New schedule !!!

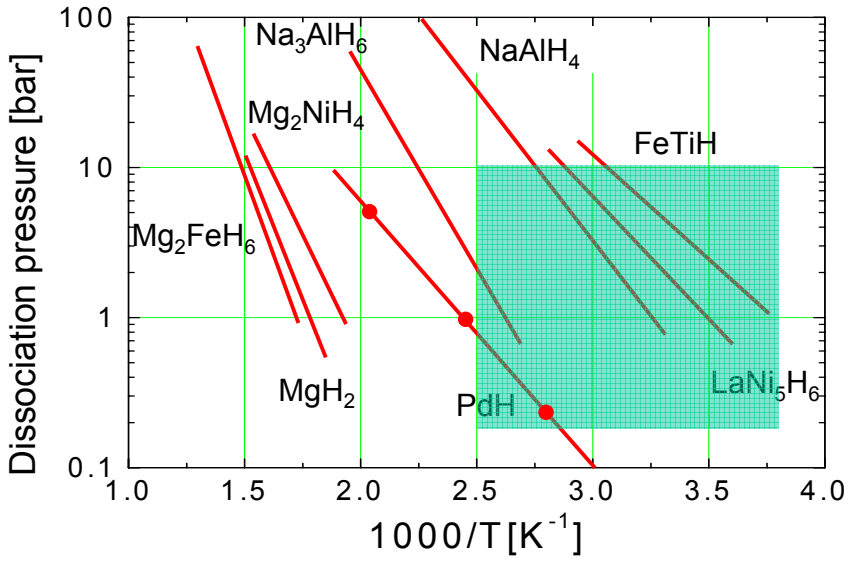
Date		Subject	Lecturer
February 12, 2008	Tuesday	Introduction: Energy, Environment & Sustainability	Griessen
February 15, 2008	Friday	Review of H, H2, Van der Waals gasses	Griessen
February 19, 2008	Tuesday	Thermodynamics (self-study and werkcollege)	Griessen
February 22, 2008	Friday	Thermodynamics	Griessen
February 26, 2008	Tuesday	Critical behaviour and H-H interaction	Griessen
February 29, 2008	Friday	Elasticity	Griessen
March 4, 2008	Tuesday	Band structure of transition metals/ effect of H on electronic states	Griessen
March 7, 2008	Friday	Band structure of complex hydrides	Griessen
March 11, 2008	Tuesday	Transport properties	Griessen
March 14, 2008	Friday	Practicum: Fuel cell, Electrolyser, Photovoltaic cell	Heeck
March 18, 2008	Tuesday	Hydrogen storage in various systems (metals, borohydrides, MOF's, graphite,....)	Zuettel

Hydrogen storage and complex hydrides

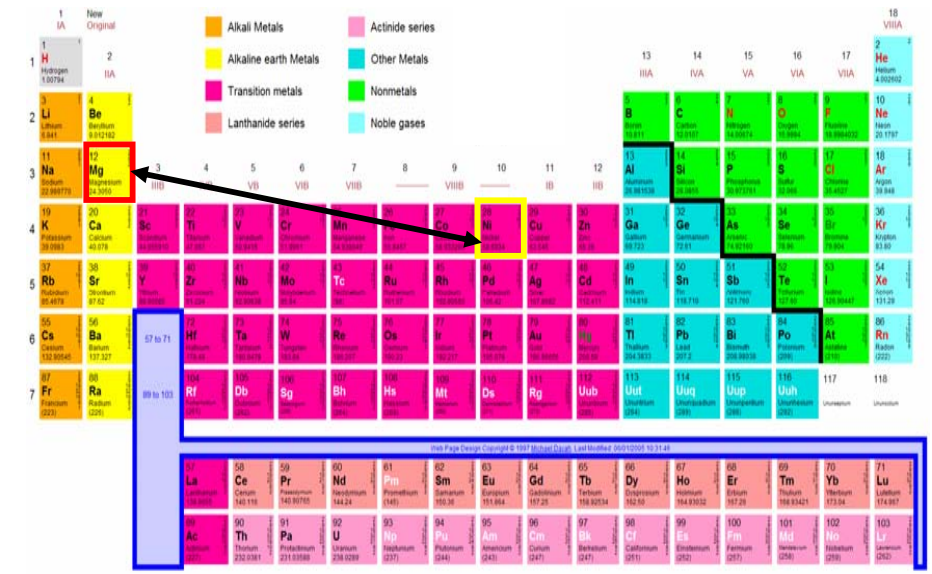
Ronald Griessen
Vrije Universiteit, Amsterdam
March 7, 2008

