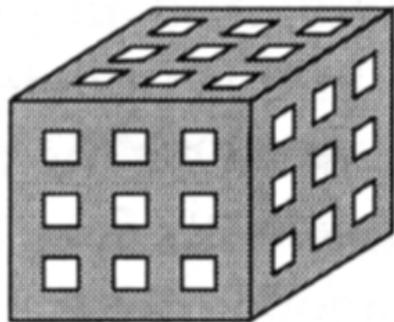


# Host-Guest Structures

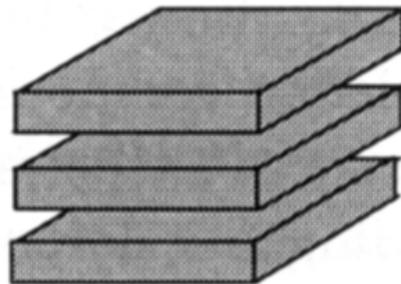
**TOPOTACTIC SOLID-STATE REACTIONS = modifying existing solid state structures while maintaining the integrity of the overall structure**

## Host dimensionality

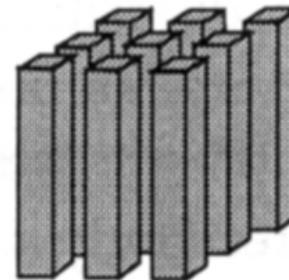
**3D**



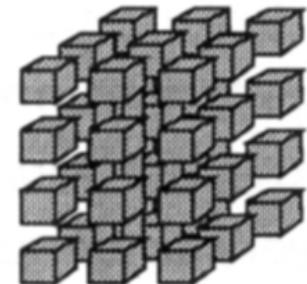
**2D**



**1D**

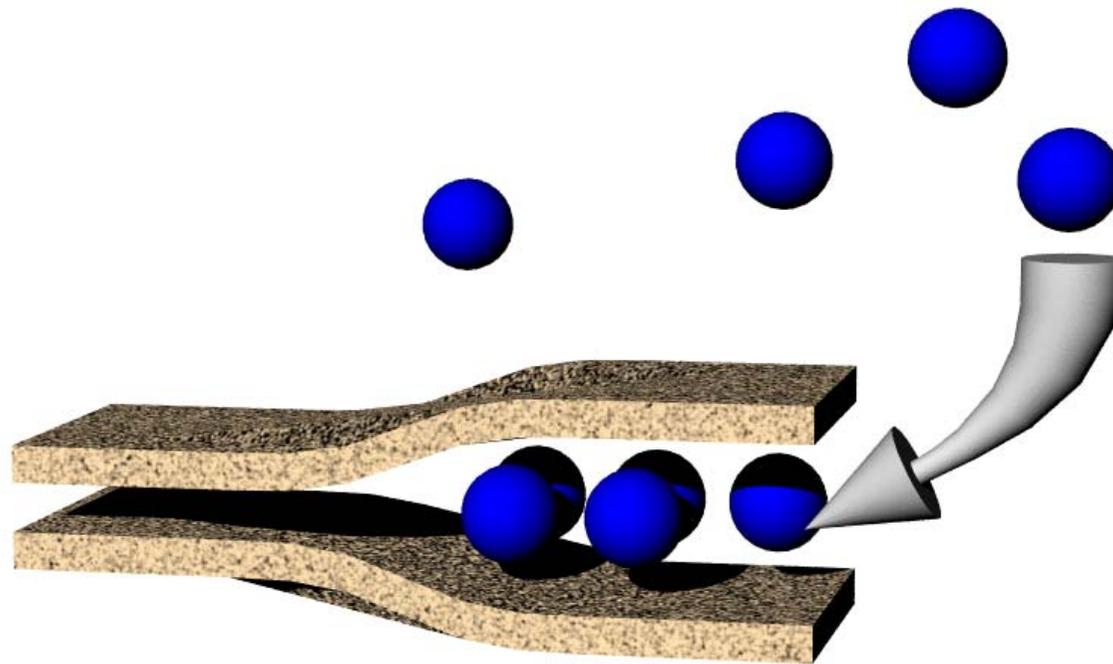


**0D**



# Layered Compounds

## Intercalation



# Layered Compounds

## GRAPHITE INTERCALATION



Graphite  $sp^2$  sigma-bonding in-plane p- $\pi$ -bonding out of plane

