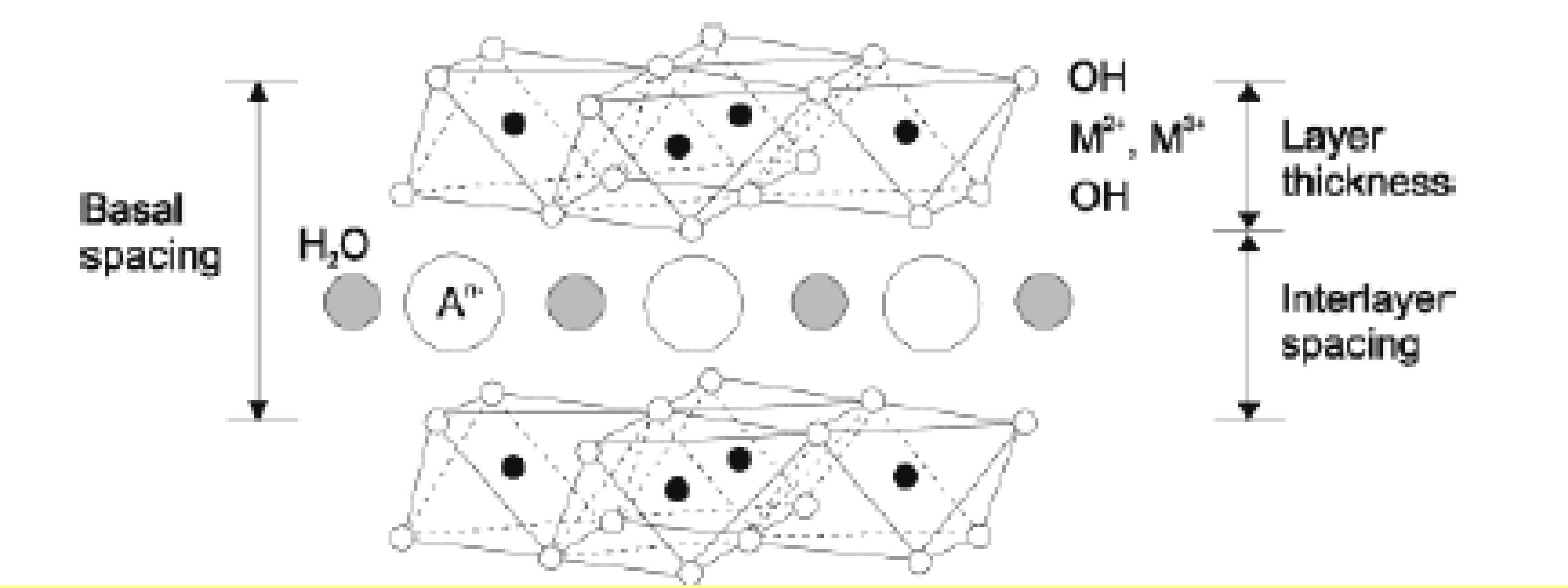


Layered Compounds

LDH = layered double hydroxides
hydrotalcites
mineral $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