Mg_2NiH_4 $LaNi_5H_6$ H_2 (liquid) H_2 (200 bar)

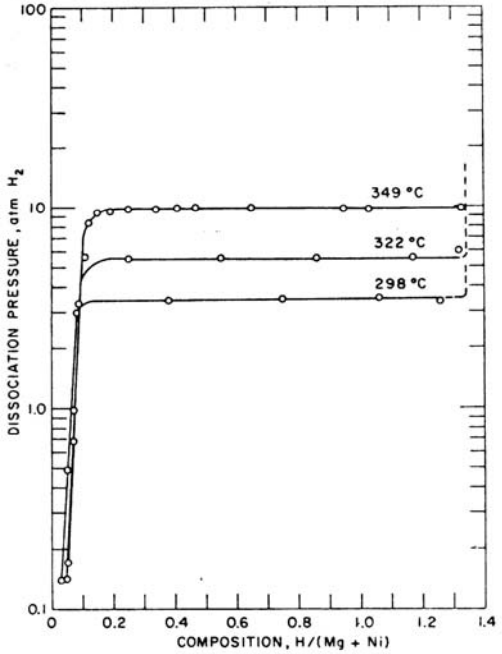
Van t'Hoff plots of some metal-hydrides



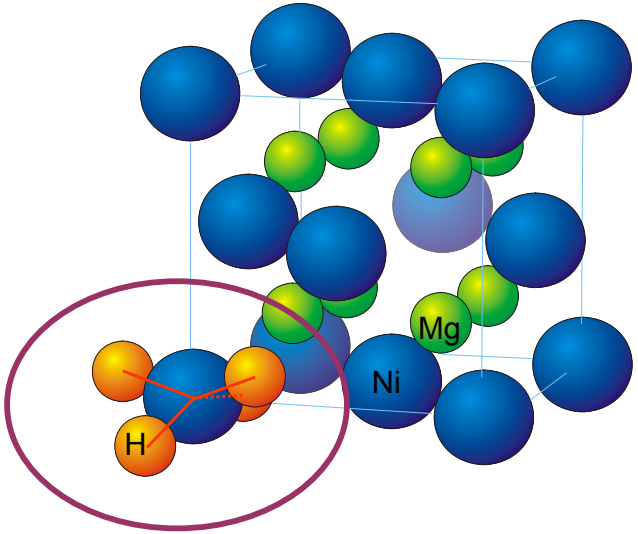
Mg_2NiH_4 Mg_2CoH_5 Mg_2FeH_6



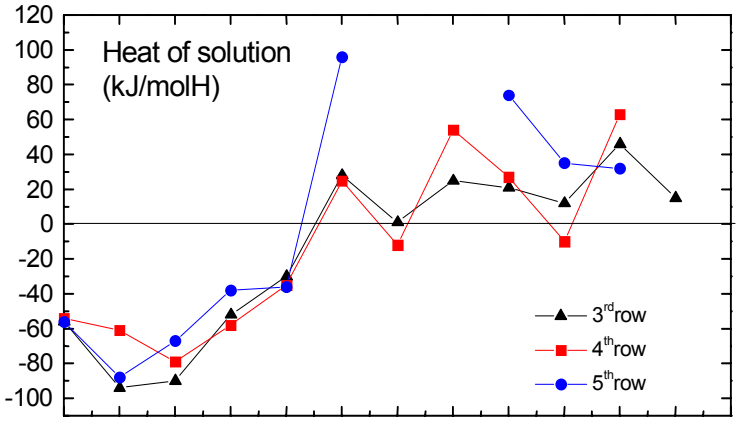
Mg_2NiH_4



Complex hydrides: Mg_2NiH_4

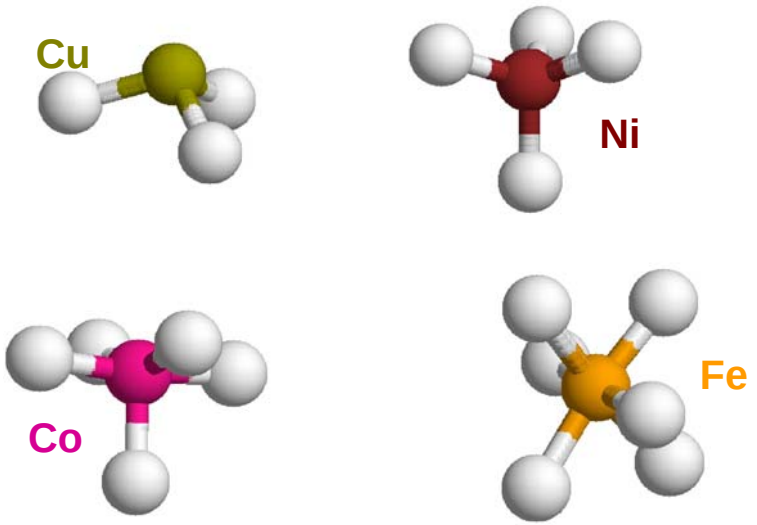


