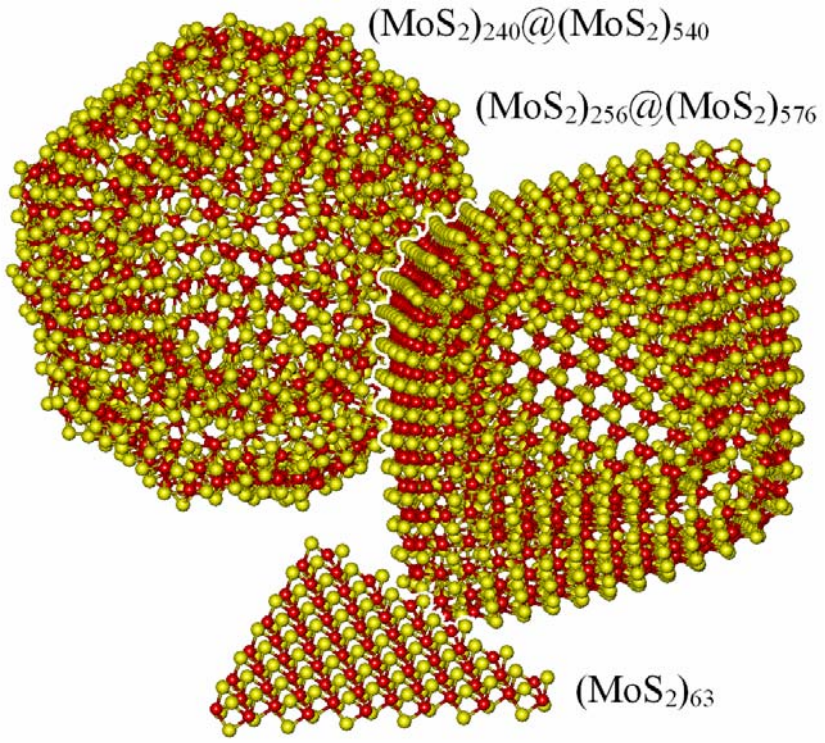
Molybdenum Sulfide Nanostructures for Functional Thin Films



(in collaboration with TUD group of Prof. Seifert)

References:

Enyashin, A.N., Gemming, S., et al.,

"Structure and Stability of Molybdenum Sulfide Fullerenes.",
Angew. Chem. Int. Ed. **46** (2007) 623-627.

Gemming, S., Seifert, G.,

"Nanoplatelets: Catalysts on the edge.",
Nature Nanotech. **2**, 21-22 (2007)

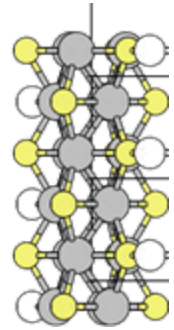
Popov, I., ; Gemming, S.; Seifert, G.,

"Structural and Electronic Properties of a Mo_6S_8 Cluster deposited on a Au(111) Surface",
Phys. Rev. B. **75**, (2007), online first.

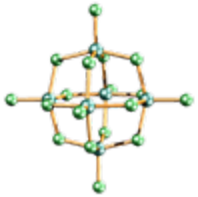
S. Gemming

Institut für Ionenstrahlphysik
und Materialforschung

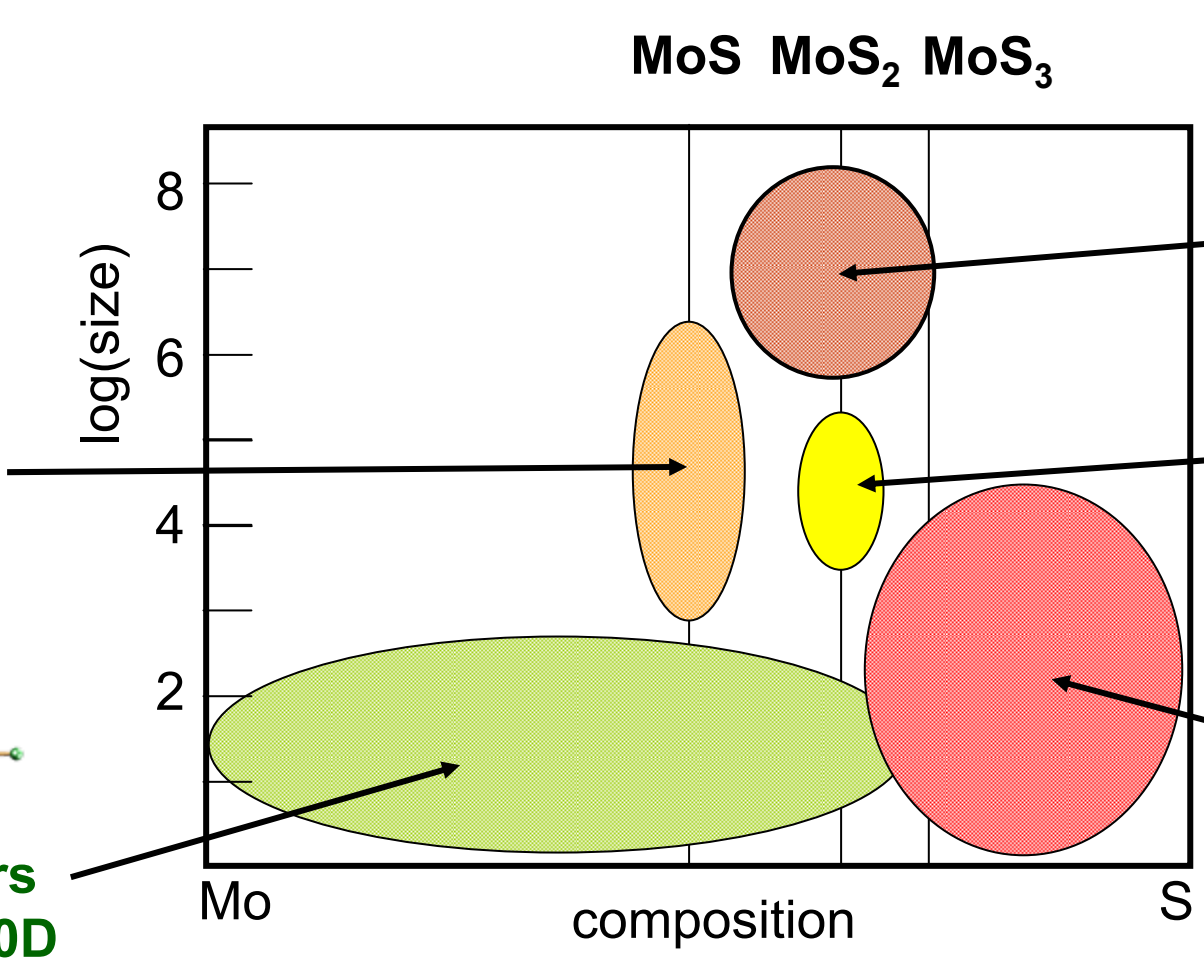
Molybdenum sulfide based structures
Morphological phase diagram



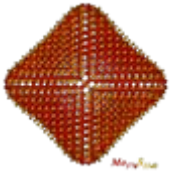
tubes,
wires
1D



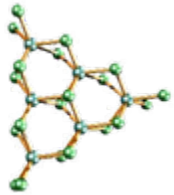
clusters
quasi-0D



fullerenes
3D



octahedra
3D



platelets
2D

Overview

I. Clusters and fullerenes – the 0D limit

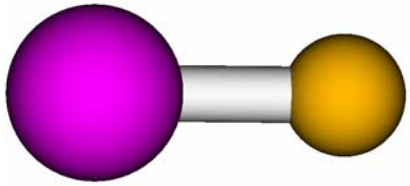
II. Cluster-platelet transition – the 2D limit

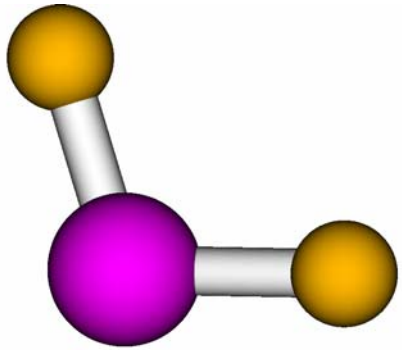
III. Cluster-wire transition – the 1D limit

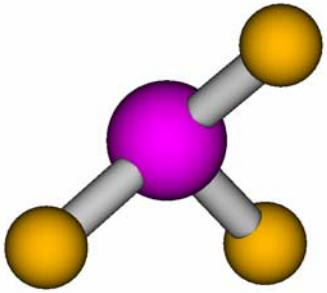
I. Small clusters – 0D limit: MoS_n n=1…6

