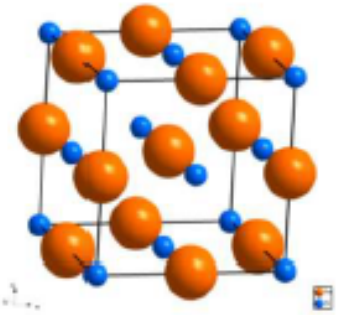
Defects in oxides

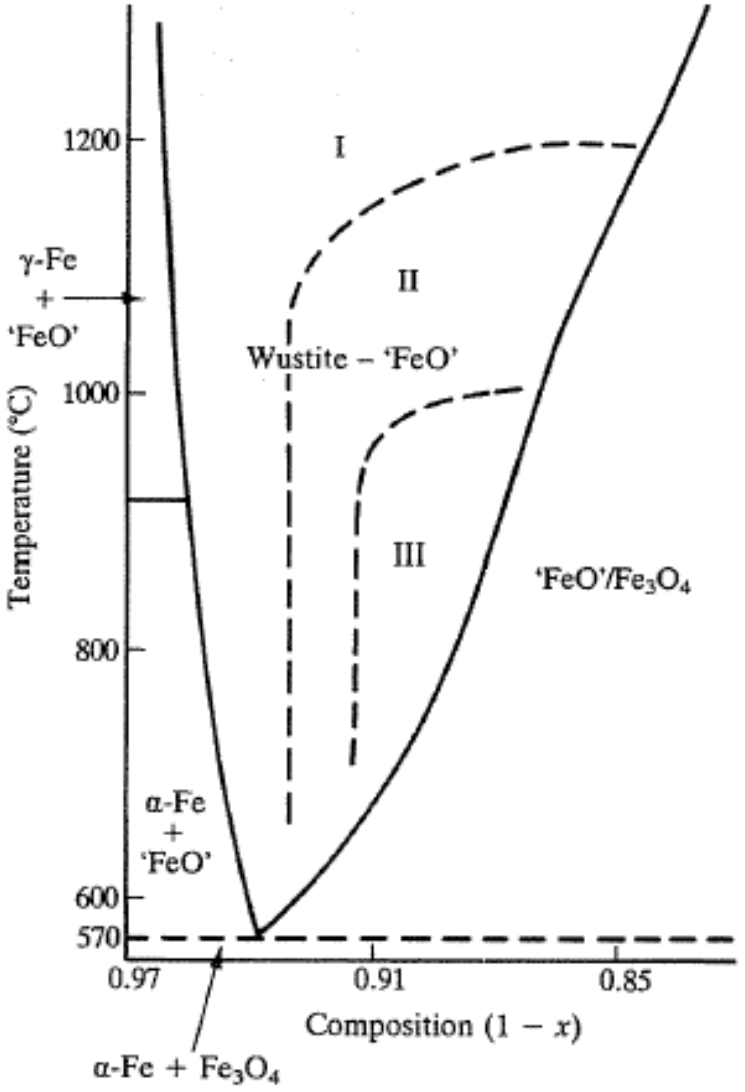
Non-stoichiometry in Wustite (FeO)