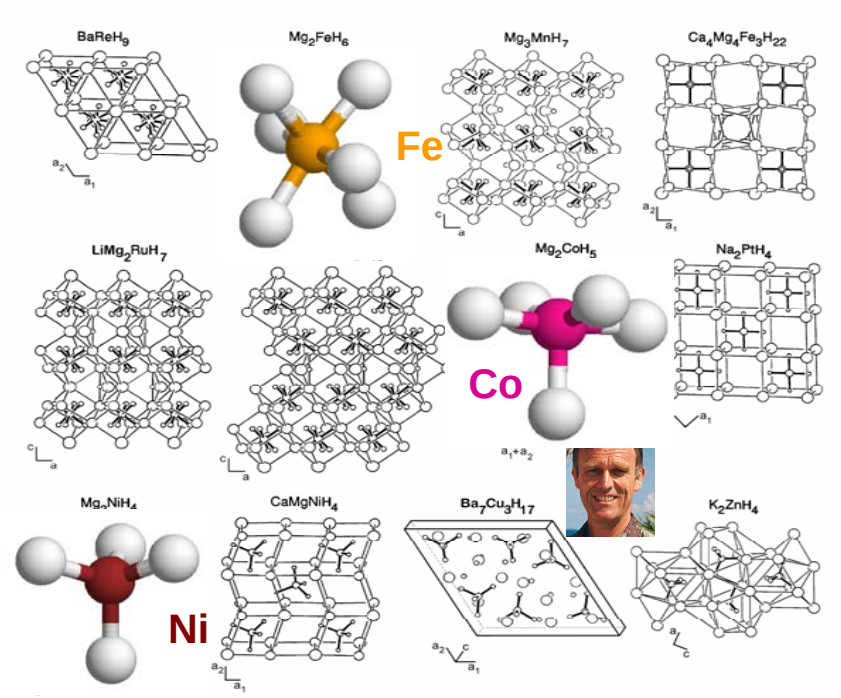
Heat of solution of metal-hydrides

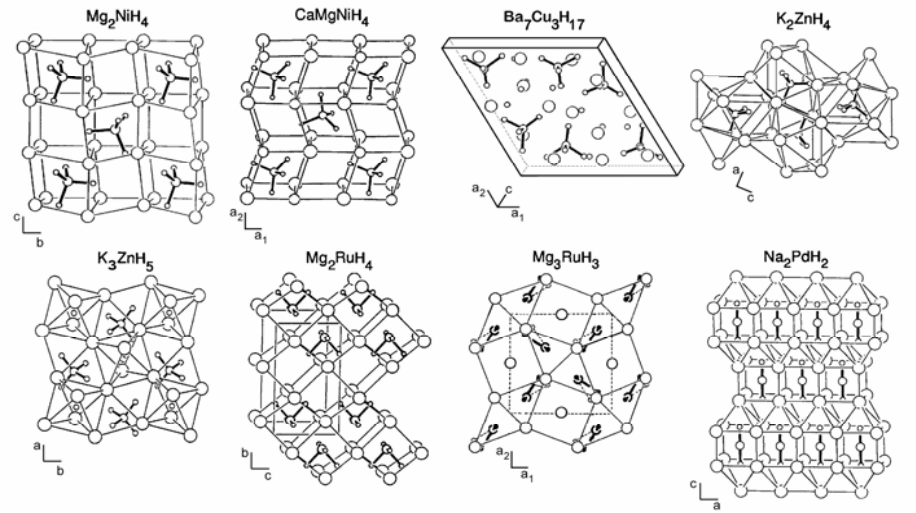


K	Ca	Sc	Ti		V	Cr	Mn	Fe	Co	Ni	Cu	Zn					
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg						

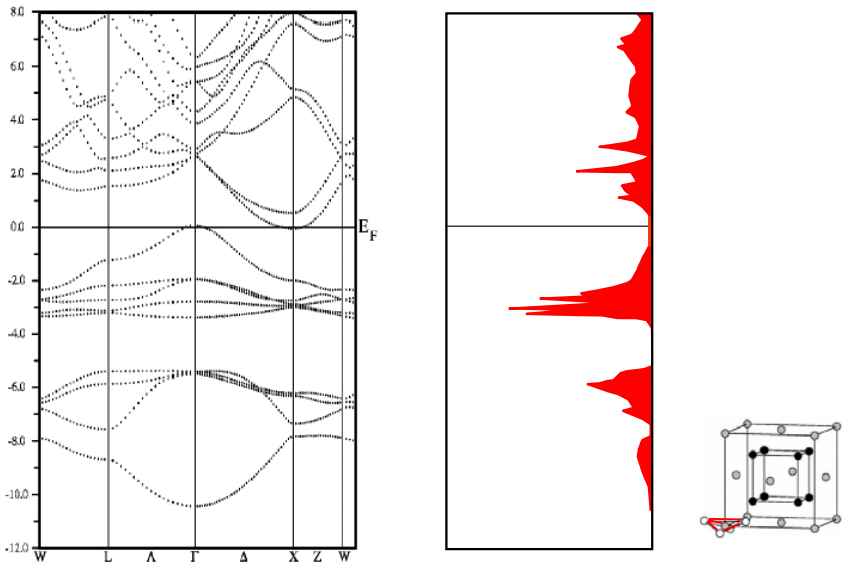
Structures of transition metal complexes