Structural elements and functional groups

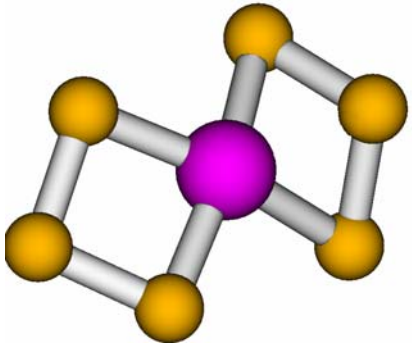
Mo=S
double bond

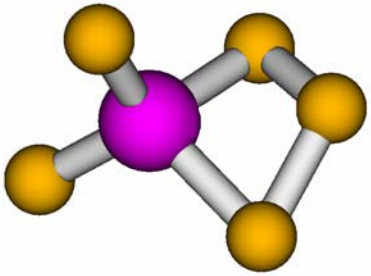


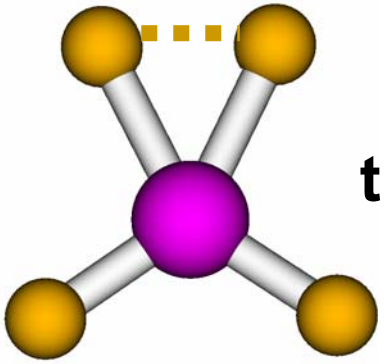




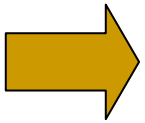
MoS_3
unit







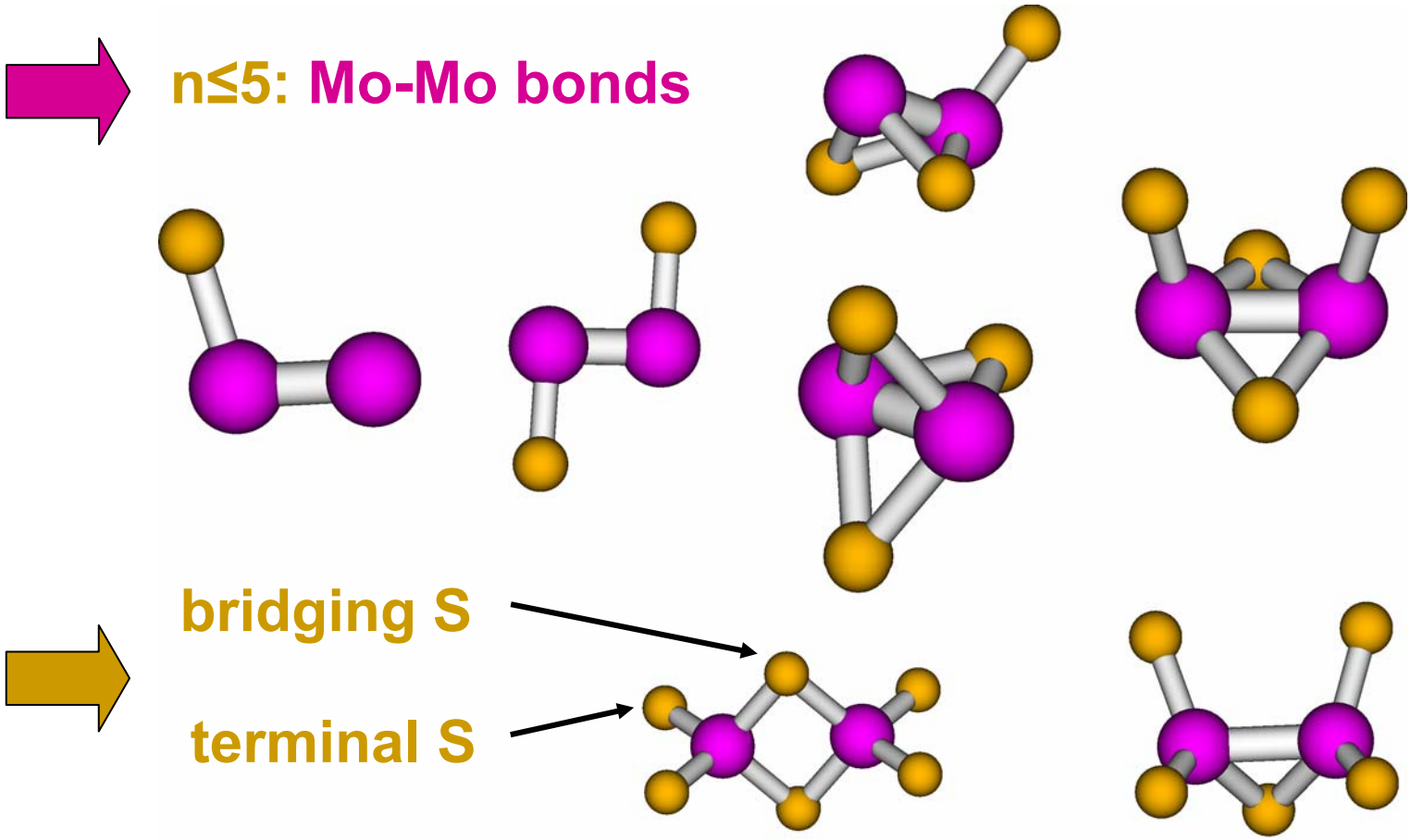
MoS_2
triangle



anions: S^{2-}, S_2^{2-}, S_3^{2-}

I. Small clusters – 0D limit: Mo_2S_n n=1…6

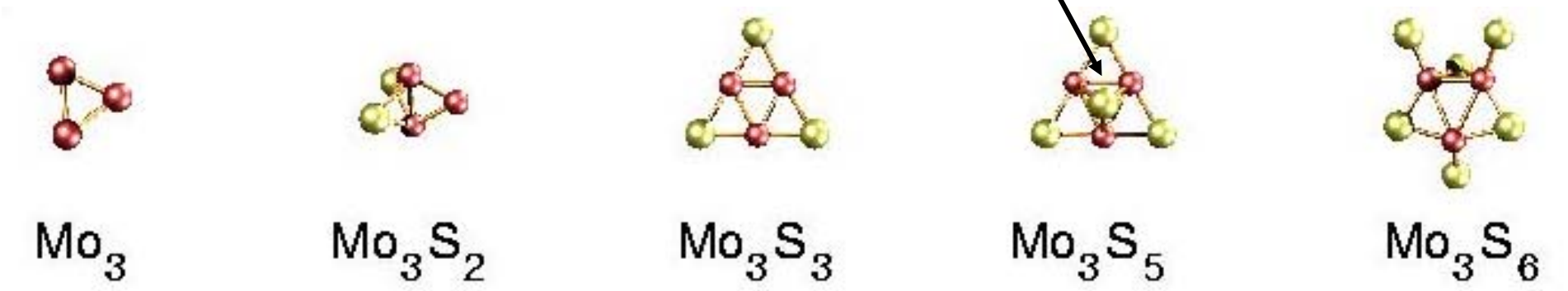
Structural elements and functional groups



Gemming, Tamuliene, Seifert, Bertram, Kim, Ganteför, *Appl. Phys. A* **82** (1): 161-166 (2006)

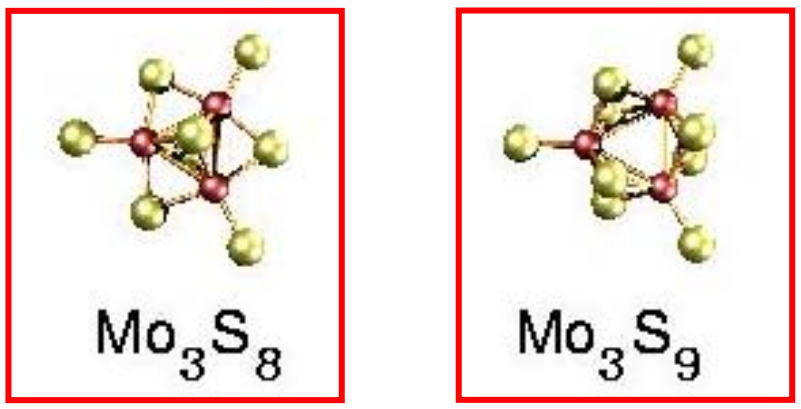
I. Small clusters – 0D limit:
Structures – Mo_3S_n n=1…12