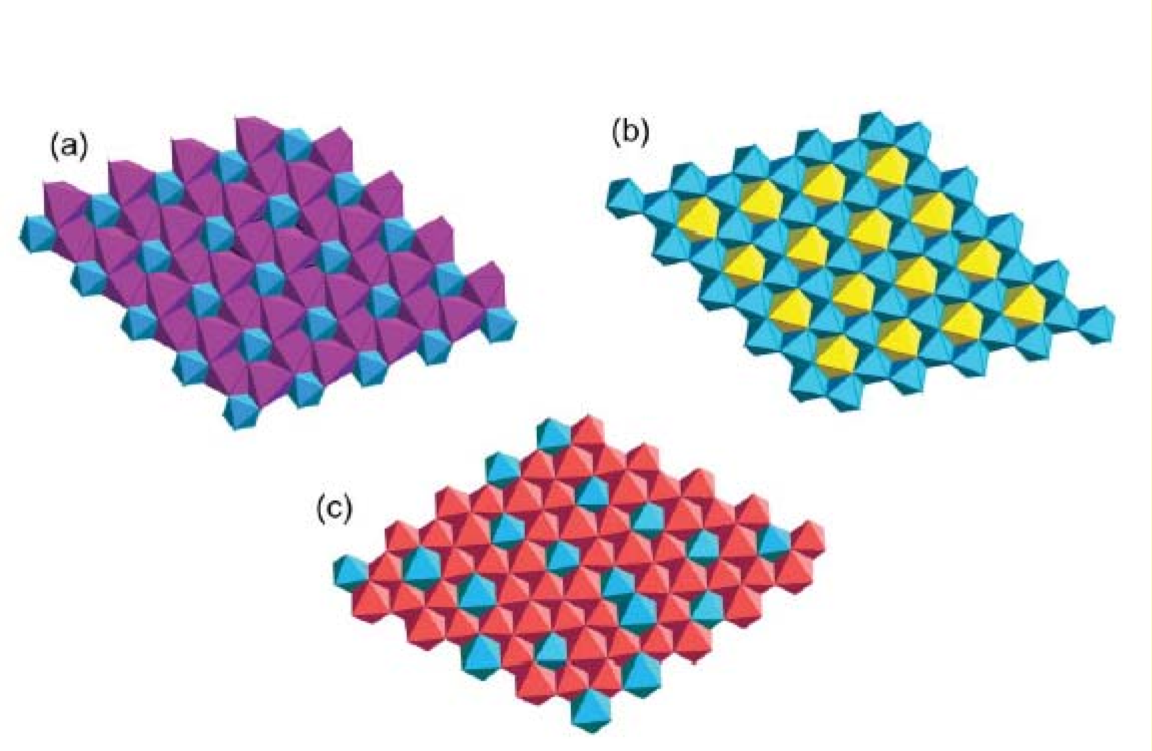
Brucite layers, Mg^{2+} substituted partially by Al^{3+}

Layers have positive charge



Layered Compounds

Brucite layers, Mg^{2+} substituted partially by Al^{3+}
Layers have positive charge



(a) $[Ca_2Al(OH)_6]_2SO_4.6H_2O$ (b) $[LiAl_2(OH)_6]Cl$ (c) $[Mg_{2.25}Al_{0.75}(OH)_6]OH$