Hexagonal graphite = two-layer ABAB stacking sequence

SALCAOs of the p- $\pi$ -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

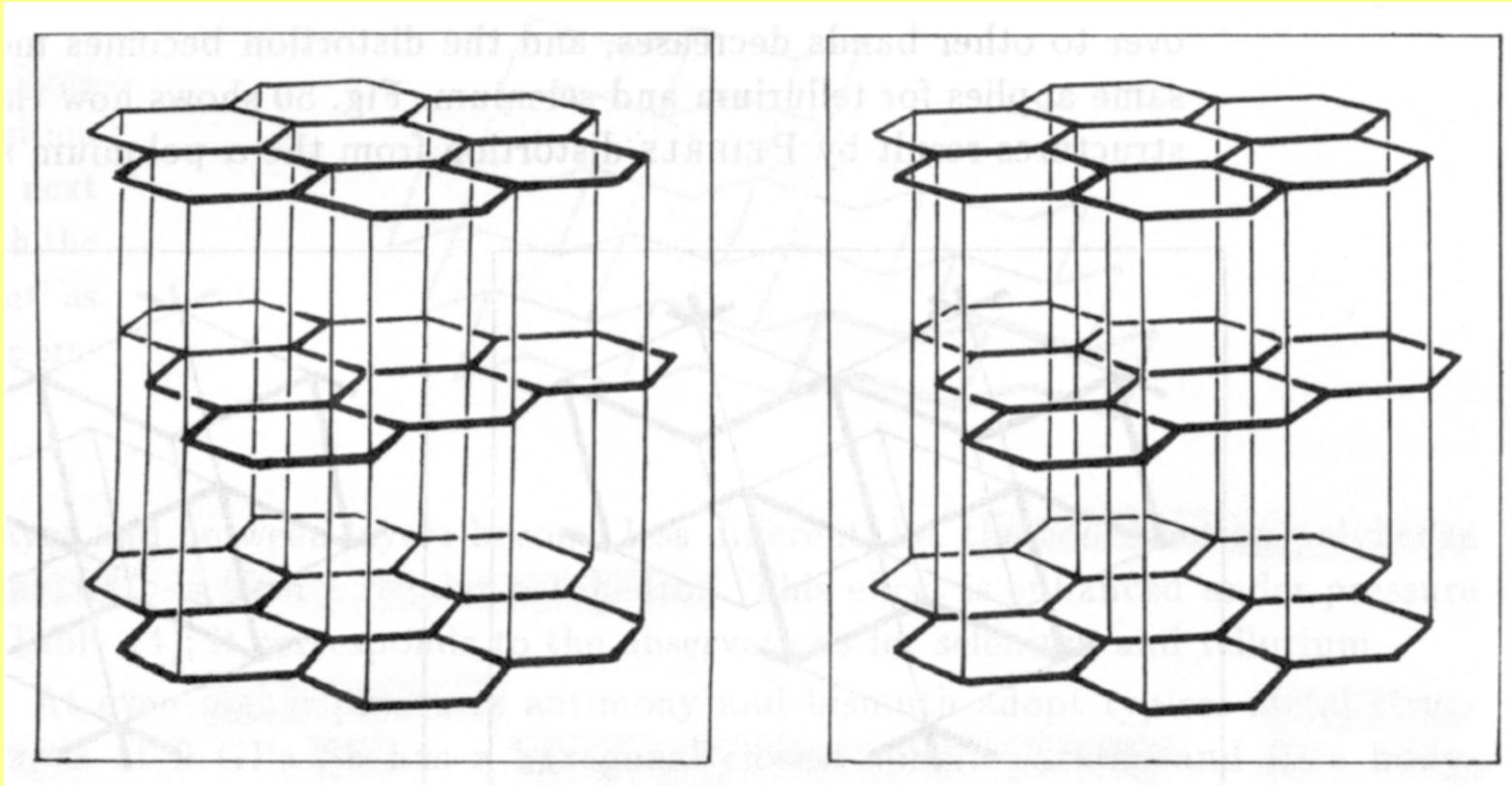
$\text{C}_8\text{K}$  potassium graphite ordered structure

Ordered K guests between the sheets, K to G charge transfer

AAAA stacking sequence, reduction of graphite sheets, electrons enter CB

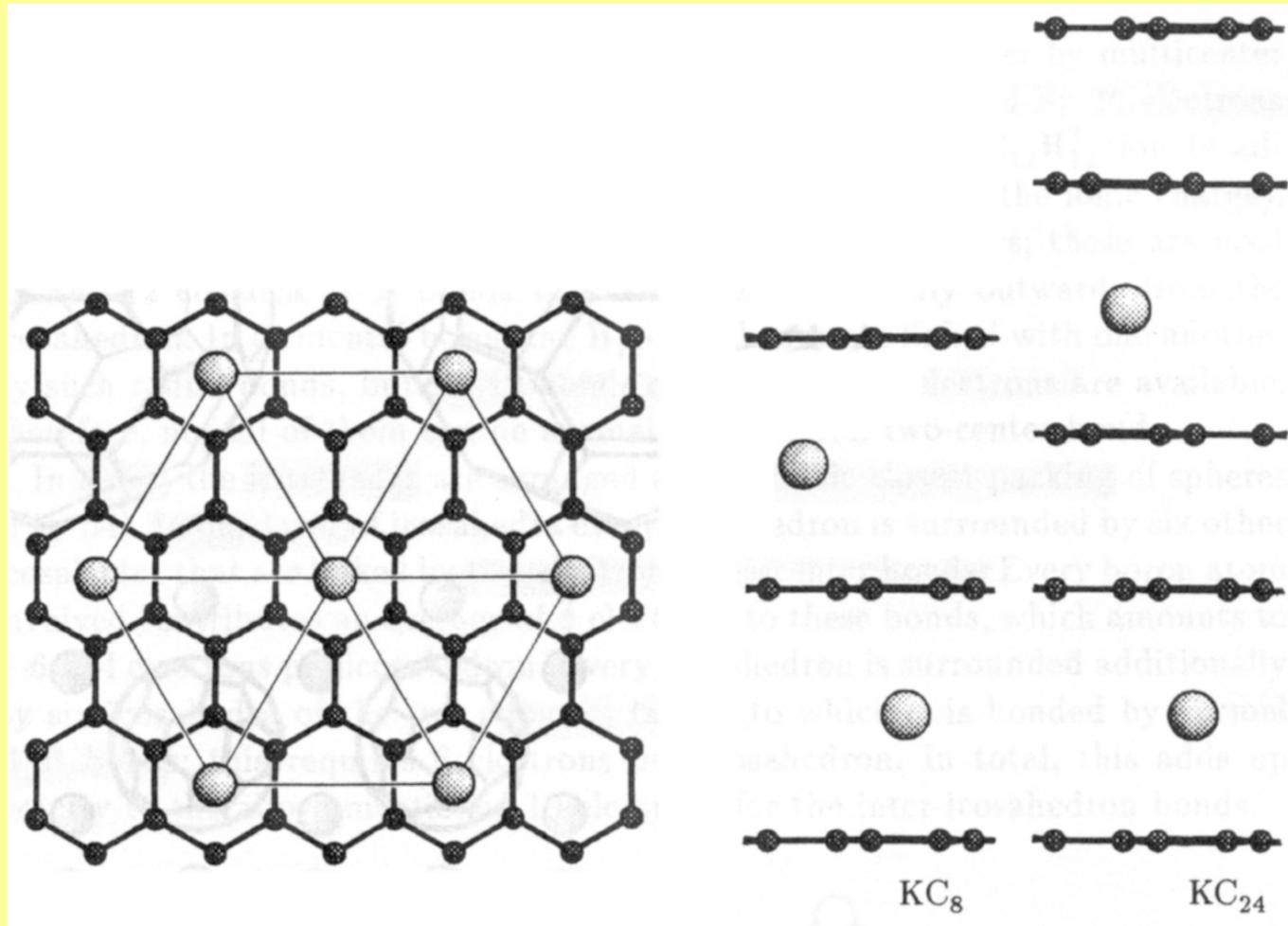
K nesting between parallel eclipsed hexagonal planar carbon six-rings