Mo-Mo **S_2^{2-}** **bridging S** **facial S** **terminal S**



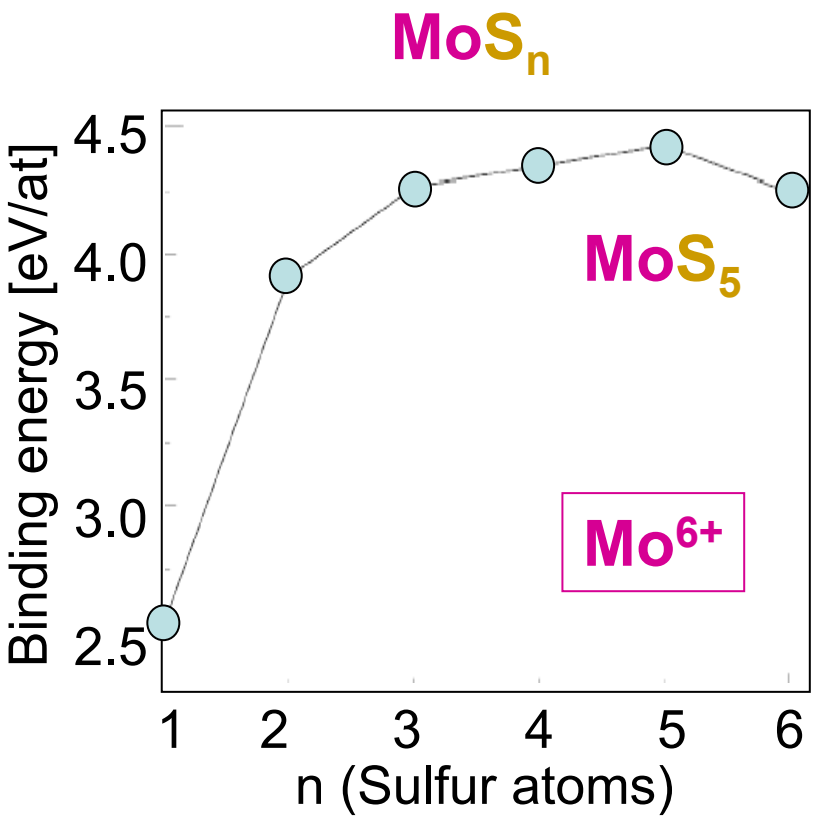
Mo_3 Mo_3S_2 Mo_3S_3 Mo_3S_5 Mo_3S_6

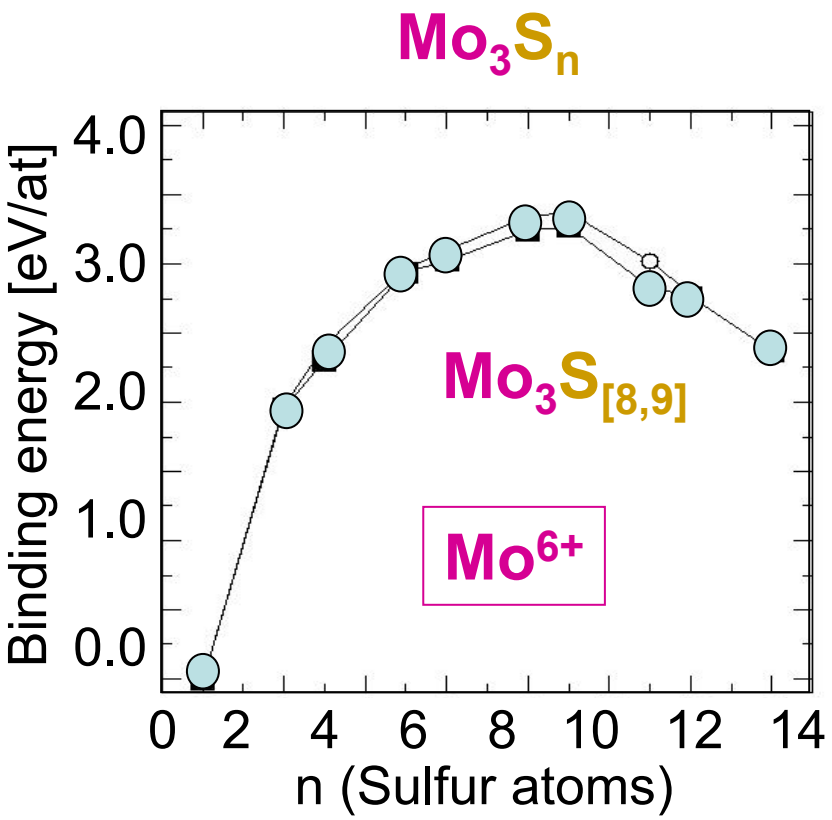
most stable



Mo_3S_8 Mo_3S_9 Mo_3S_{11} Mo_3S_{12}

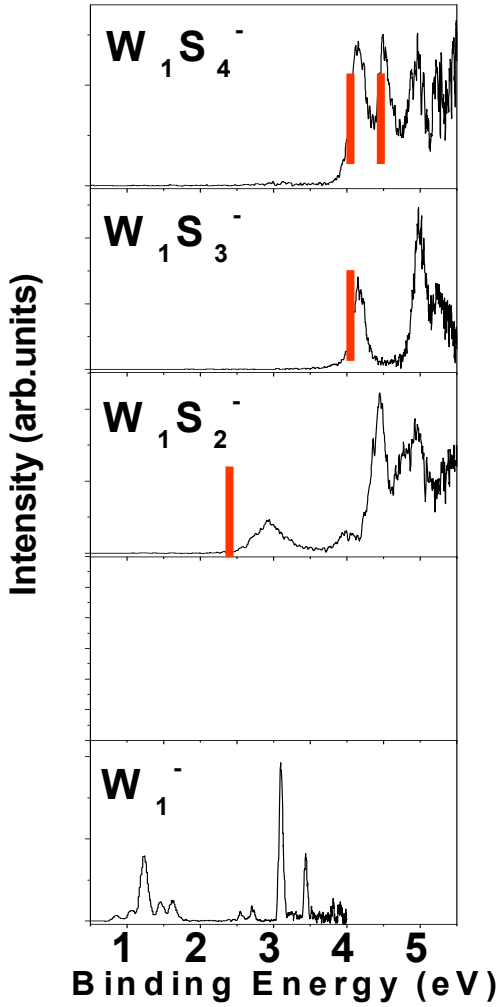
I. Small particles – 0D limit:
Stability





Stable Mo oxidation state +6

I. Small particles – 0D limit:
Electronic structure & photoelectron spectra



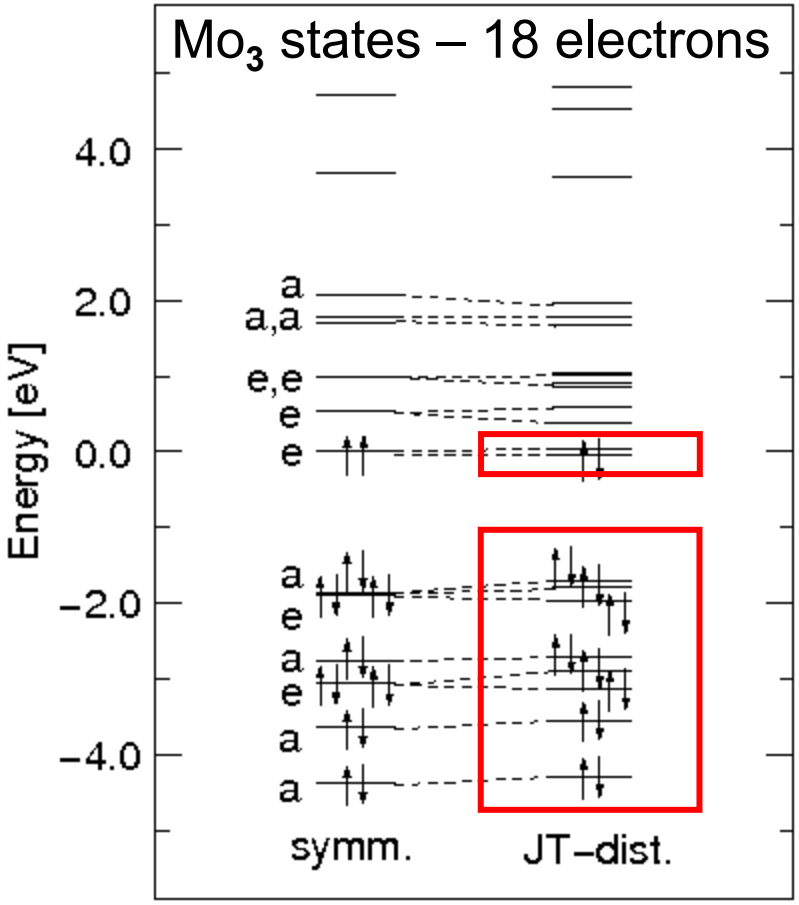
Matchin HOMO-LUMO gaps:
MoS_2: 2.2 eV, MoS_3: 2.1 eV, MoS_4: 1.8 eV

Matching vertical detachment energy:
E_{tot}(anion) – E_{tot}(neutral*)

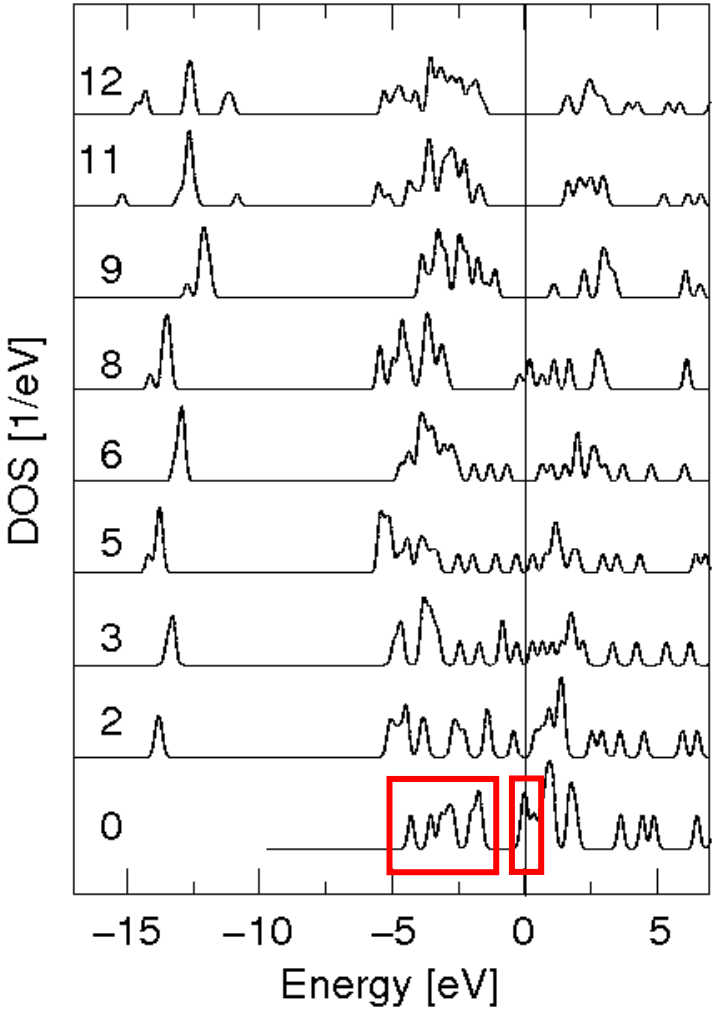
Compounds	$^2E^-$-$^1E^0$, *eV*	$^2E^-$-$^3E^0$, *eV*	$^2E^-$-$^1E^0$(ag), *eV*	$^2E^-$-$^3E^0$(ag), *eV*
MoS	1.37	0.40	2.50	1.28
MoS_2	2.16	1.53	2.28	1.64
MoS_2*	1.30*	0.67*	2.28	4.60*
MoS_3	3.46	3.99	3.89	4.15
MoS_4	2.42	1.87	4.56	3.77
MoS_5	3.01	3.65	3.66	3.95
MoS_6	2.99	2.90	3.15	3.16

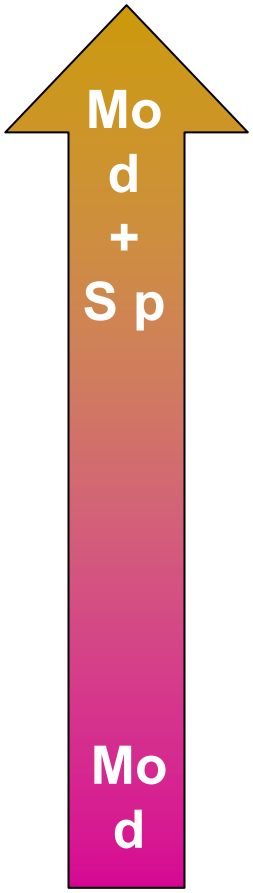
Gemming, et al., *Appl. Phys. A* **82** (1): 161-166 (2006)