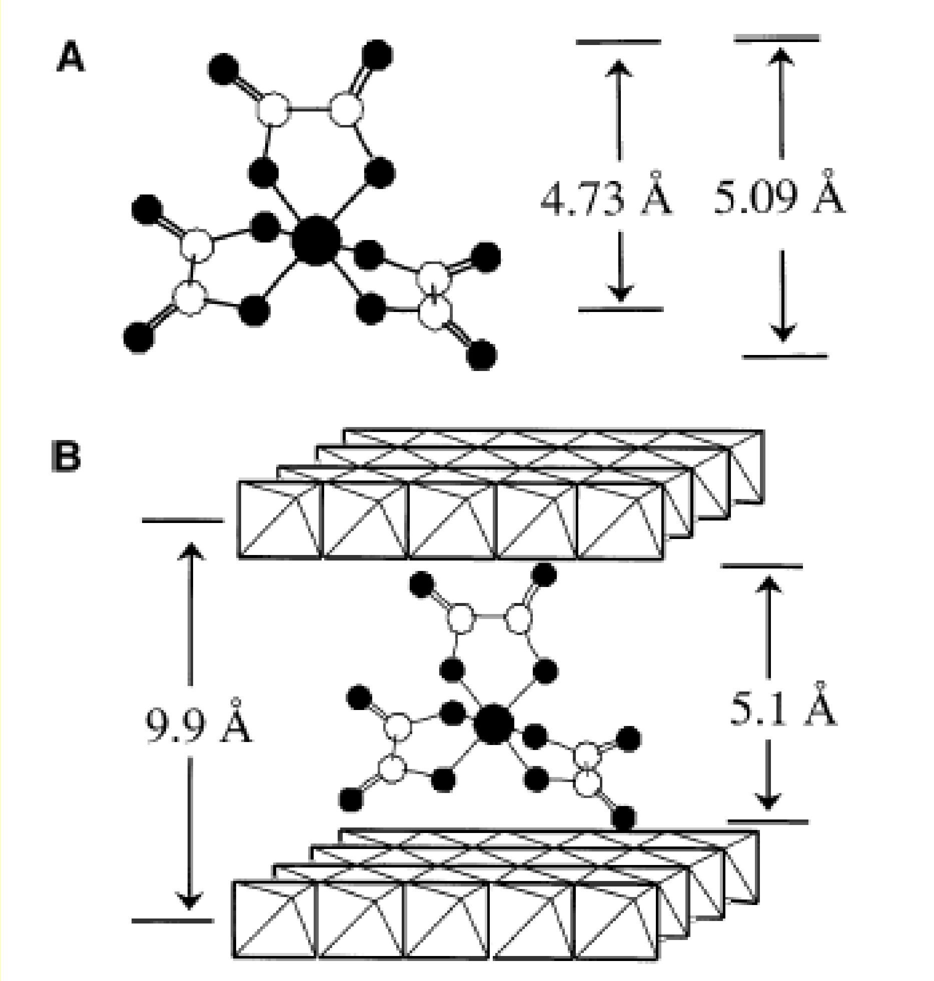
Layered Compounds

LDH = layered double hydroxides
hydrotalcites
mineral $Mg_6Al_2(OH)_{16}CO_3.4H_2O$

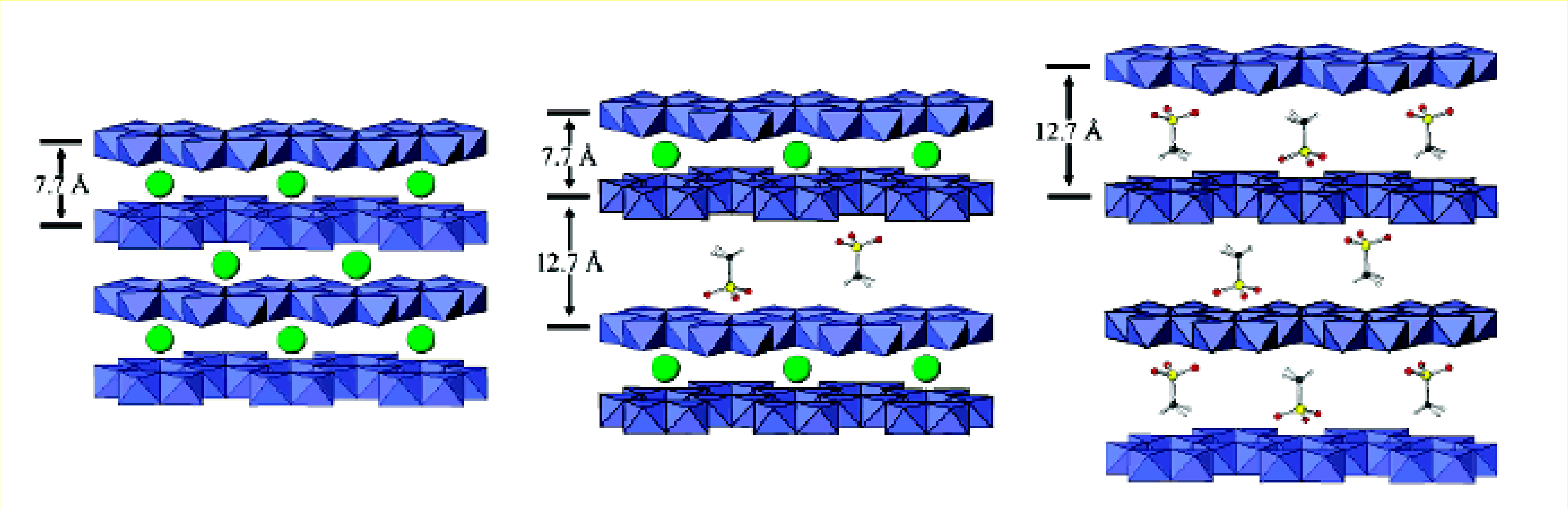
Brucite layers, Mg^{2+} substituted partially by Al^{3+}