# Layered Compounds

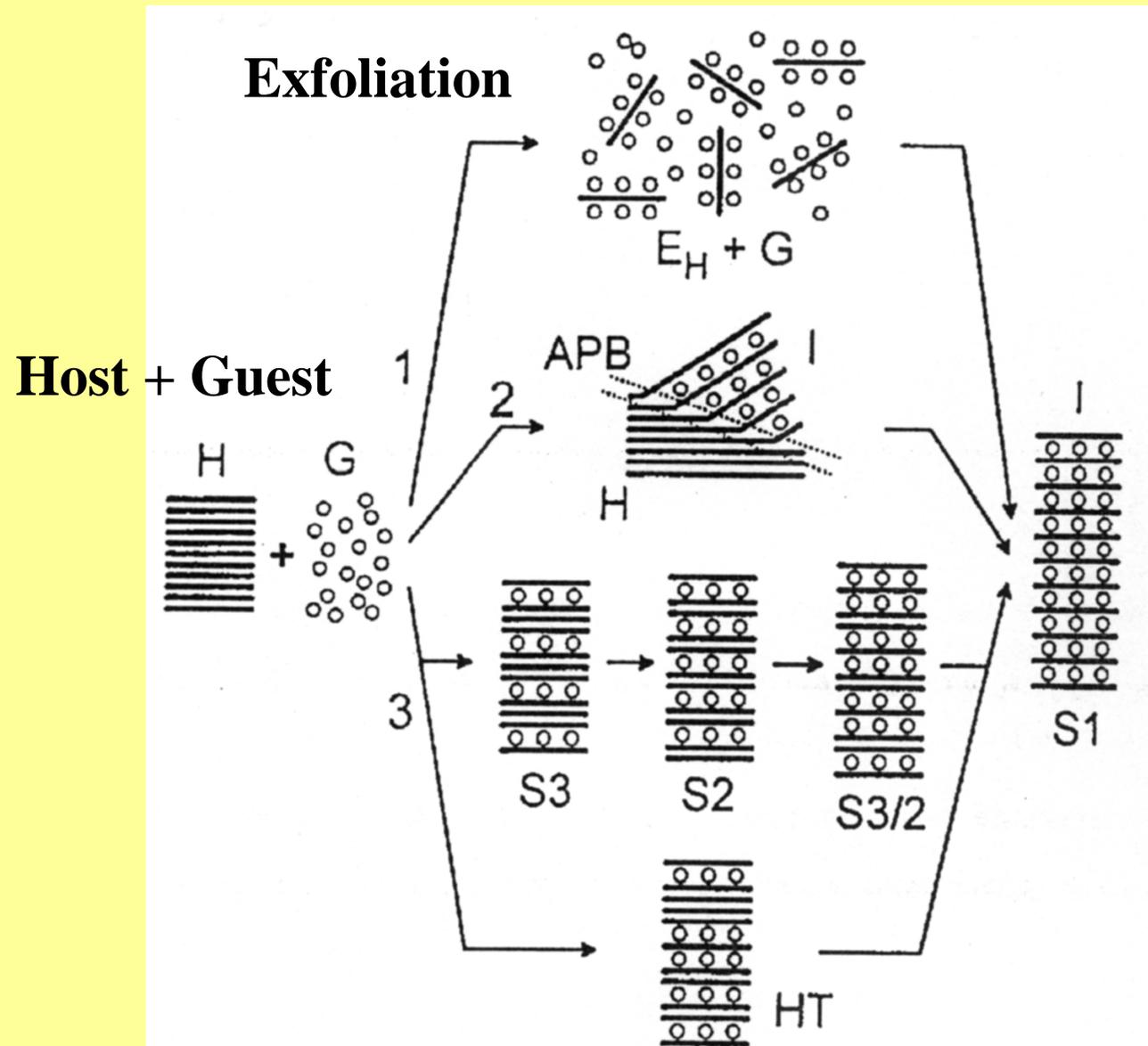


**ABABAB**

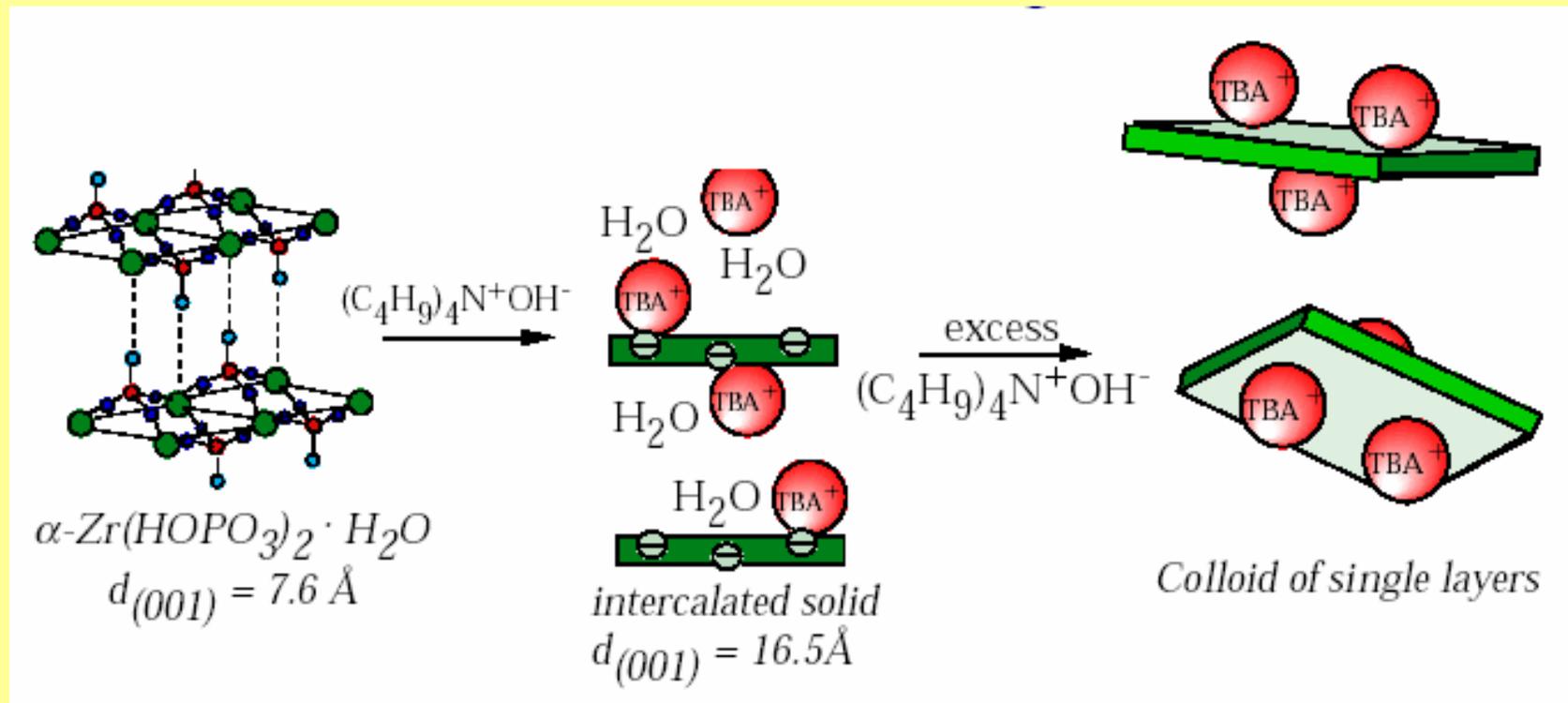
# Layered Compounds



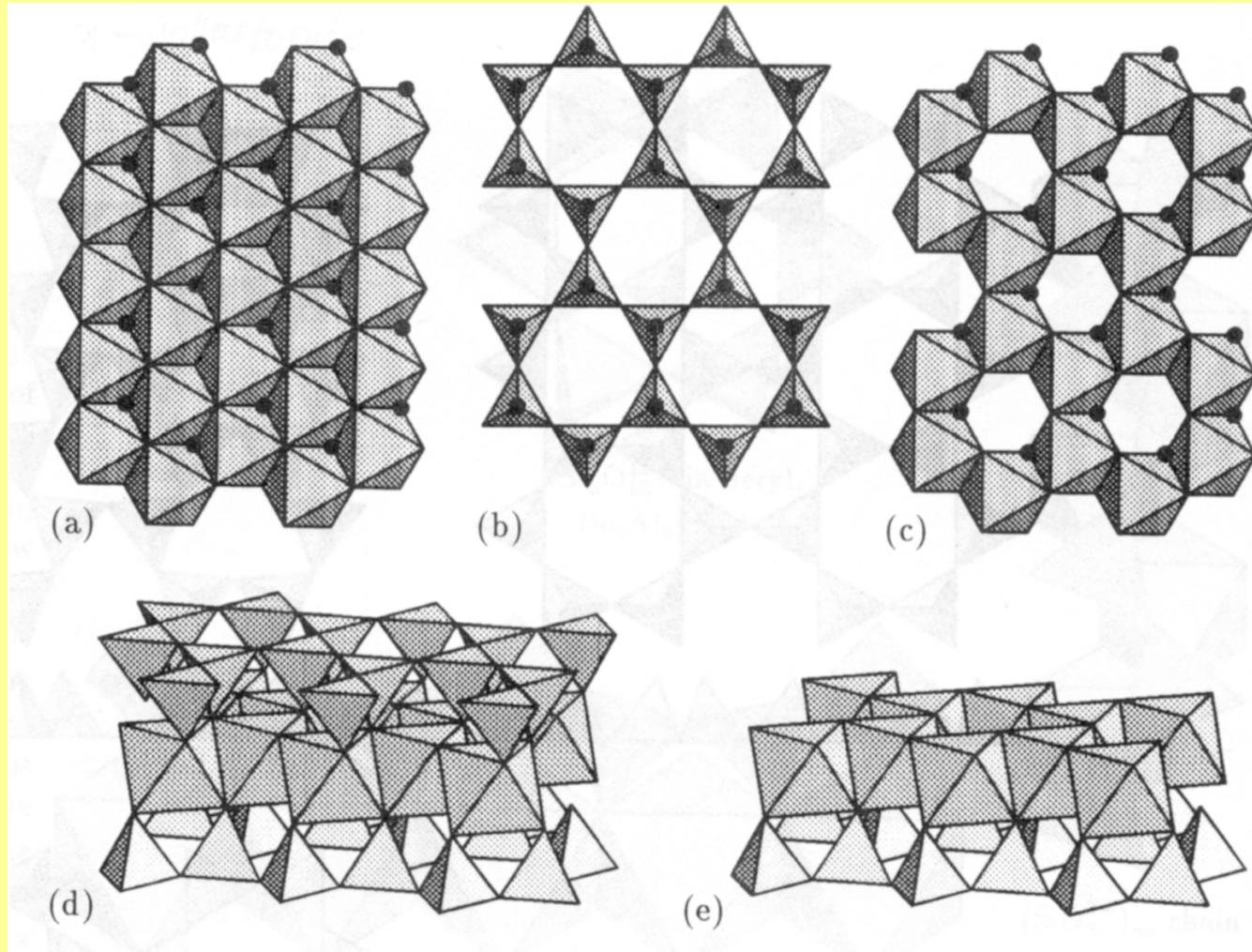
# Layered Compounds



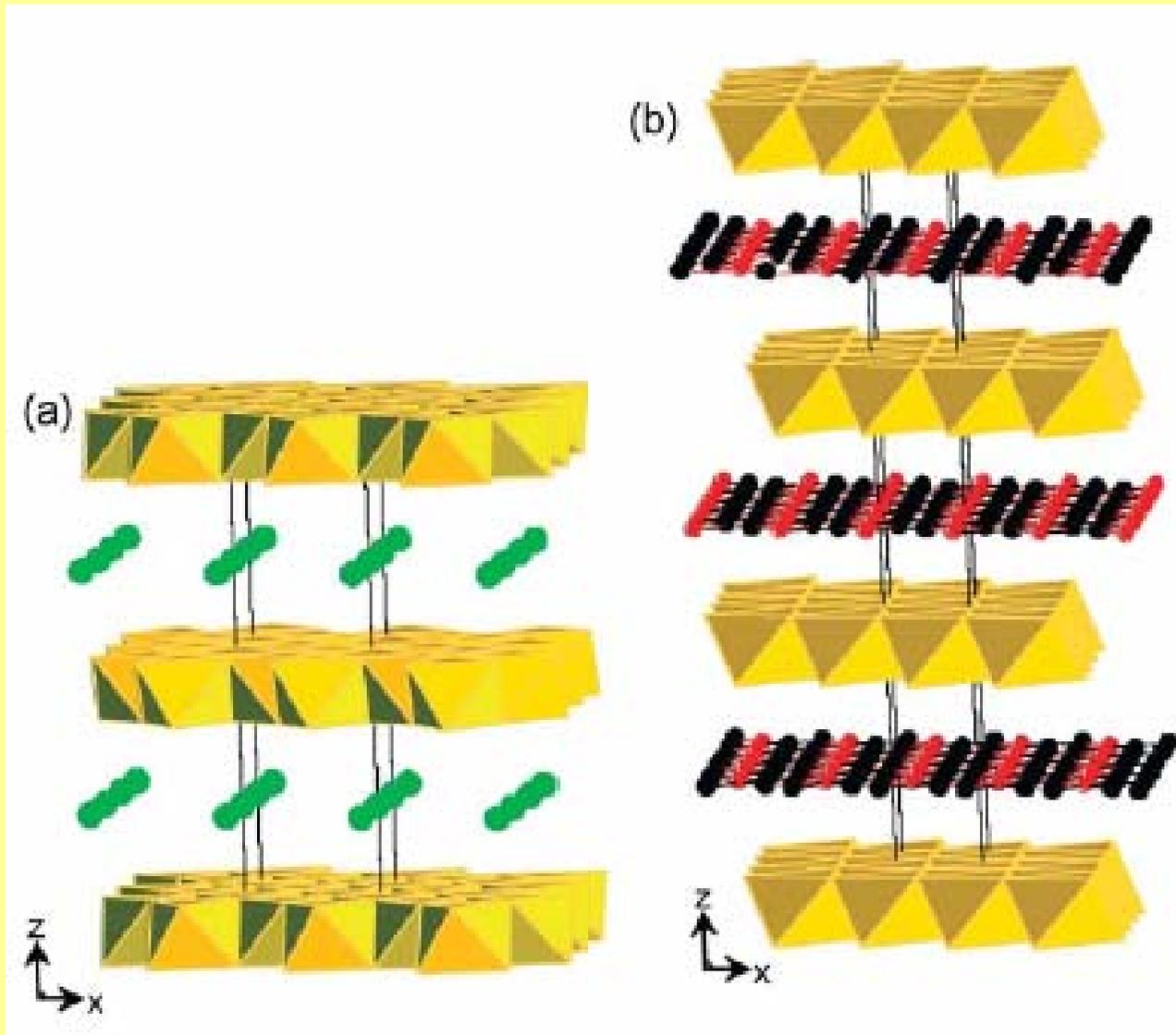