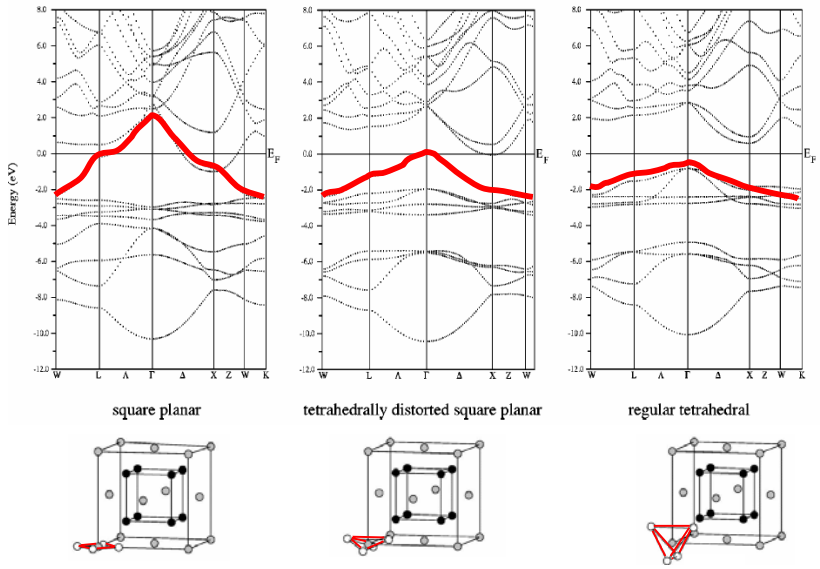




Density of states Mg_2NiH_4



Influence of the H-positions in Mg_2NiH_4



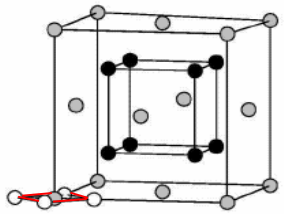
A TM atom surrounded by 4 H in a square

$$\left[-\frac{\hbar^2}{2m}\Delta+V_M(\mathbf{r})+V_{H_1}(\mathbf{r})+V_{H_2}(\mathbf{r})+V_{H_3}(\mathbf{r})+V_{H_4}(\mathbf{r})\right]\Psi=E\Psi$$

$$\left[-\frac{\hbar^2}{2m}\Delta+V_M(\mathbf{r})\right]\left|M_l\right\rangle=E_{M_l}\left|M_l\right\rangle$$

$$\left[-\frac{\hbar^2}{2m}\Delta+V_{H_j}(\mathbf{r})\right]\left|H_j\right\rangle=E_H\left|H_j\right\rangle$$

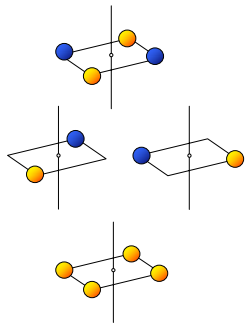
$$\Psi=\sum_{l=1}^{9}a_l\left|M_l\right\rangle+\sum_{j=1}^{4}b_j\left|H_j\right\rangle$$



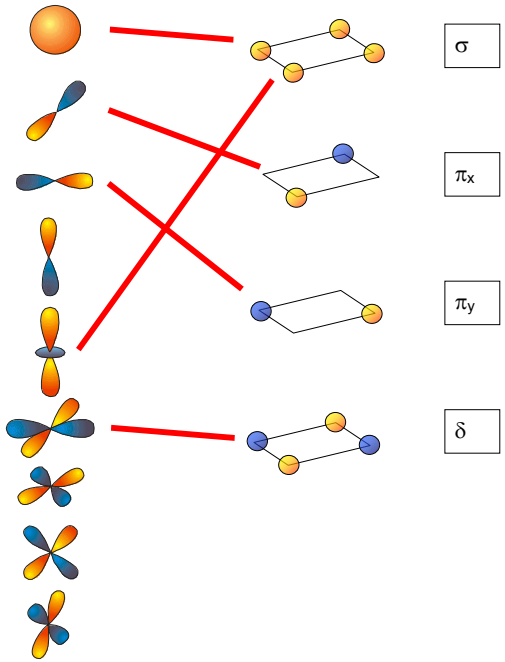
Determinant for the 4 H only

$$\begin{vmatrix} E_H-2V-E & -w & 0 & -w \\ -w & E_H-2V-E & -w & 0 \\ 0 & -w & E_H-2V-E & -w \\ -w & 0 & -w & E_H-2V-E \end{vmatrix}=0$$