I. Small particles – 0D limit:
Electronic structure: DOS of Mo_3S_n – Jahn-Teller effect



n(S)↑ : occupancy↓





I. Small particles – 0D limit:
Structure elements – electronic structure

Mo-Mo bonds

terminal S^{2-}

bridging S^{2-}

facial S^{2-}

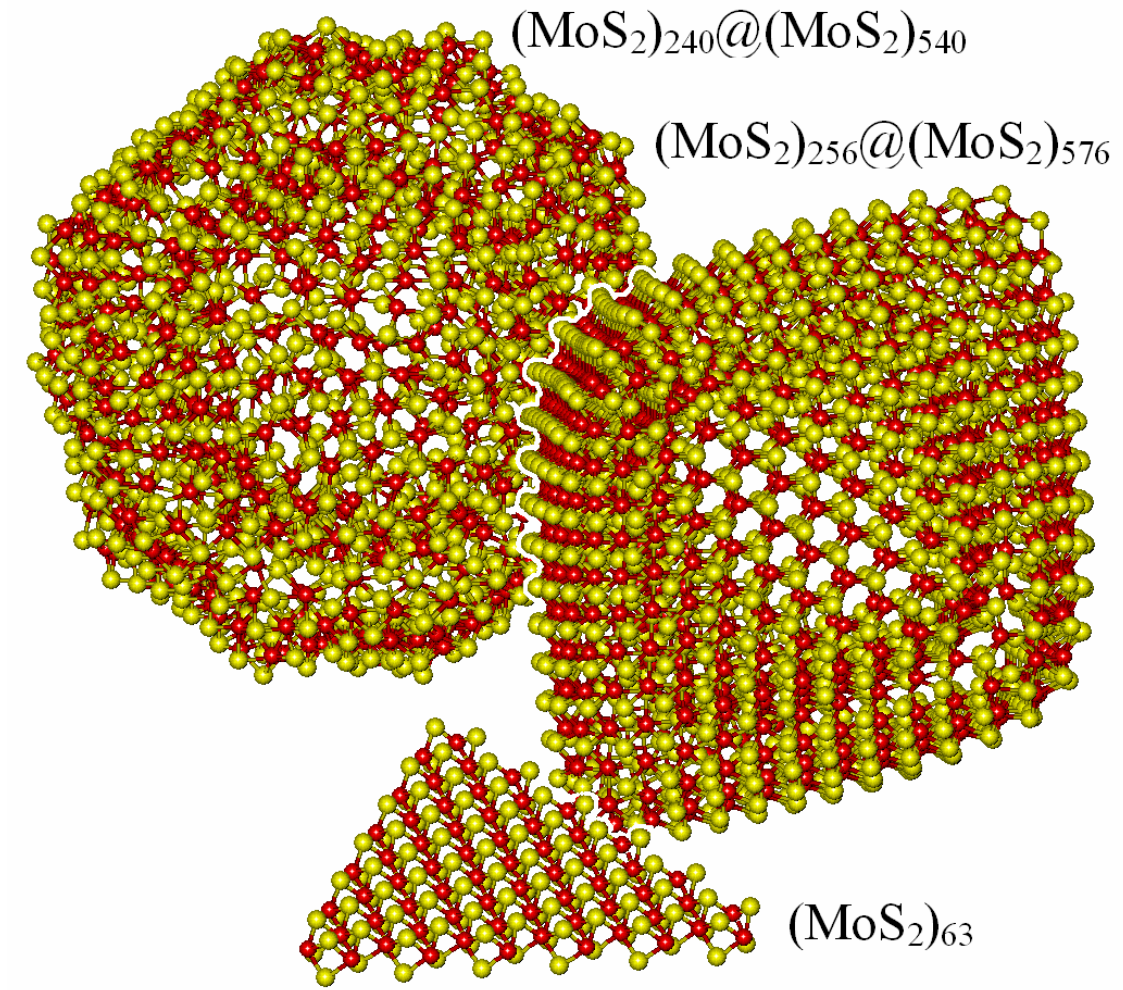
polyanions

S_2^{2-}

S_3^{2-}

optimum stability at Mo:S ~ 1:3
Jahn-Teller distortions

I. Clusters & fullerenes – 0D limit:
Larger hollow structures



~~Mo-Mo bonds~~

terminal S^{2-}

bridging S^{2-}

~~facial S^{2-}~~

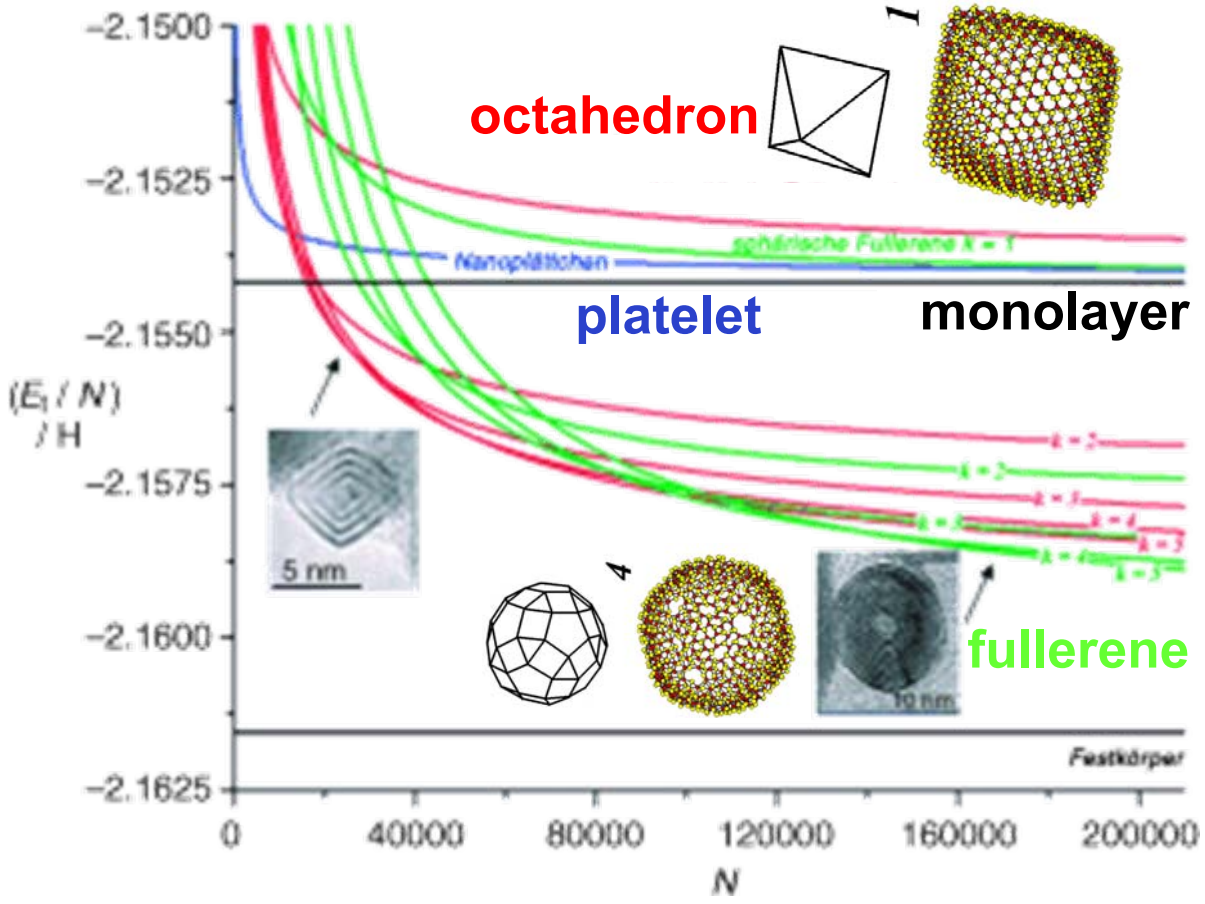
~~polyanions~~

stoichiometric (!)

I. Clusters & fullerenes – 0D limit:
Model for the stability

Effective Hamiltonian: $E_{tot} = E_{facets} + E_{edges} + E_{corners}$

(energies from first principles)



size-dependent morphology: plat. < oct. < full.

filled clusters more stable than hollow ones

(*Angew. Chem.* **119** (2007) 631; *J. Phys. Chem. B* **110** (2006) 25399.)

Overview

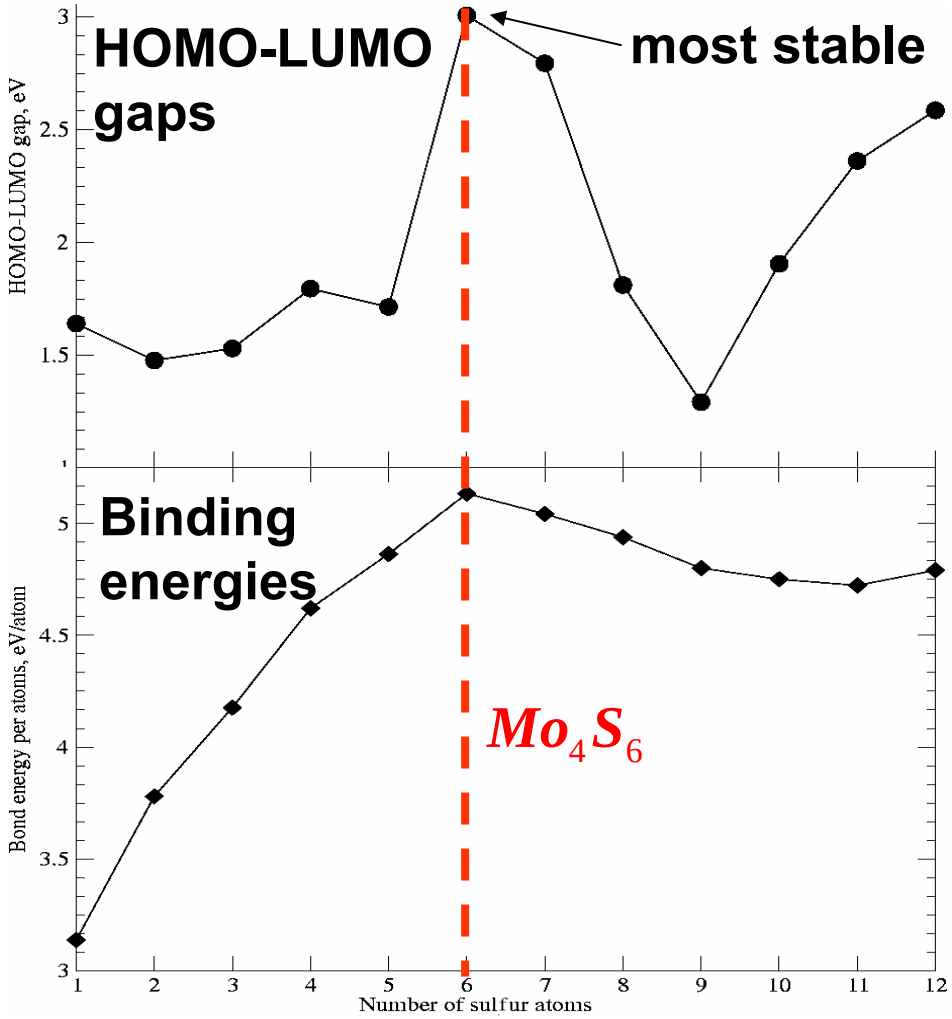
I. Clusters and fullerenes – the 0D limit

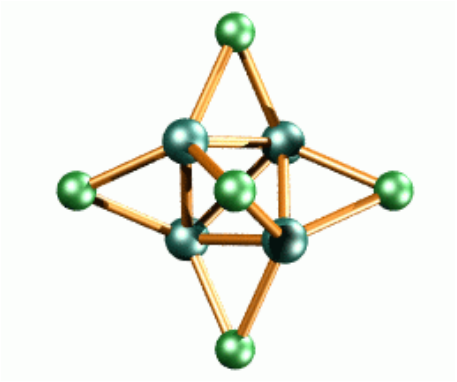
II. Cluster-platelet transition – the 2D limit