# Exfoliation



# Layered Compounds



# Layered Compounds



# Layered Compounds

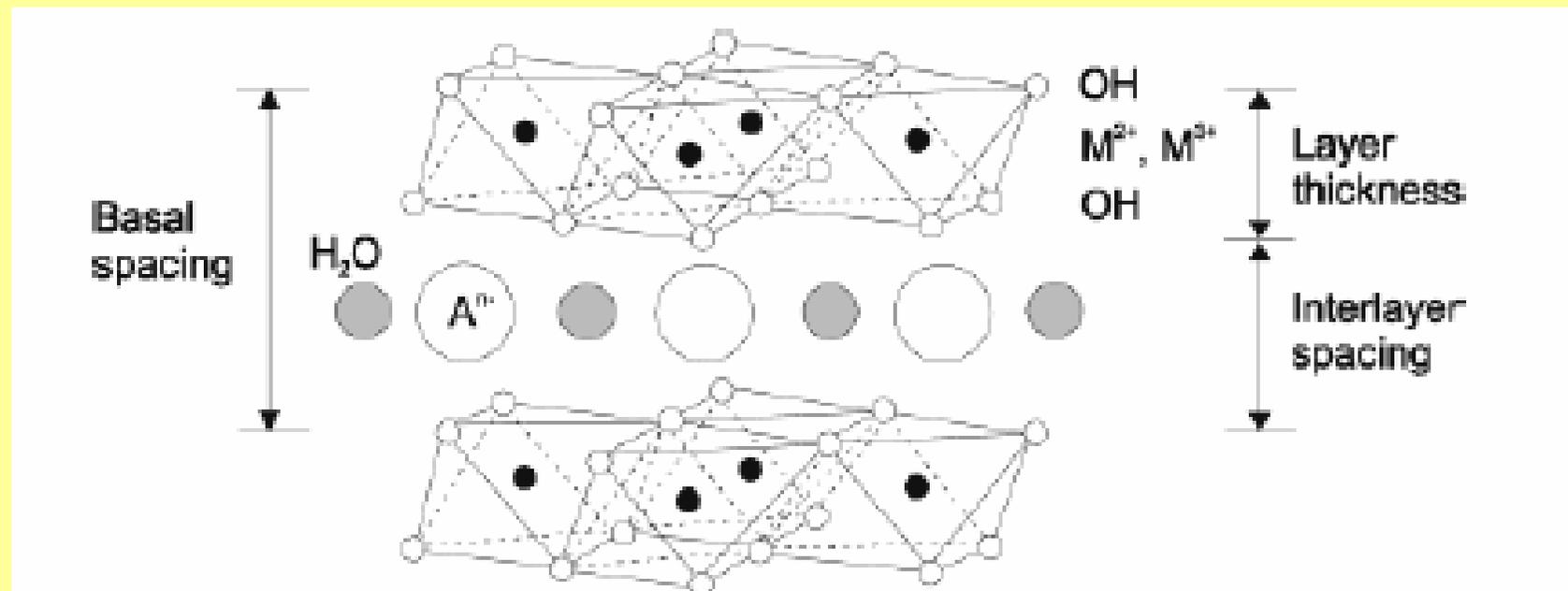
LDH = layered double hydroxides

hydrotalcites