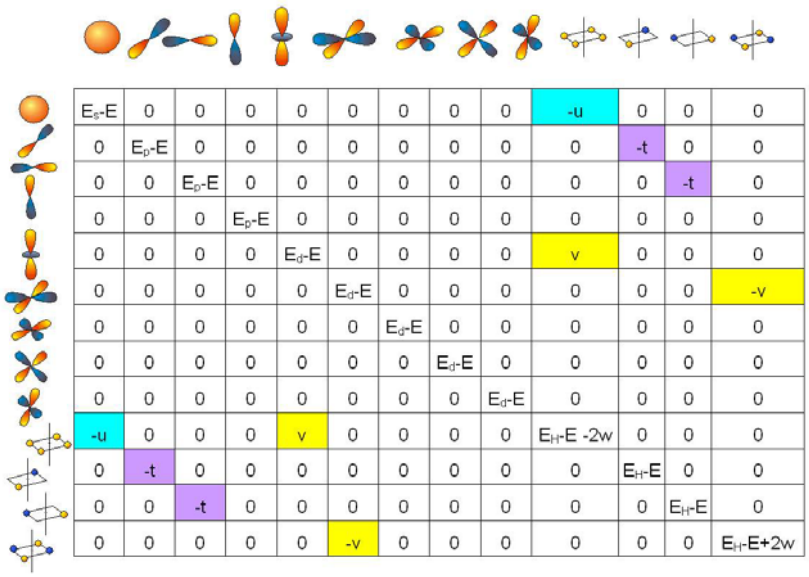
Eigenvalues	Eigenvectors
$E=E_H-2V+2w$	(1/2) (1, -1, 1, -1)
$E=E_H-2V$	(1/√2) (-1, 0, 1, 0) (1/√2) (0, -1, 0, 1)
$E=E_H-2V-2w$	(1/2) (1, 1, 1, 1)