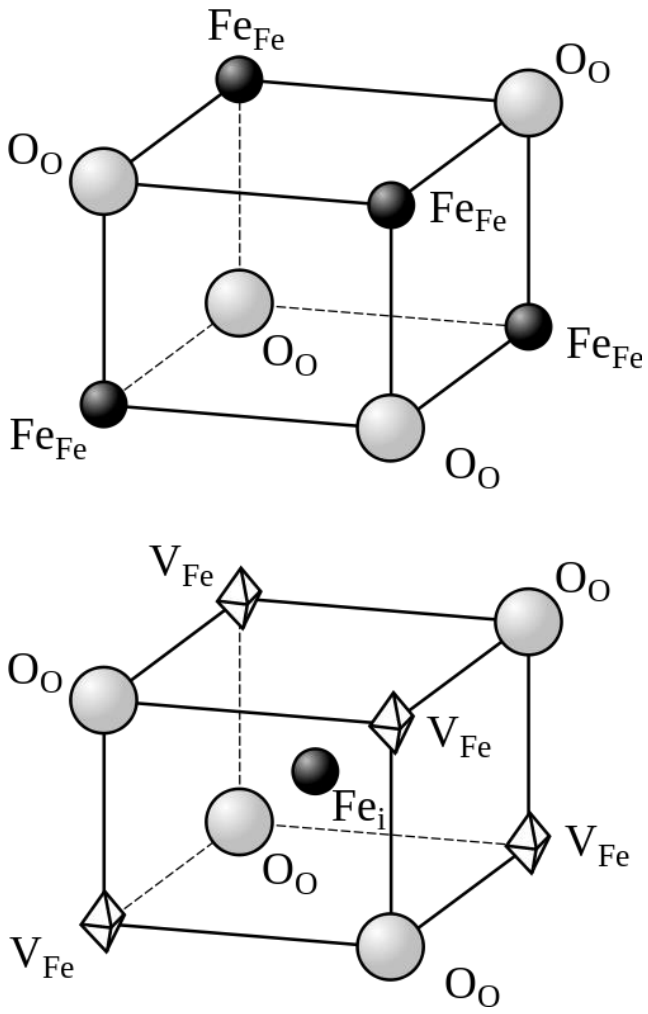
Ferrous oxide, or wustite (FeO) has the NaCl structure type.



- Chemical analysis indicates it is non-stoichiometric and always deficient in iron. Stoichiometric FeO isn't stable, and below 570°C disproportionates into α-Fe and Fe_3O_4.
- Iron deficiency may be accommodated in the structure on one of two ways:

1. Iron vacancies, giving $Fe_{1-x}O$
2. Excess of oxygen in interstitial positions, giving FeO_{1+y}



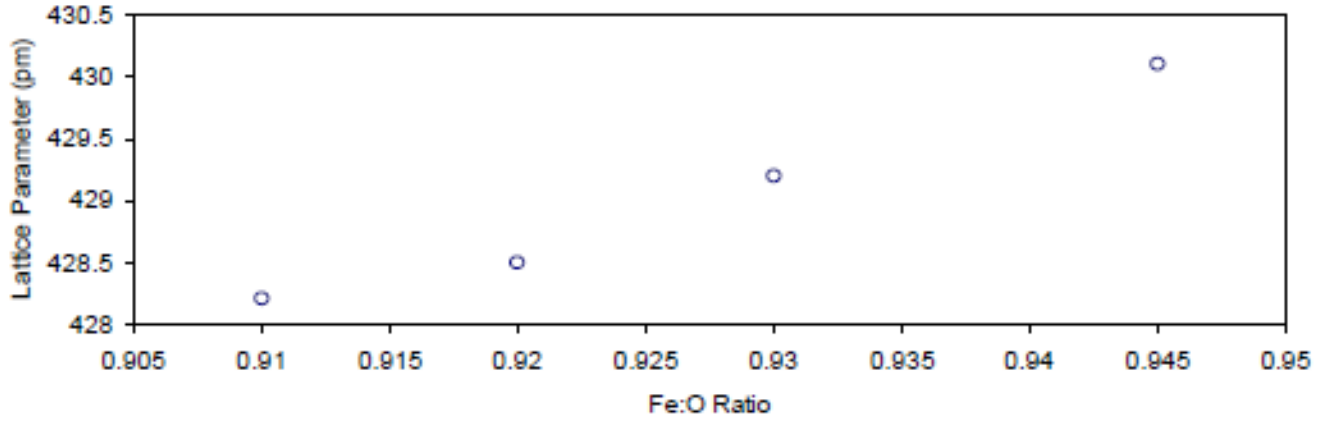


Defects cluster in wüstite (FeO):
four iron vacancies V_{Fe} and an interstitial iron atom Fe_i.