III. Cluster-wire transition – the 1D limit

II. Platelets – 2D limit:

Onset of the transition: Stability of Mo_4S_n n=1…12





Optimized Mo_4S_6 cluster

formally $Mo^{+1.5}$

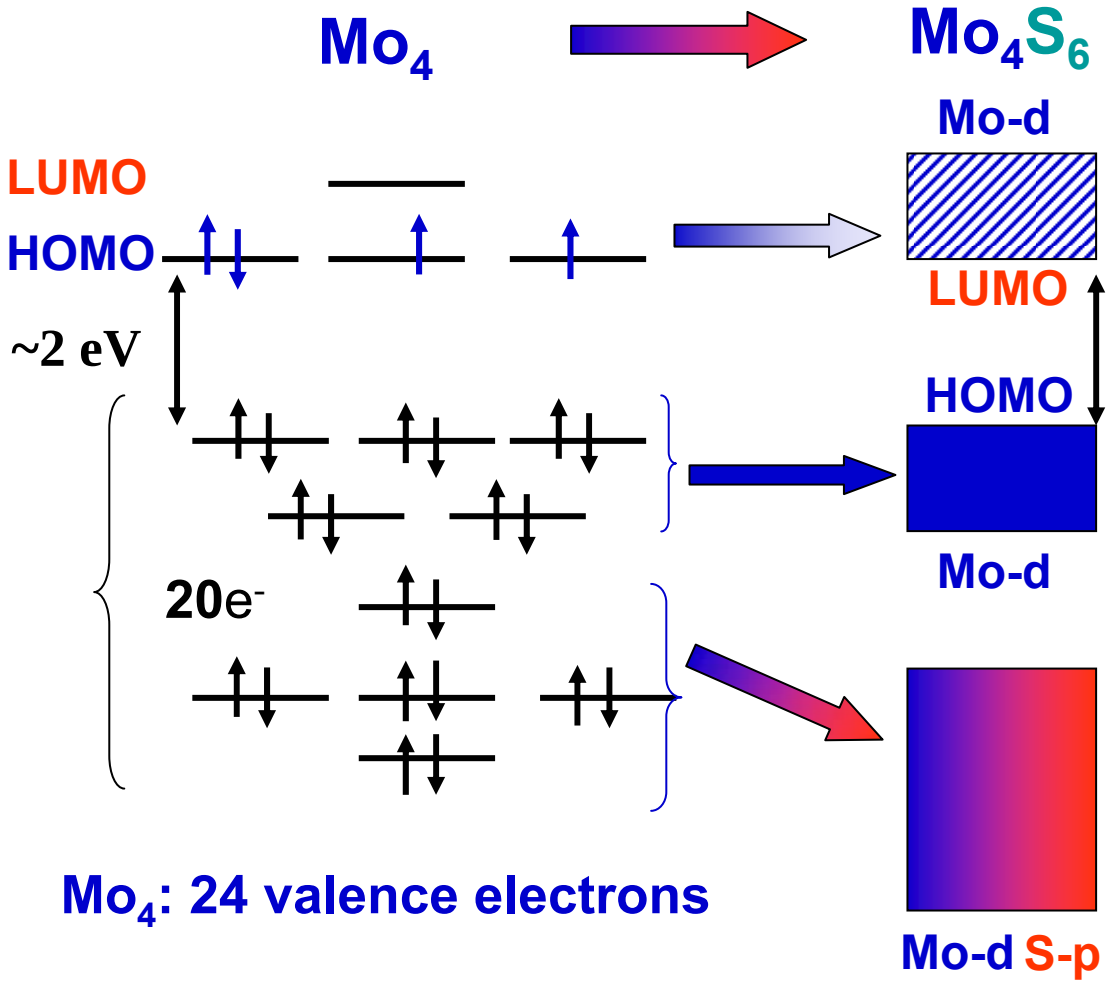
HOMO-LUMO gap ~ 3 eV

VDE ~ 2.6 eV

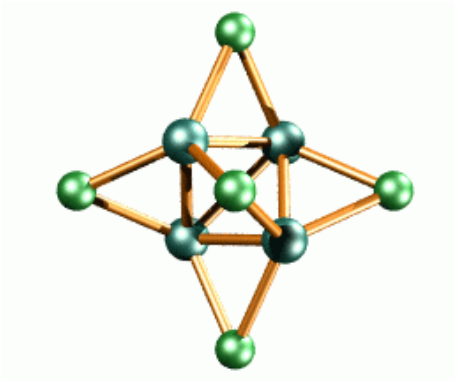
Seifert, Tamuliene, Gemming,
Comp. Mater. Sci. **35** (3): 316-320 (2006).

II. Platelets – 2D limit:

Electronic structure of Mo_4S_n n=1…12



Mo_4: 24 valence electrons



Optimized Mo_4S_6 cluster

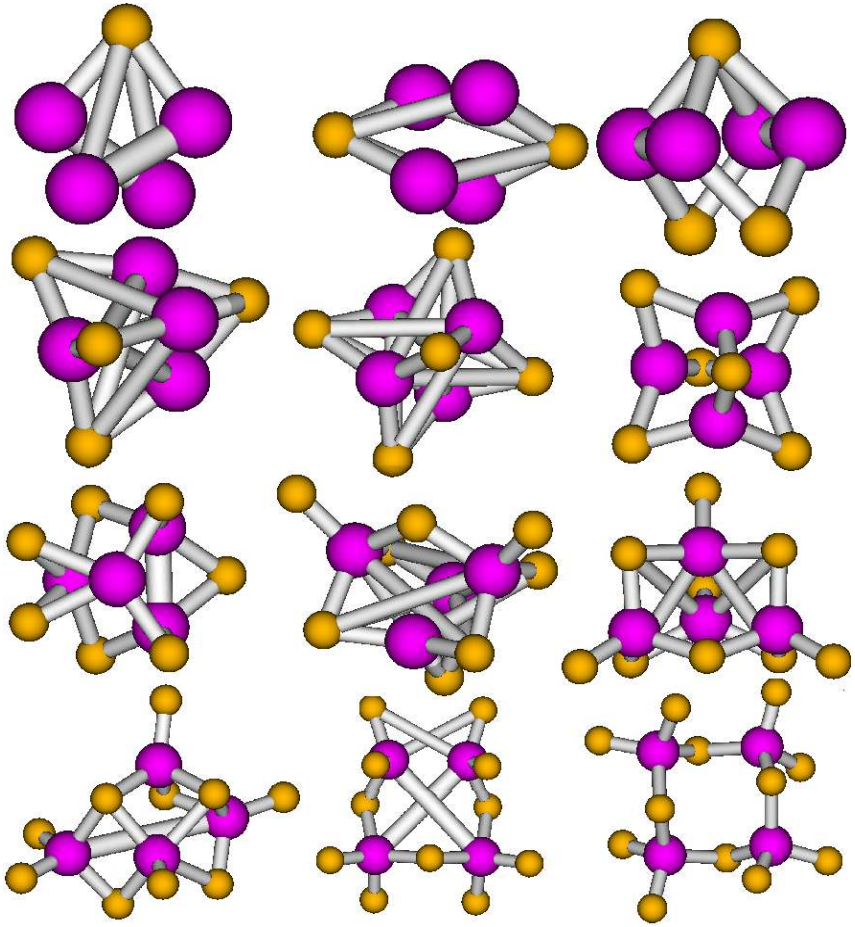
formally $Mo^{+1.5}$

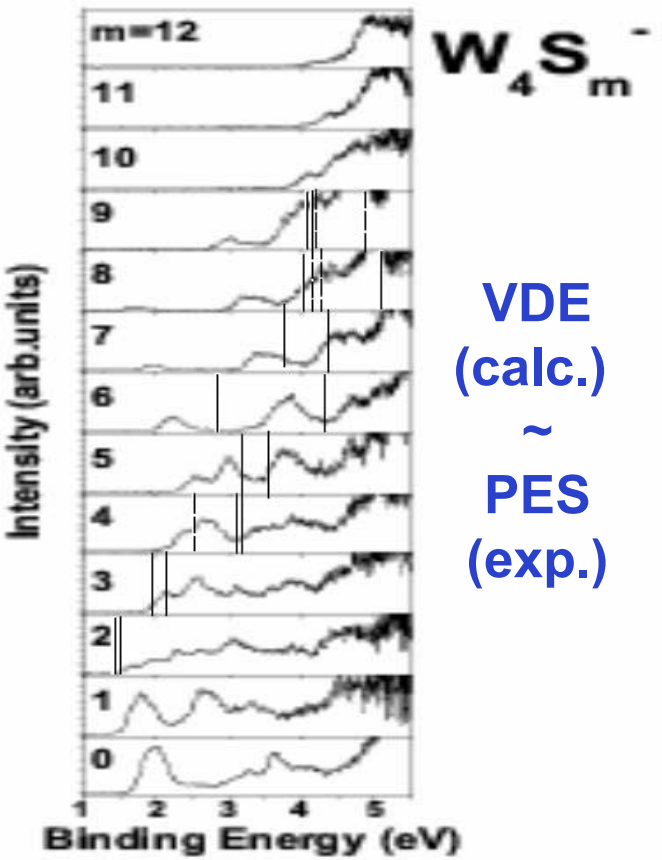
Mo-Mo: 0.26 nm

Mo-S-Mo bridges

II. Platelets – 2D limit:

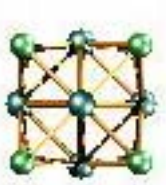
Mo_4S_n n=1…12



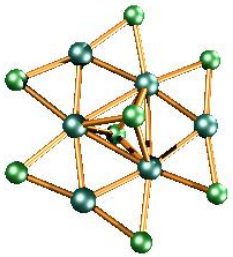


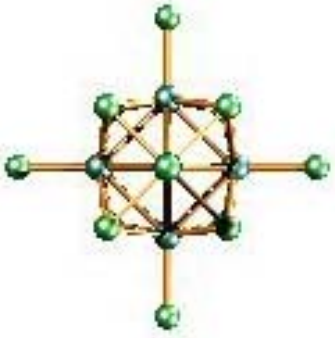
Bertram, Cordes, Kim, Ganteför, Gemming, Seifert, *Chem. Phys. Lett.* **418** (1-3): 36-39 (2006).