Non-zero tunneling matrix elements

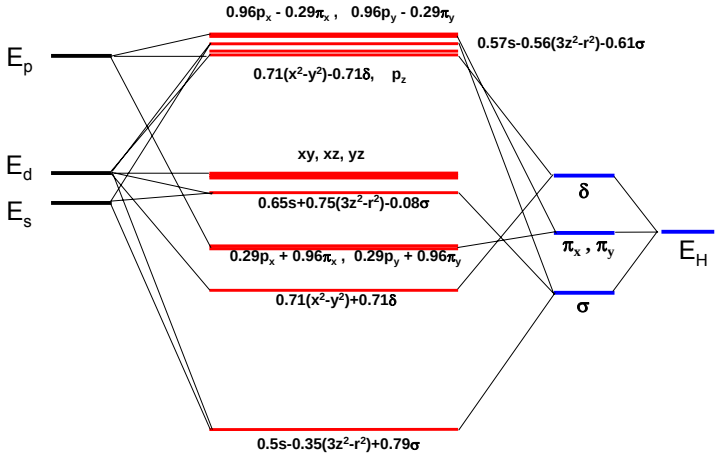


Determinant for a TM surrounded by a square of 4 H

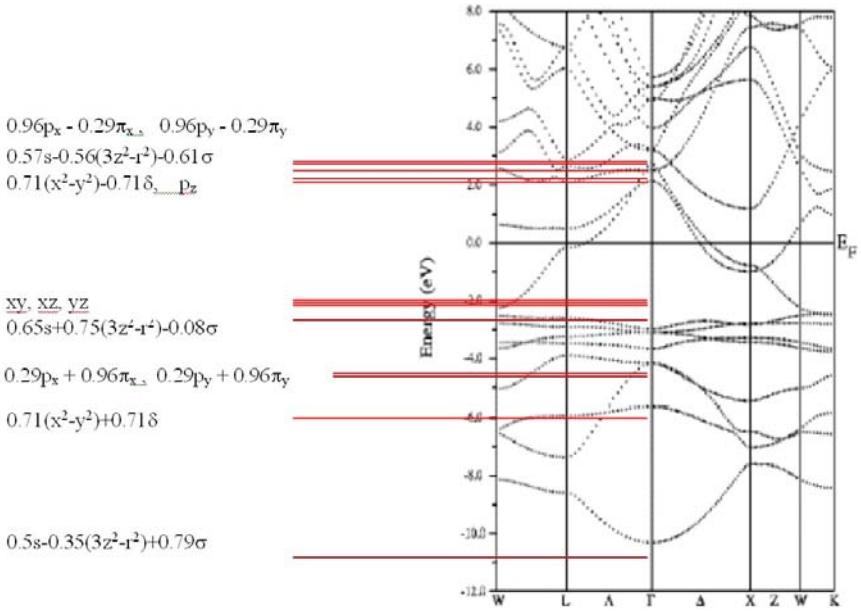


E_s-E	0	0	0	0	0	0	0	0	-u	0	0	0
0	E_p-E	0	0	0	0	0	0	0	0	-t	0	0
0	0	E_p-E	0	0	0	0	0	0	0	0	-t	0
0	0	0	E_p-E	0	0	0	0	0	0	0	0	0
0	0	0	0	E_d-E	0	0	0	0	v	0	0	0
0	0	0	0	0	E_d-E	0	0	0	0	0	0	-v
0	0	0	0	0	0	E_d-E	0	0	0	0	0	0