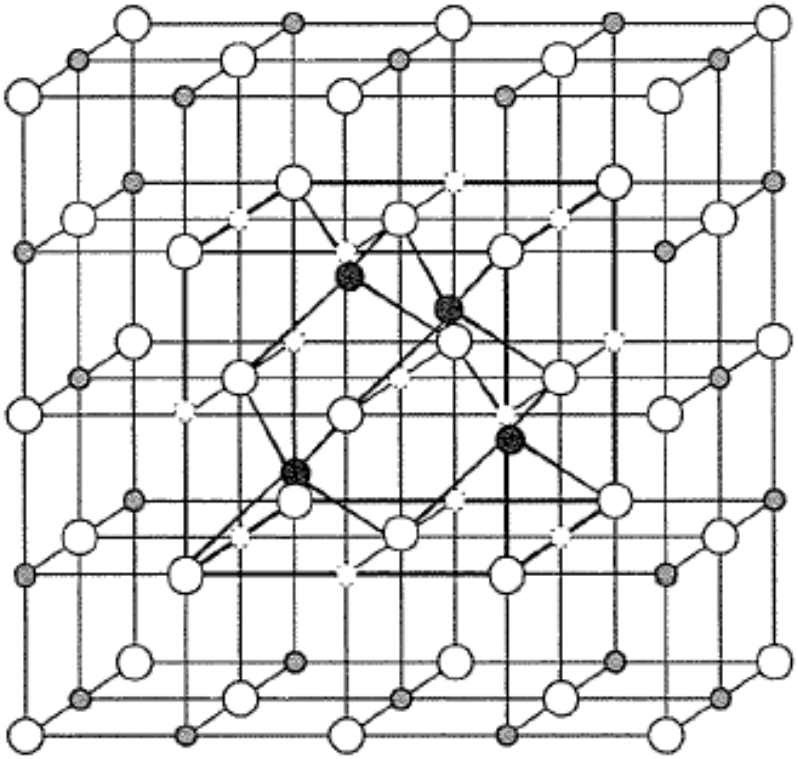
Vegard's Law

It is often found that non-stoichiometric compounds have a unit cell size that varies smoothly with composition but has symmetry that is unchanged, which is known as Vegard's Law.

O:Fe ratio	Fe:O ratio	Lattice parameter /pm	Observed density (g/cm^3)	Interstitial O (g/cm^3)	Fe Vacancies (g/cm^3)
1.058	0.945	430.1	5.728	6.075	5.742
1.075	0.930	429.2	5.658	6.136	5.706
1.087	0.920	428.5	5.624	6.181	5.687
1.099	0.910	428.2	5.613	6.210	5.652



Koch-Cohen Cluster



O

*Front and back plans cut away for clarity

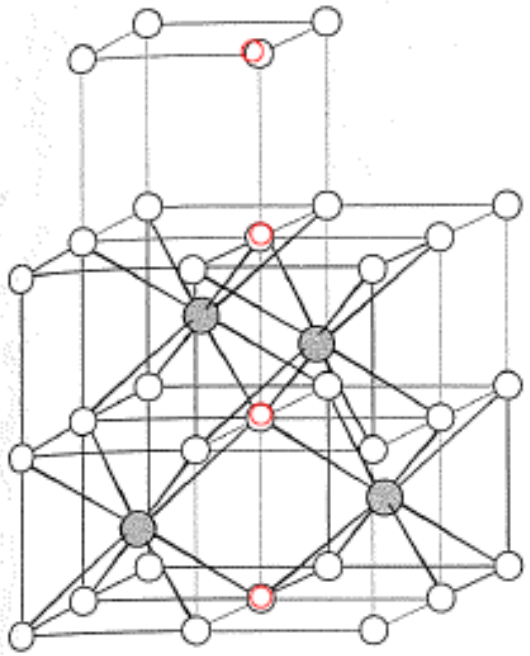
Fe^{3+}_{tet}

Vacancy

Fe_{oct}

- A *defect cluster* is a region of the crystal where defects form an *ordered structure*.
- Surrounding the central defect unit cell, the other octahedral iron sites (Fe_{oct}) are occupied, but may contain either Fe^{2+} or Fe^{3+}.
- Clusters sometimes referred to the ratio of cation vacancies to interstitial Fe^{3+} in tetrahedral holes (13:4).