mineral  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

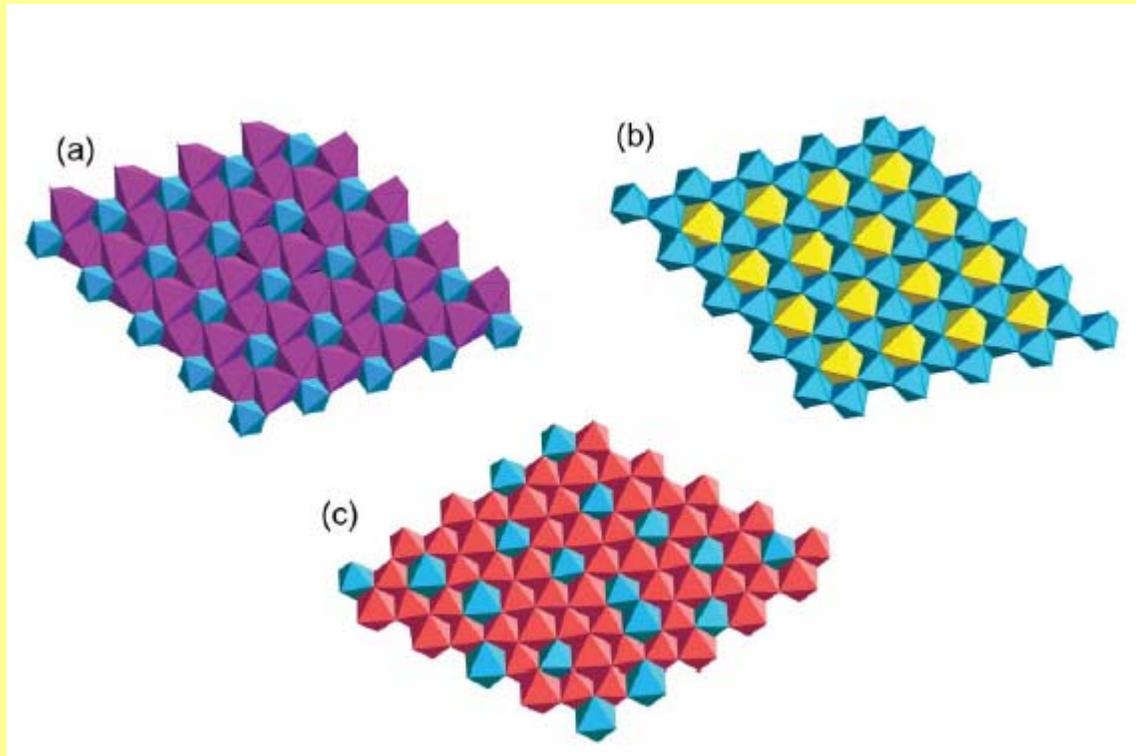
Brucite layers,  $\text{Mg}^{2+}$  substituted partially by  $\text{Al}^{3+}$

Layers have positive charge



# Layered Compounds

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



(a)  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (b)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}$  (c)  $[\text{Mg}_{2.25}\text{Al}_{0.75}(\text{OH})_6]\text{OH}$