II. Platelets – 2D limit:
Cluster-Platelet transition

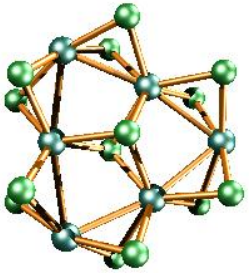


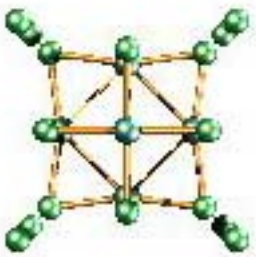
Mo_6S_8





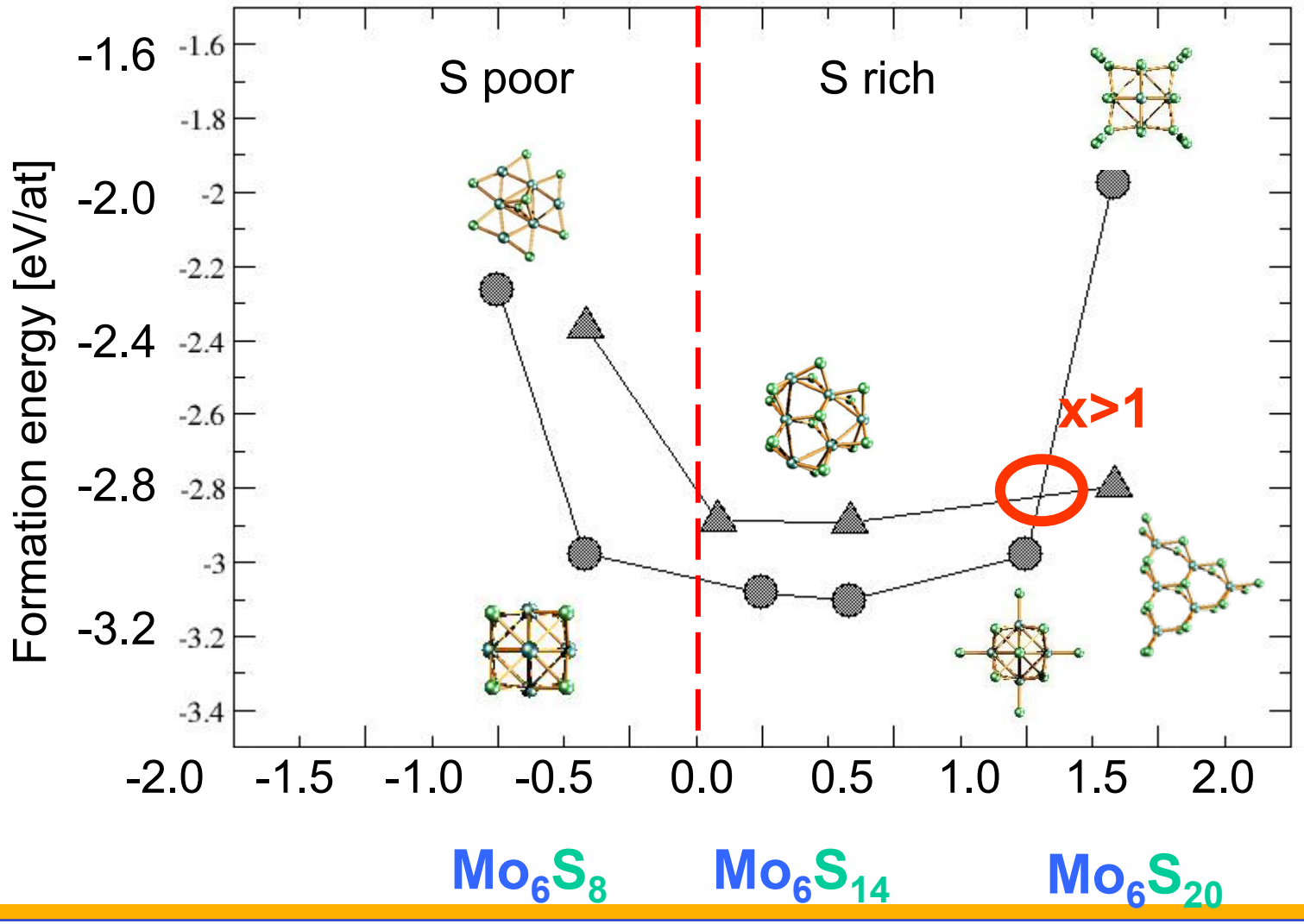
Mo_6S_{14}





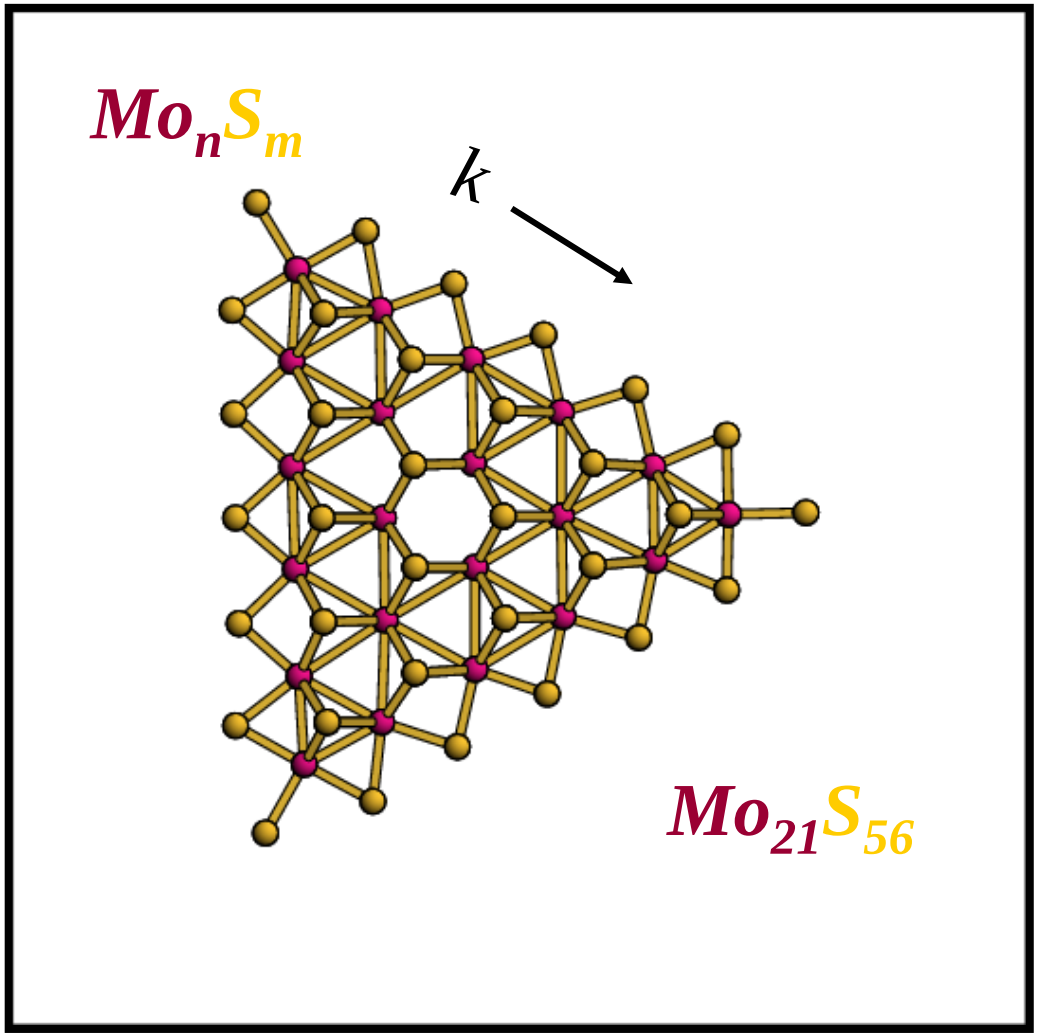
Mo_6S_{20}

II. Platelets – 2D limit:
Cluster-Platelet transition



transition for x > 1

II. Platelets – 2D limit:
Platelet structure and composition



$$n = \frac{k(k+1)}{2}$$

$$m = k(k+1) + 2(k+1)$$

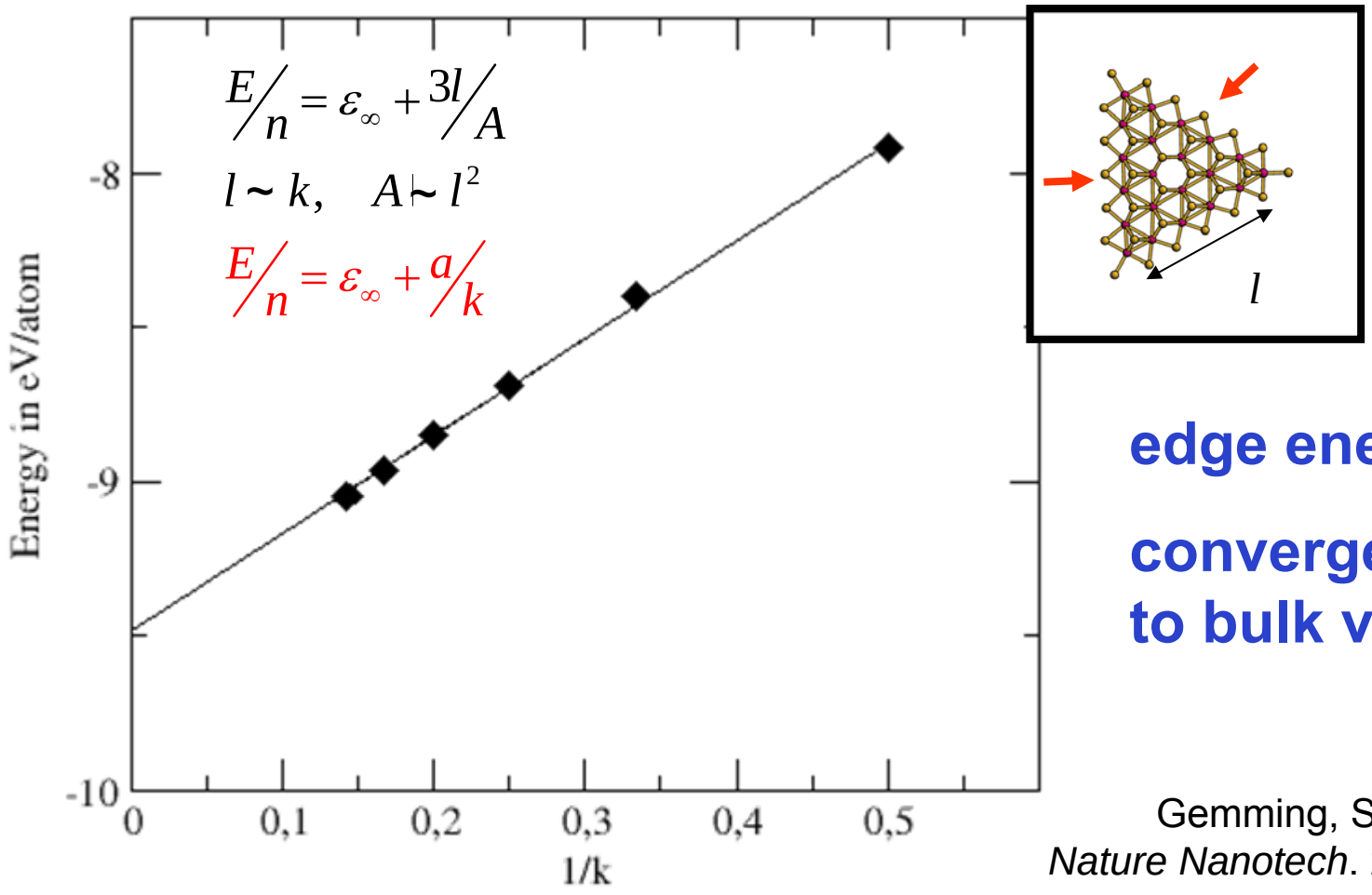
$$\frac{m}{n} = 2 + \frac{4}{k}$$

$$k = 6 \rightarrow$$

$$n = 21 \quad m = 56$$

$$\frac{m}{n} = 2.66667$$

II. Platelets – 2D limit:
Platelet properties



edge energy

convergence to bulk values

Gemming, Seifert,
Nature Nanotech. **2** (2007) 21.