Uranium Dioxide



- Above 1127°C, a single oxygen-rich non-stoichiometric phase of UO_2 is found with formula UO_2 to $UO_{2.25}$ (U_4O_9)
- Interstitial anions are present in the fluorite structure.
- Interstitial O′ causes O″ displacement.
- A defect cluster, considered as two vacancies, one interstitial of one kind O′, and two of another O″, is called a 2:1:2 Willis cluster.
- The movement of the interstitial oxide O′ is along the direction towards the diagonal of the cube face (110) direction, whereas the O″ is along cube diagonal (111)
- Can consider UO_2 as containing microdomains of U_4O_9 structure within UO_2.

Electronic Properties of Non-stoichiometric Oxides

Four basic types of compounds are non-stoichiometric:

Metal excess (reduced metal)

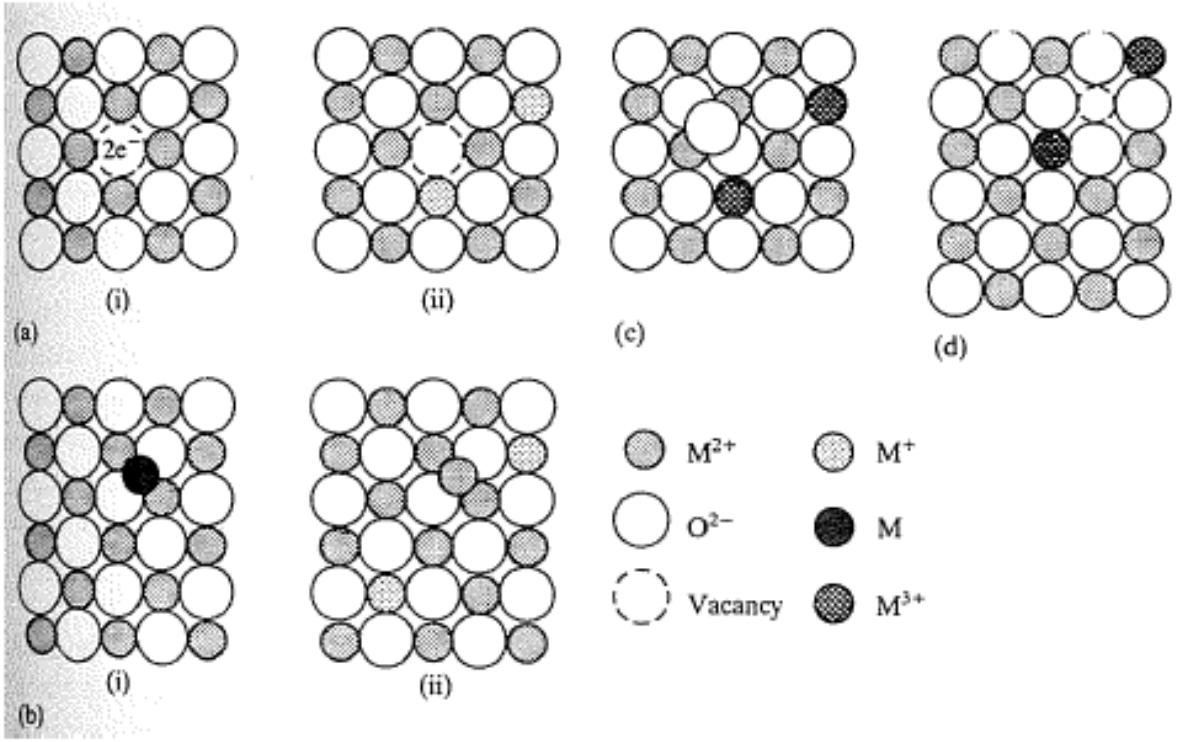
Type A: anion vacancies present → formula MO_{1-x} (e.g. TiO, VO, ZrS)

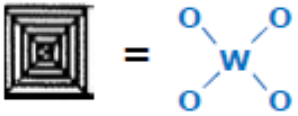
Type B: interstitial cations → formula $M_{1+x}O$ (e.g. CdO, ZnO)

Metal deficiency (oxidized metal)