0	0	0	0	0	0	0	E_d-E	0	0	0	0	0
0	0	0	0	0	0	0	0	E_d-E	0	0	0	0
-u	0	0	0	v	0	0	0	0	E_H-E -2w	0	0	0
0	-t	0	0	0	0	0	0	0	0	E_H-E	0	0
0	0	-t	0	0	0	0	0	0	0	0	E_H-E	0
0	0	0	0	0	-v	0	0	0	0	0	0	E_H-E+2w

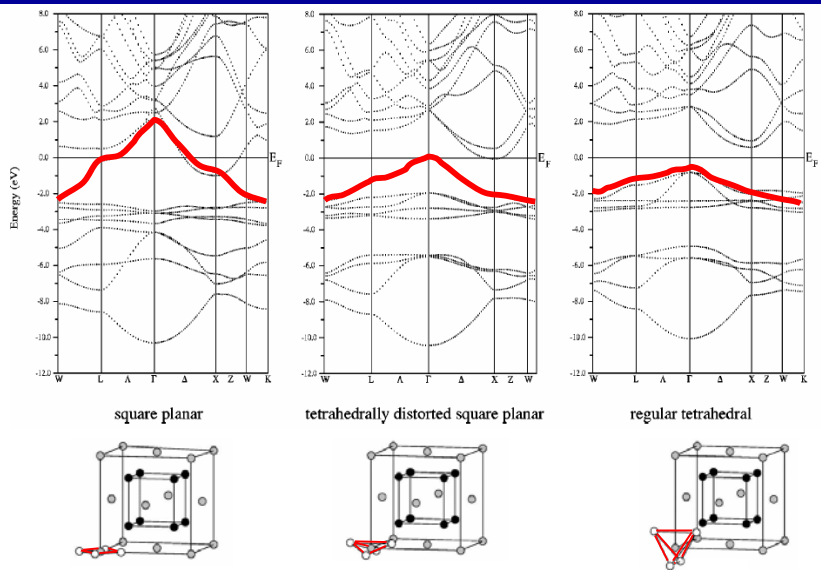
Level scheme of Mg_2NiH_4



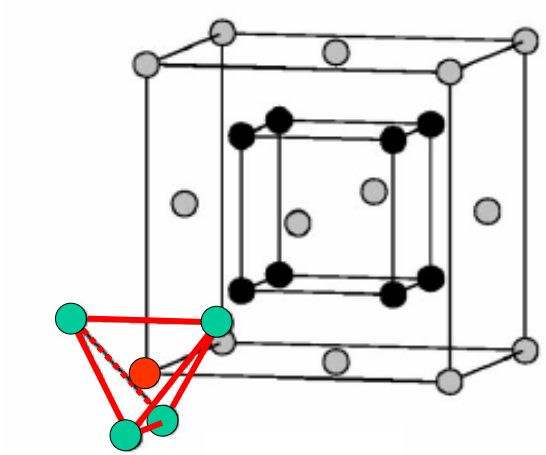
E_s= -3 , E_p=2, E_d=-2, E_H=-4 and t=2, u=5, v=4 and w=1