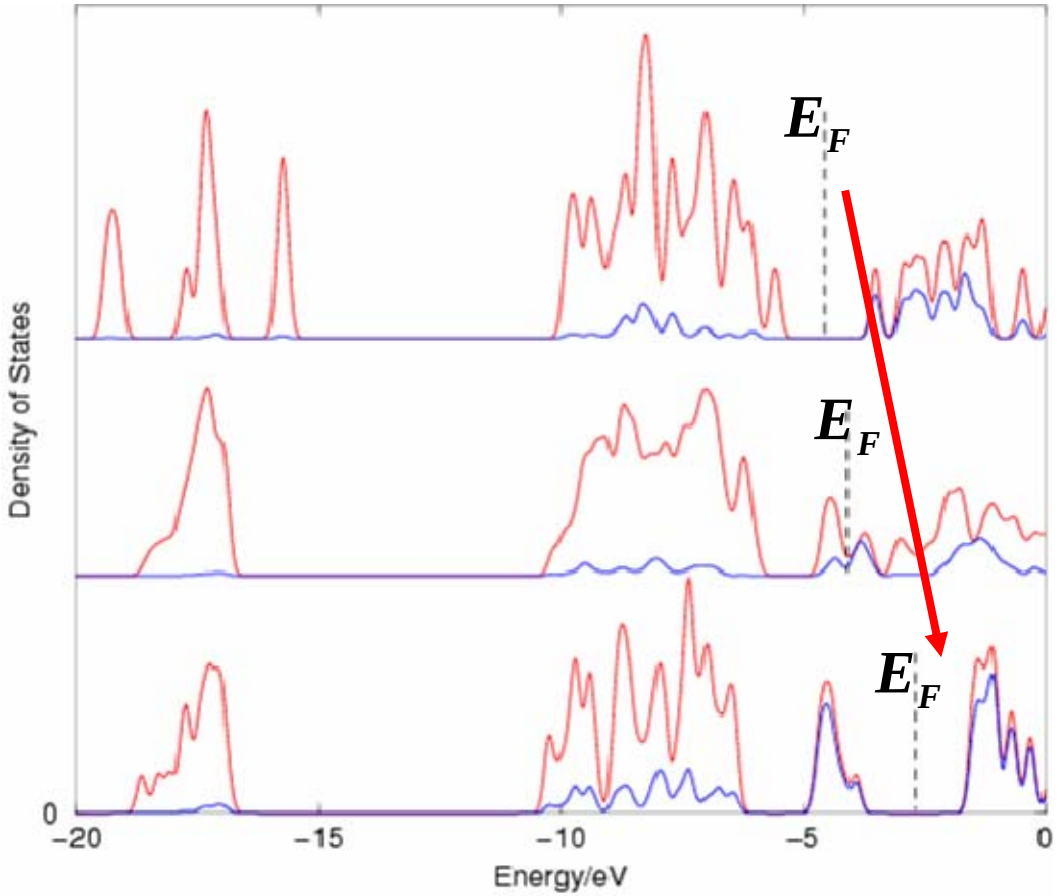
II. Platelets – 2D limit:

Platelet properties – densities of electronic states

1 : 4

1 : 2.5

1 : 2



Mo_3S_{12}

$Mo_{36}S_{90}$

MoS_2

bulk layer

Fermi level shift; large platelet ~ bulk sheet

II. Platelets – 2D limit

Mo-Mo bound clusters | **transition region** | **platelets polyanions S_2^{2-}**

optimum stability below Mo:S ~ 1:3
excess (active) Sulfur incorporated at edges
platelets ~ bulk compound

Overview

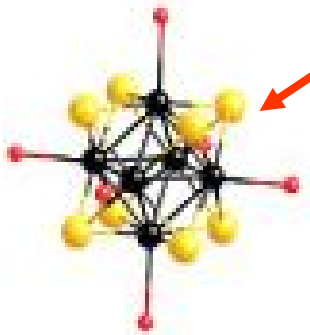
I. Clusters and fullerenes – the 0D limit

II. Cluster-platelet transition – the 2D limit

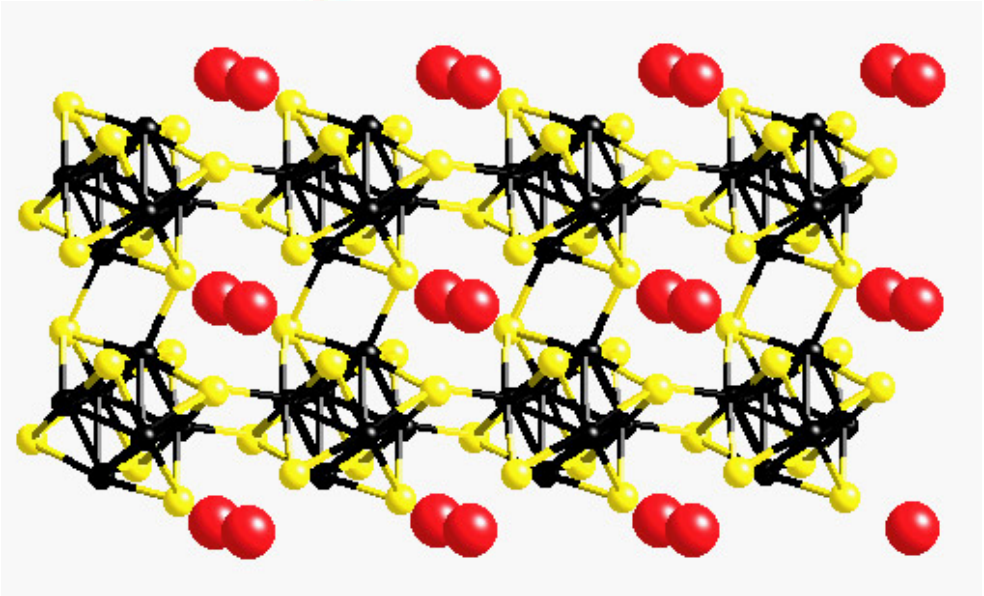
III. Cluster-wire transition – the 1D limit

III. Wires – 1D limit: Chevrel clusters at low Sulfur content

Cluster: L-Mo_6S_8 L-Pb $(Mo_6S_8)^{4-}$

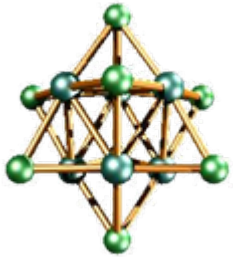
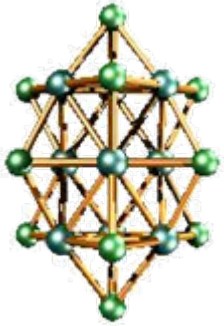
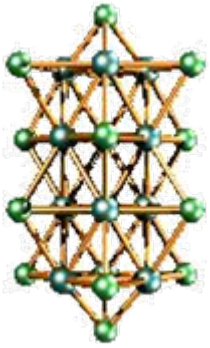
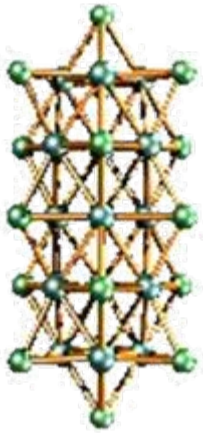
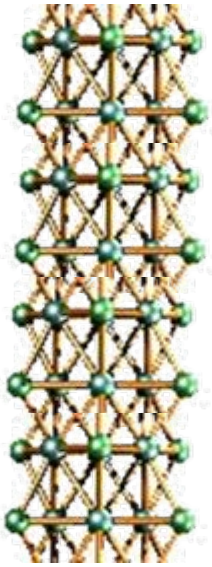


Chevrel Phases



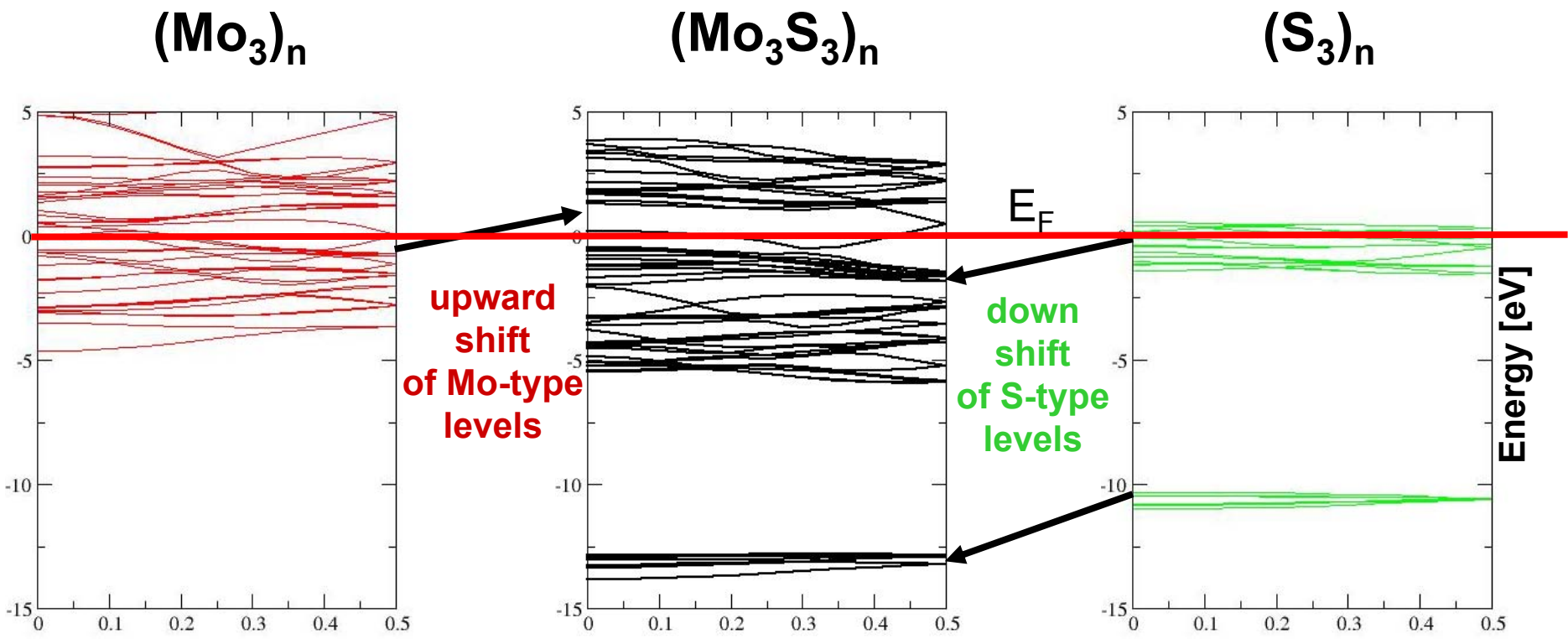
Gemming, S., Seifert, G., in Proc. 19th IWEPNM, Eds. H. Kuzmany, et al., Proc. (2005).