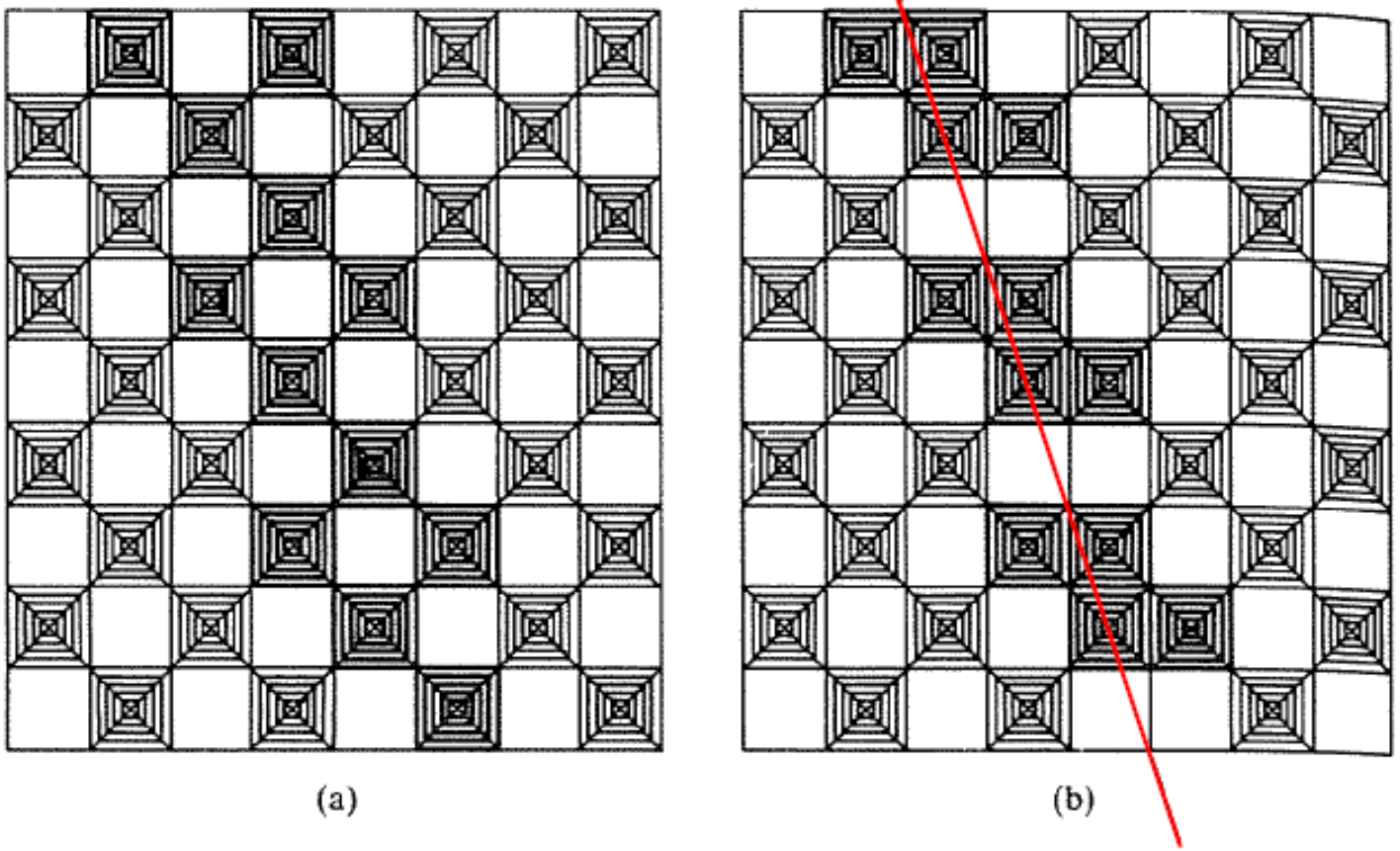
Type C: interstitial anions → formula MO_{1+x}

Type D: cation vacancies → $M_{1-x}O$ (e.g. TiO, VO, MnO, FeO, CoO)