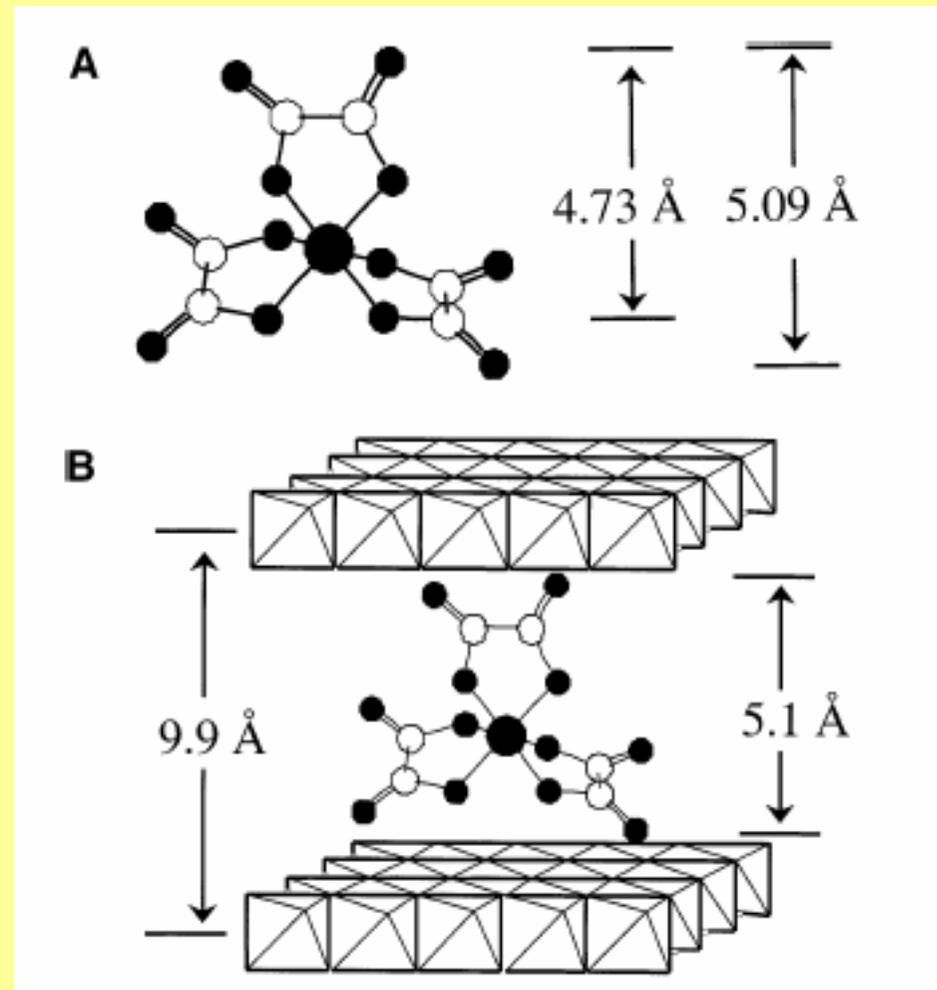
# Layered Compounds

LDH = layered double hydroxides  
hydrotalcites  
mineral  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$

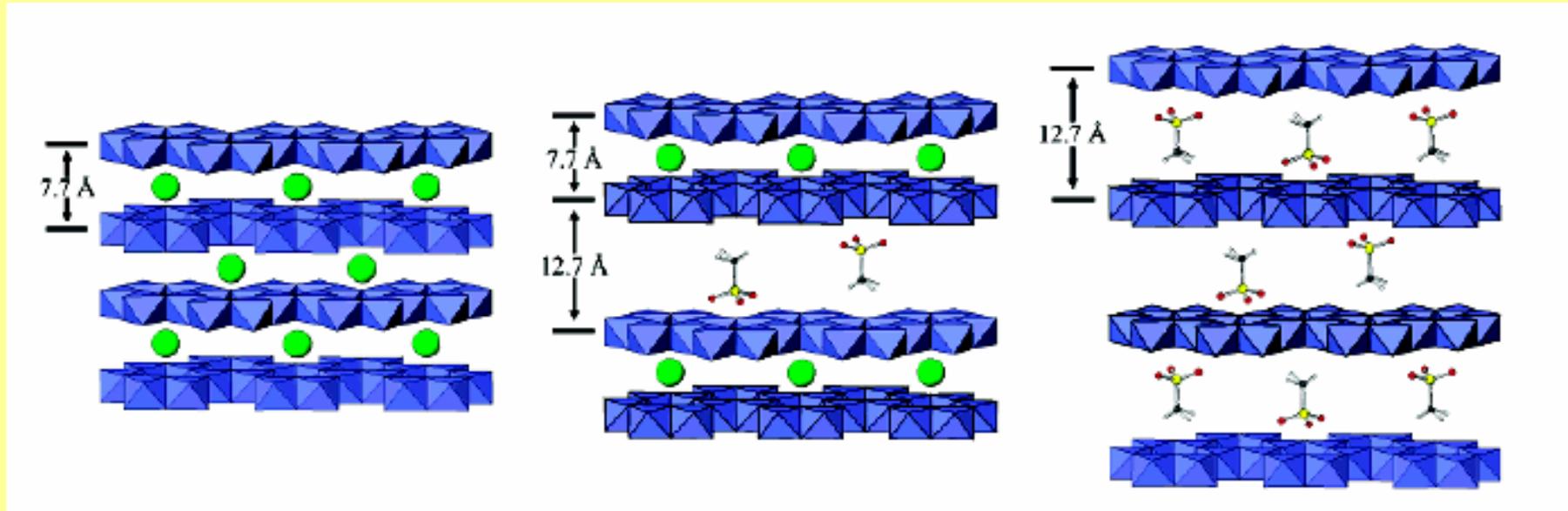
Brucite layers,  $\text{Mg}^{2+}$  substituted  
partially by  $\text{Al}^{3+}$

Layers have positive charge

Intercalate anions  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$



# Layered Compounds



the intercalation of methylphosphonic acid into Li/Al LDH

(a)  $[\text{LiAl}_2(\text{OH})_6]\text{Cl}\cdot\text{H}_2\text{O}$

(b) second-stage intermediate, alternate layers occupied by Cl and MPA anions

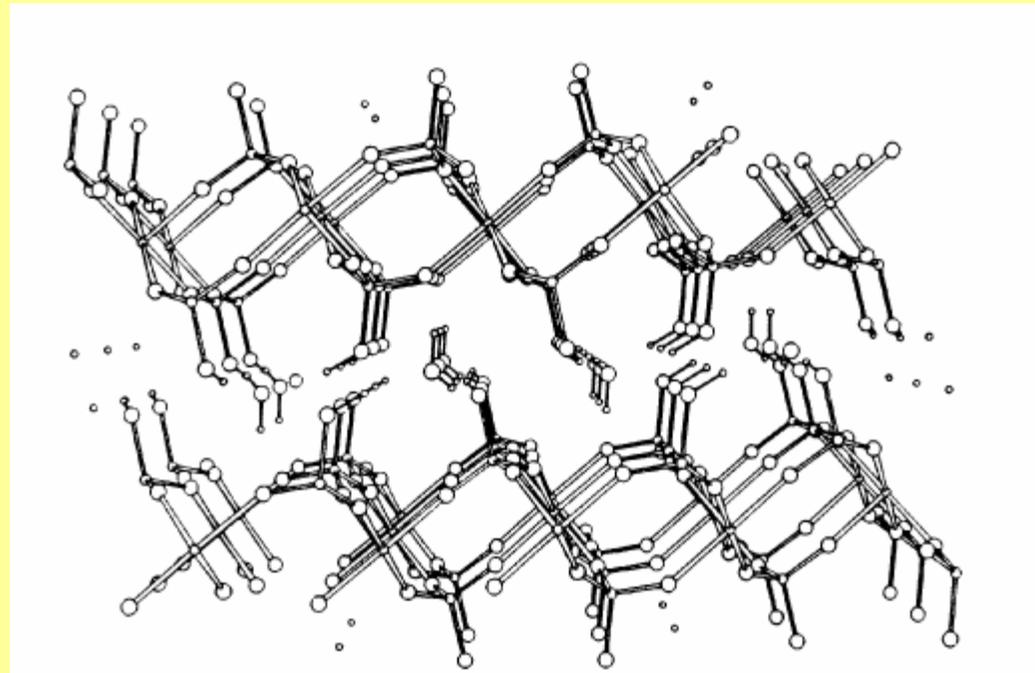
(c) first-stage product with all interlayer regions occupied by MPA.