III. Wires – 1D limit:
Clusters $(M_3S_3)_nS_2$

	Mo_6S_8	Mo_9S_{11}	$Mo_{12}S_{14}$	$Mo_{15}S_{17}$	∞Mo_6S_6
					
ΔE_{HL}	0.48 eV	0.05 eV	0.04 eV 0.11 eV *	0.02 eV 0.18 eV *	
VDE	4.12 eV	3.02 eV	2.81 eV	2.29 eV	
ADE	3.78 eV	2.99 eV	2.68 eV	2.25 eV	

Jahn-Teller d(Mo-Mo): 0.264 nm outer Mo_3, 0.274 inner Mo_3

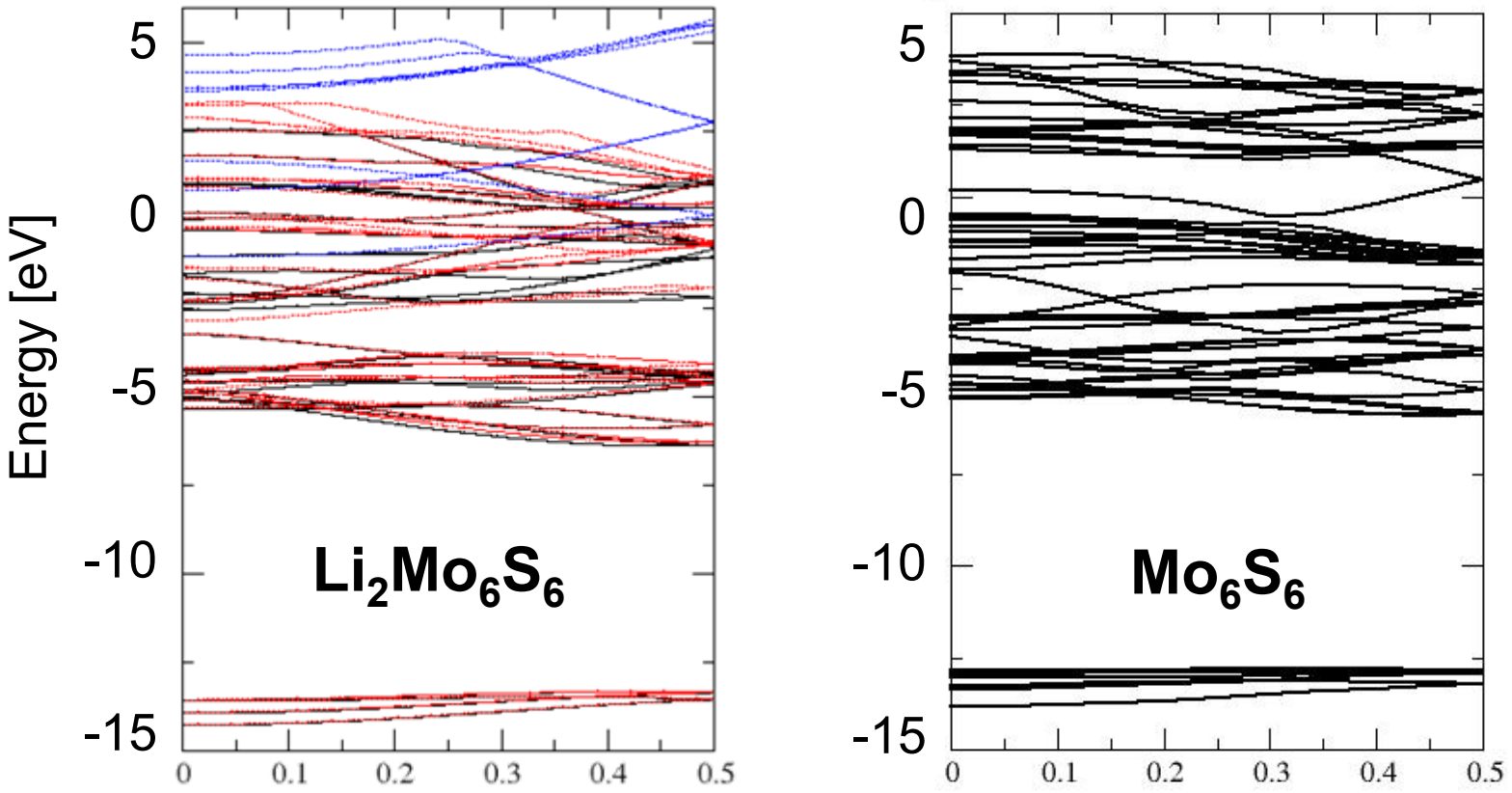
III. Wires – 1D limit:
Electronic structure - conductivity



metallic wire, with Mo-derived states at Fermi level

III. Wires – 1D limit:

Electron doping by addition of $Li_2Mo_6S_6$



(black: $Li_2Mo_6S_6$ bands, blue: Li bands, red: Mo_6S_6 bands)

Gemming, S., Seifert, G., Vilfan, I., *phys. stat. sol. b* **243** (13): 3320-3324 (2006).

III. Wires – 1D limit:

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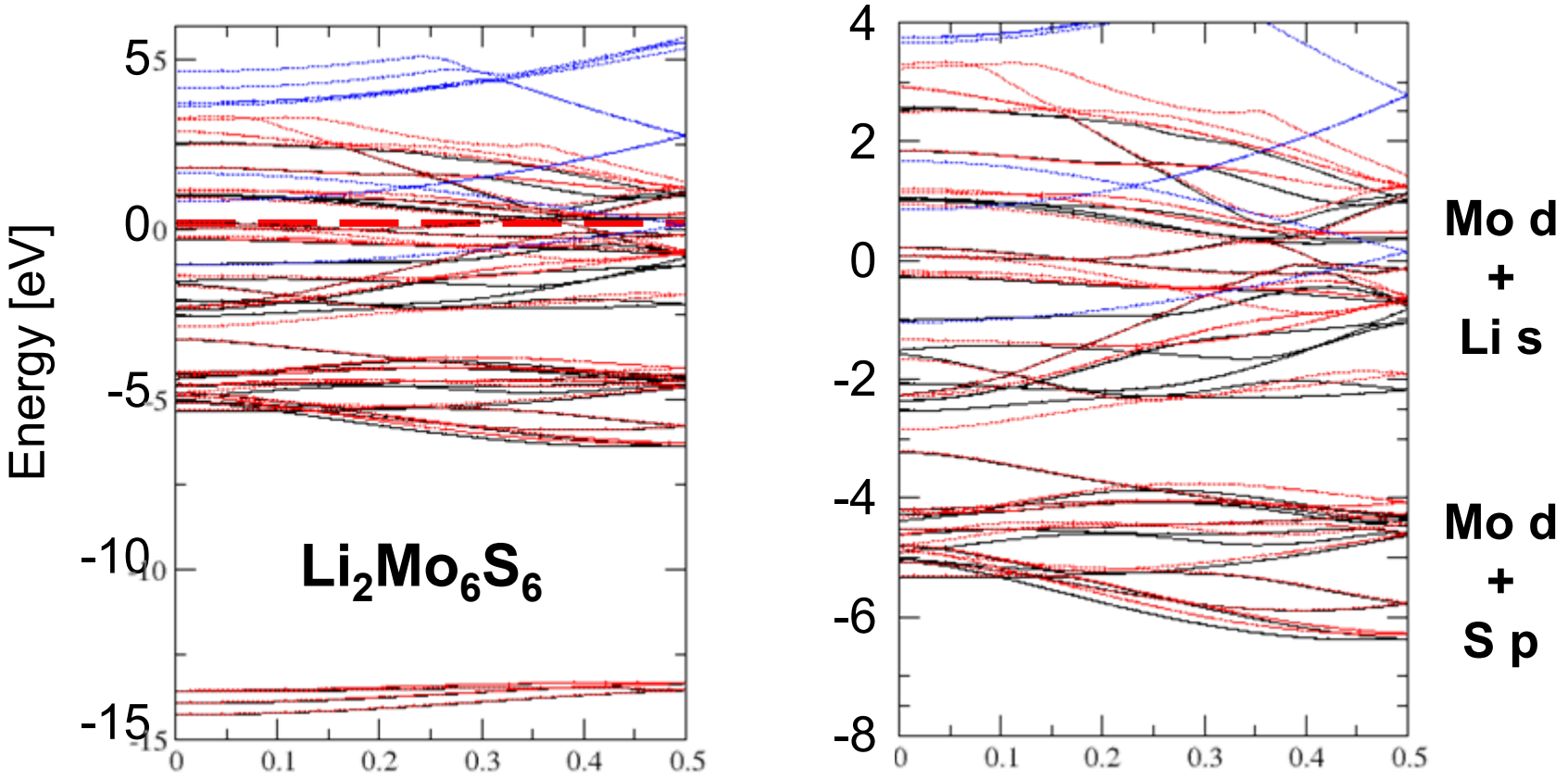

(black: $Li_2Mo_6S_6$ bands, blue: Li bands, red: Mo_6S_6 bands)

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III. Wires – 1D limit: Doping with Li to $Li_2Mo_6S_6$

Mo-Mo bound wire | **elongated Chevrel cluster** | **JT-distorted clusters**

optimum stability at Mo:S ~ 1:1
Mo-Mo-triangles bridged by S
metallic Mo-based core, doping by Li

Molybdenum sulfide based structures and their properties - Conclusions

MoS	MoS_2	MoS_3
wires/tubes 1D	bulk crystal 3D	platelets 2D
clusters 3D	fullerenes 3D	octahedra 3D
+ions		+Au
ion./el. conductors Mo-Mo & Mo-S bonds	semiconductor Mo-S bonds	metallic conductors Mo-S & S-S bonds
contact agents	lubricant	catalysts

Why Mo_mS_n?

Versatile building blocks – structural variety

Mo-Mo bonds

terminal S^{2-}
bridging S^{2-}

facial S^{2-}
polyanions S_2^{2-}, S_3^{2-}

Different bond types – reactivity & bonding variety

multiple/single
Mo-Mo bonds

single
Mo-S bonds

single
S-s bonds

Electronic & ionic doping – conductivity variety

metallic/metalloid
Chevrel structures

Li-doped
clusters/wires

metallic
edge states

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