Formation of Shear Structure

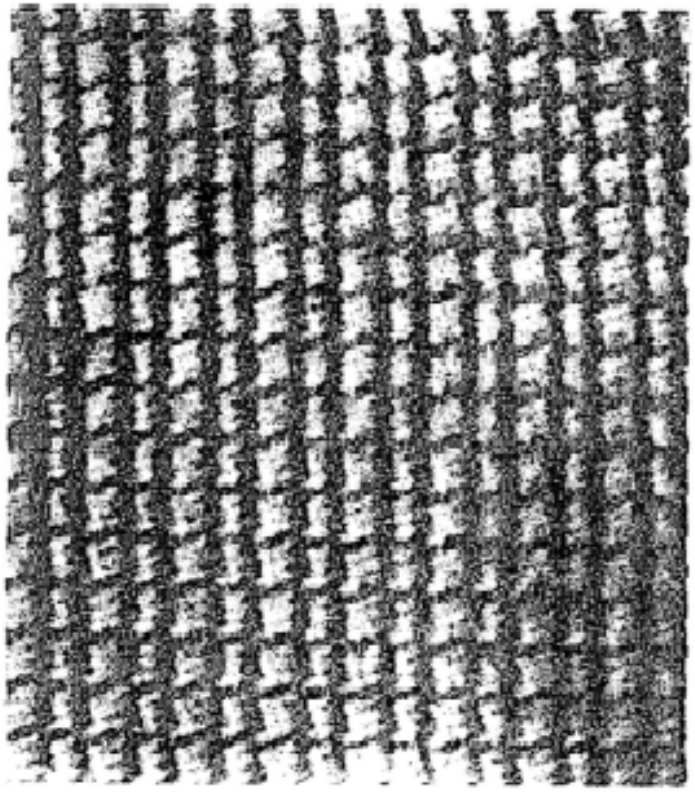


(a) (b)

Three-Dimensional Defects: Block Structures

In O-deficient Nb_2O_5, and mixed oxides of Nb and Ti, and Nb and W, the crystallographic shear planes occur in two sets at right angles to each other.

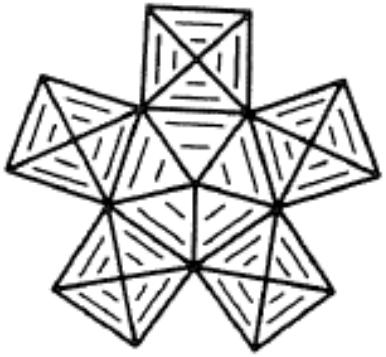
- Intervening regions of perfect structure change from infinite sheets to infinite columns or blocks, which are known as double shear or block structures.
- Characterized by the cross sectional size of the blocks.
- May also have blocks of two or three different sizes arranged in an ordered fashion, such as the 4x4 and 3x4 blocks in $W_4Nb_{26}O_{77}$.



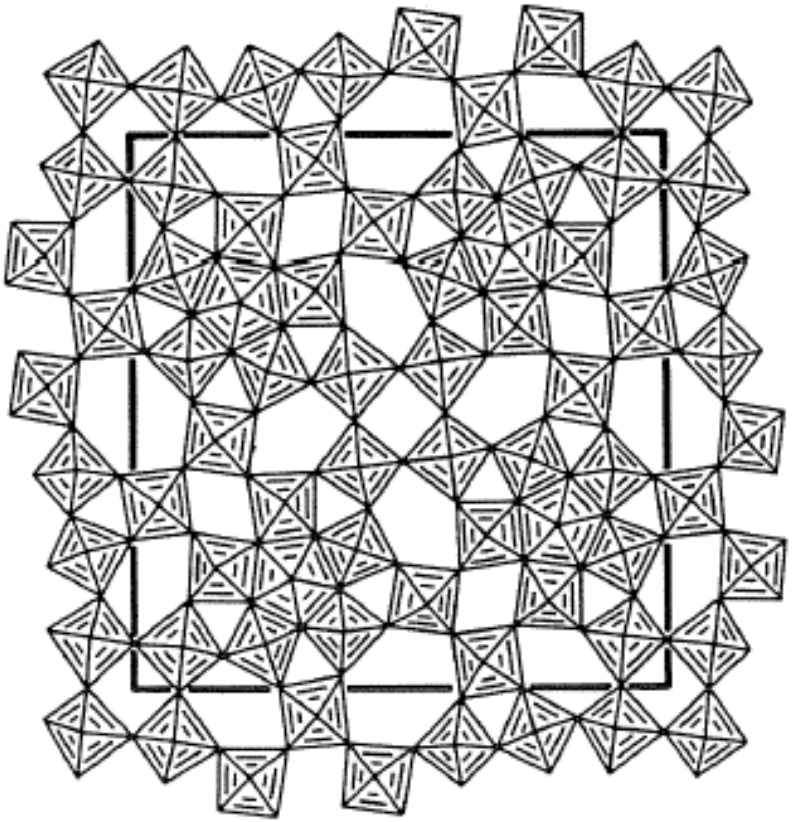
High-resolution electron micrograph of $W_4Nb_{26}O_{77}$