# Layered Compounds

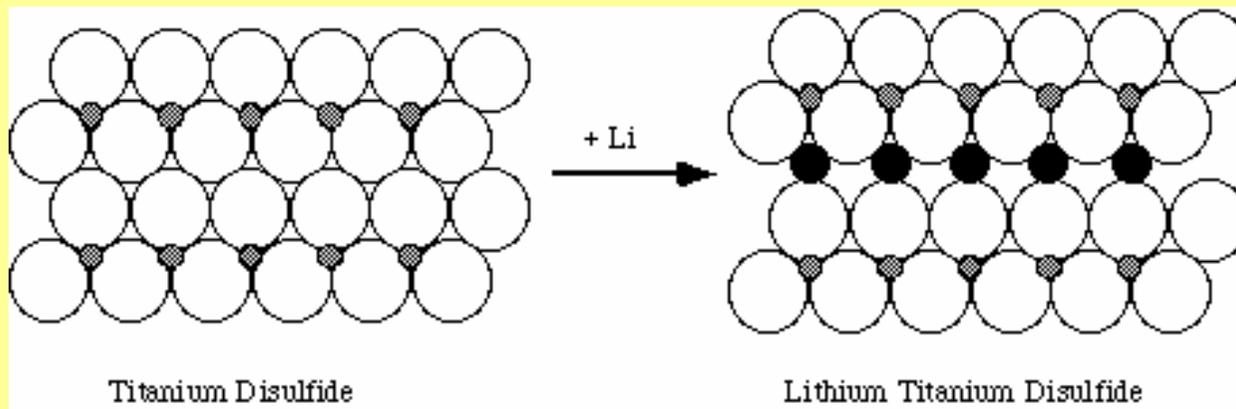
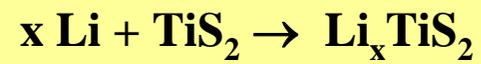
$MPS_3$  (M = V, Mn, Fe, Co, Ni, Zn)

$TiS_2$

$\alpha\text{-Zr(HPO}_4)_2 \cdot \text{H}_2\text{O}$

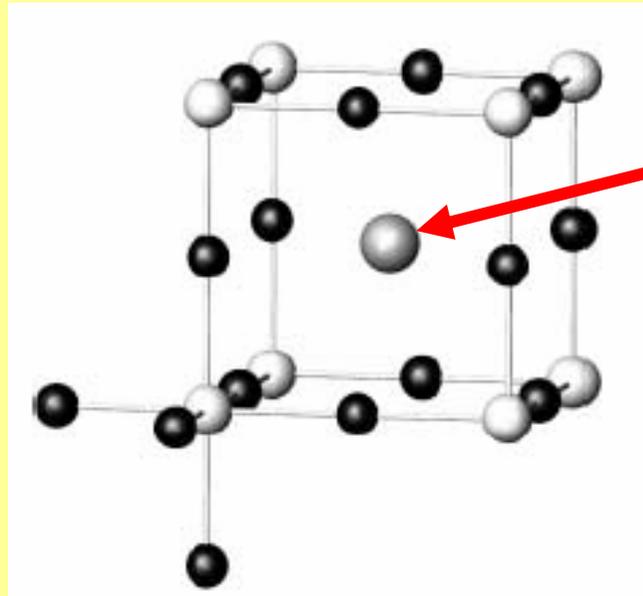


# Layered Compounds



# 3D Intercalation Compounds

$\text{Cu}_3\text{N}$  and  $\text{Mn}_3\text{N}$  crystallize in the (anti-)  $\text{ReO}_3$ -type structure



the large cuboctahedral void in the structure can be filled

By Pd to yield (anti-) perovskite-type  $\text{PdCu}_3\text{N}$

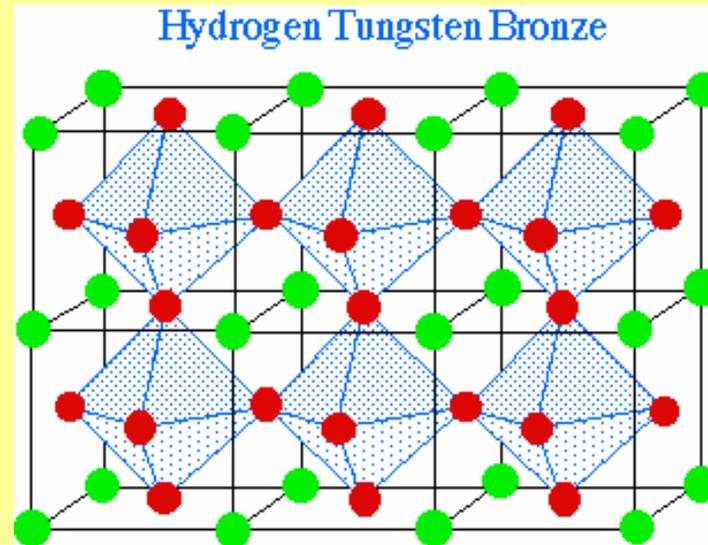
By  $\text{M} = \text{Ga}, \text{Ag}, \text{Cu}$  leading to  $\text{MMn}_3\text{N}$

# 3D Intercalation Compounds

**Tungsten trioxide structure**

=  $\text{WO}_6$  octahedra joined at their corners

= the perovskite structure of  $\text{CaTiO}_3$  with all the calcium sites vacant



The color and conductivity changes are due to the intercalation of protons into the cavities in the  $\text{WO}_3$  structure, and the donation of their electrons to the conduction band of the  $\text{WO}_3$  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