Layers have positive charge

Intercalate anions $[Cr(C_2O_4)_3]^{3-}$



Layered Compounds



the intercalation of methylphosphonic acid into Li/Al LDH

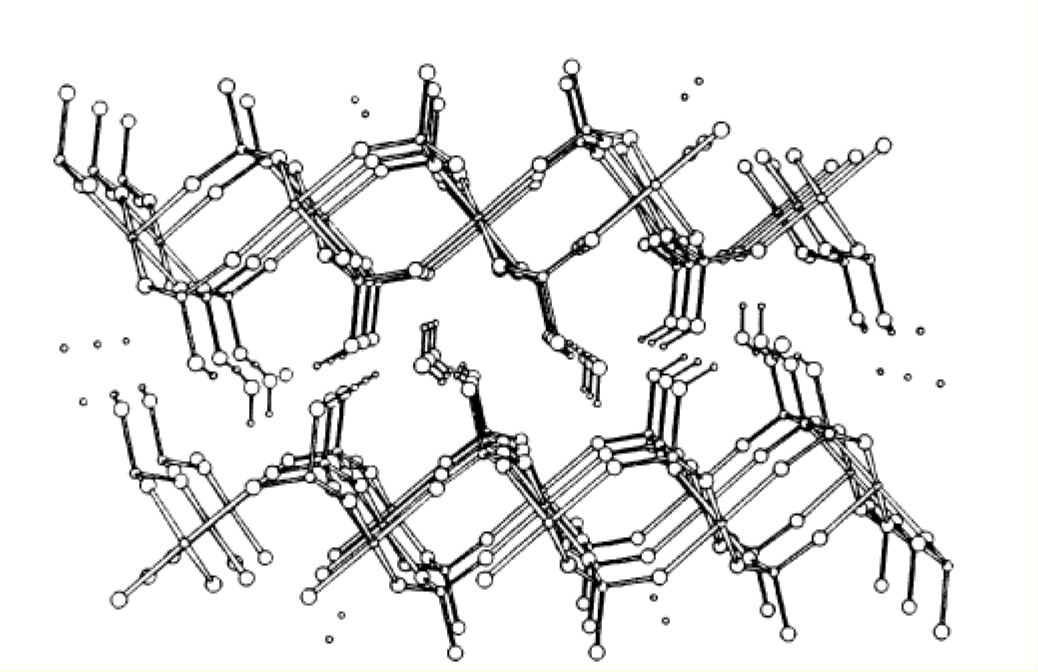
(a) $[LiAl_2(OH)_6]Cl.H_2O$
(b) second-stage intermediate, alternate layers occupied by Cl and MPA anions
(c) first-stage product with all interlayer regions occupied by MPA.

Layered Compounds

MPS_3 (M = V, Mn, Fe, Co, Ni, Zn)