Three-Dimensional Defects: Pentagonal Columns

- Structure consists of a pentagonal ring of five [MO_6] octahedra, which when stacked form a pentagonal column with alternating M and O atoms.
- The pentagonal columns fit inside an ReO_3 type structure in an ordered way and, depending on the spacing, form a homologous series.
- One example is the Mo_5O_{14} structure.



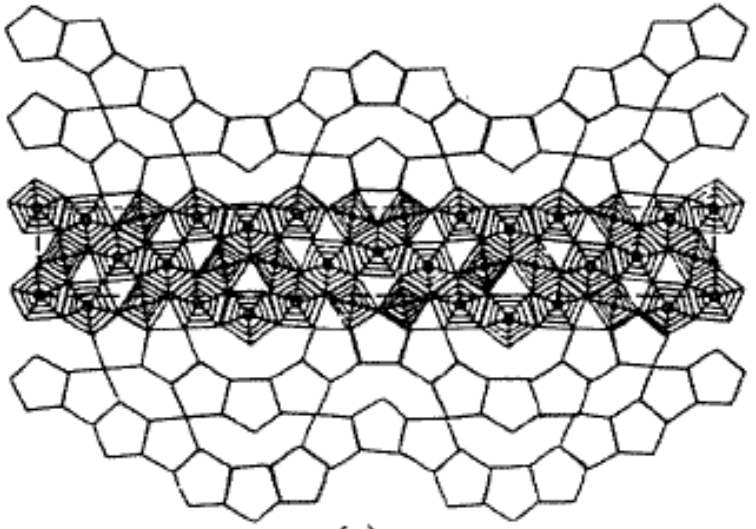
(a)



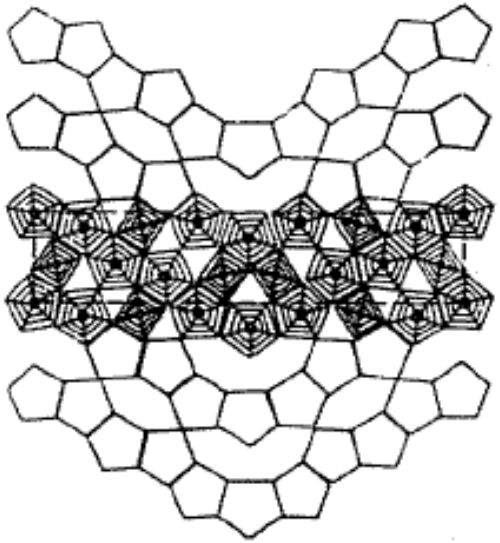
(b) Mo_5O_{14}

Three-Dimensional Defects: Infinitely Adaptive Structures

- A large number of compounds form in the Ta_2O_5-WO_3 system, built from fitting together pentagonal columns.
- Structure have a *wavelike* skeleton of pentagonal columns.
- As the composition varies, the 'wavelength' of the backbone changes, giving rise to a huge number of possible ordered structures, know as infinitely adaptive structures.



(a) $Ta_{22}W_4O_{67}$



(b) $Ta_{30}W_2O_{81}$