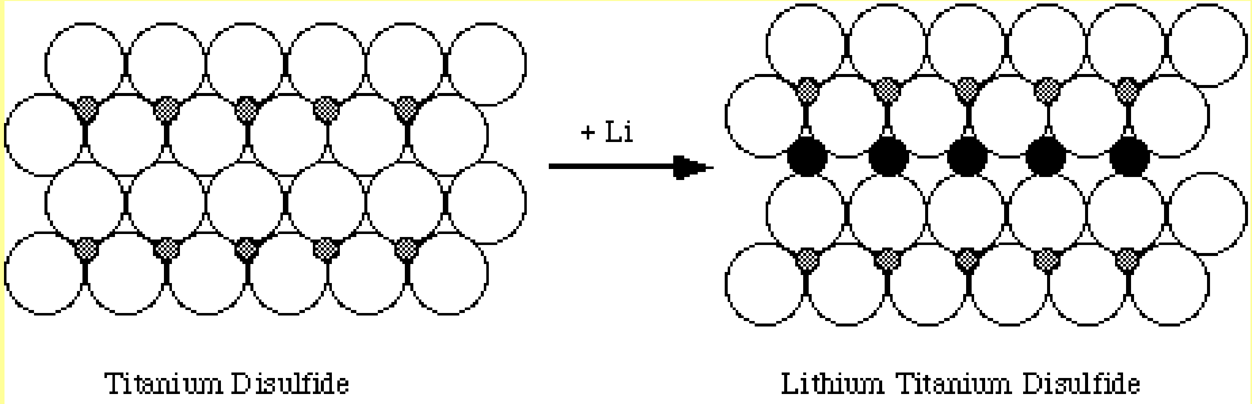
TiS_2

α-$Zr(HPO_4)_2.H_2O$



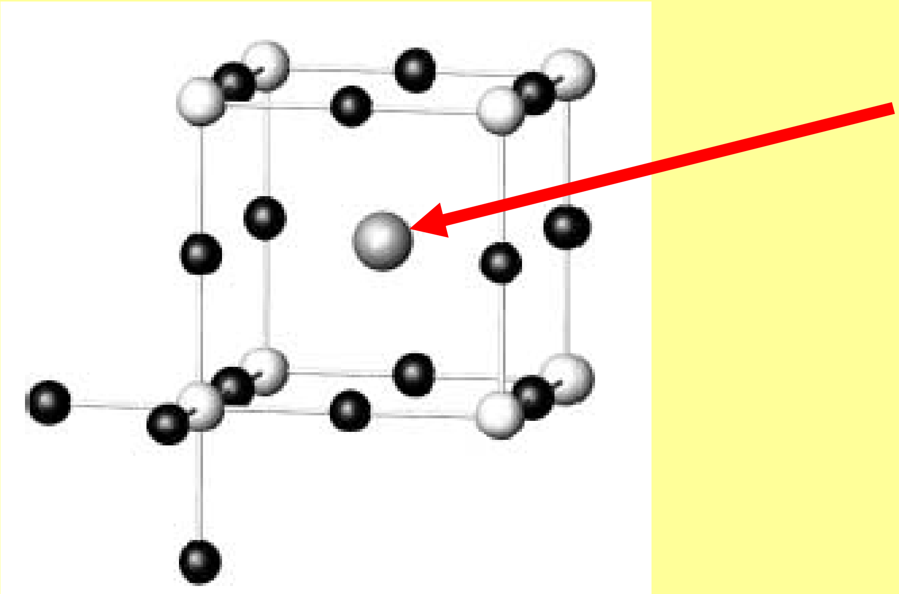
Layered Compounds

$$x\ Li + TiS_2 \rightarrow Li_xTiS_2$$



3D Intercalation Compounds

Cu_3N and Mn_3N crystallize in the (anti-) ReO_3-type structure



the large cuboctahedral void in the structure can be filled

By Pd to yield (anti-) perovskite-type $PdCu_3N$

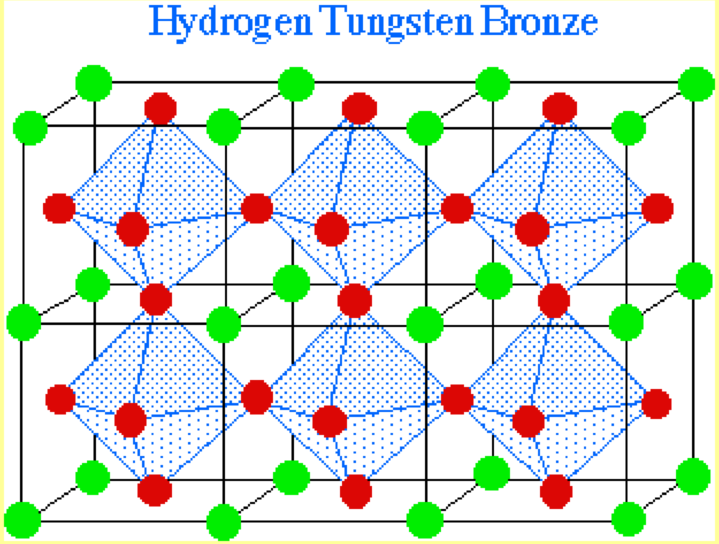
By M = Ga, Ag, Cu leading to MMn_3N

3D Intercalation Compounds

Tungsten trioxide structure
= WO_6 octahedra joined at their corners
= the perovskite structure of $CaTiO_3$ with all the calcium sites vacant

$$Zn + 2\,HCl \rightarrow 2\,H + ZnCl_2$$

$$WO_3 + x\,H \rightarrow H_xWO_3$$



The color and conductivity changes are due to the intercalation of protons into the cavities in the WO_3 structure, and the donation of their electrons to the conduction band of the WO_3 matrix. The material behaves like a metal, with both its conductivity and color being derived from free electron behavior.
The coloration reaction used in electrochromic displays for sun glasses, rear view mirrors in cars

3D Intercalation Compounds

C_{60} = FCC

$K_3 C_{60}$