Effect of NiH_4 geometry



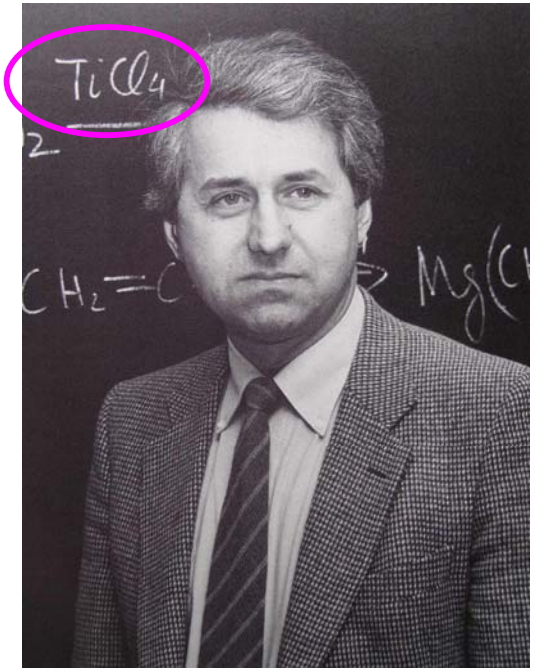
Exercise: Cluster of a TM and 4H in a tetrahedral arrangement



$NaAlH_4$

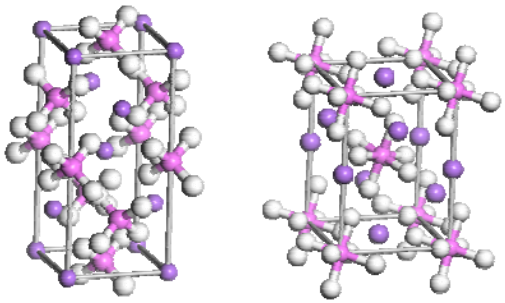
$NaAlH_4$

B. Bogdanovic and M. Swickardi, J. Alloys and Compounds 253-254 (1997), p. 1-9



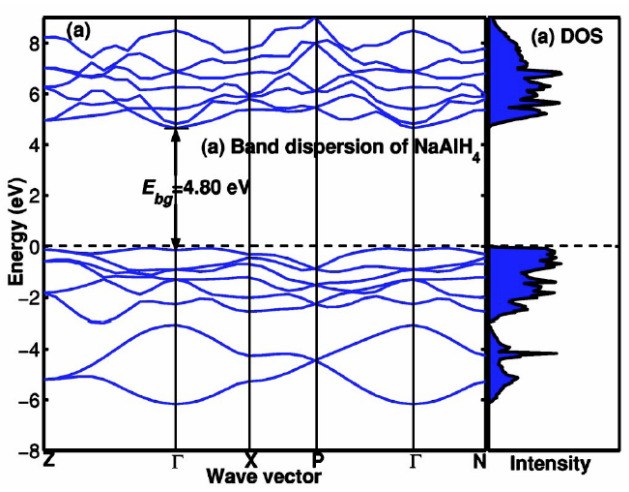
Hydrogen desorption of $NaAlH_4$

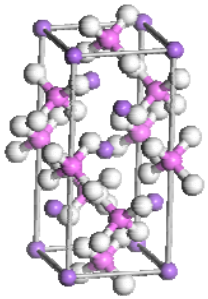
$$NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$$



$$Na_3AlH_6 \rightarrow 3NaH + Al + \frac{3}{2}H_2$$

Bandstructure of $NaAlH_4$

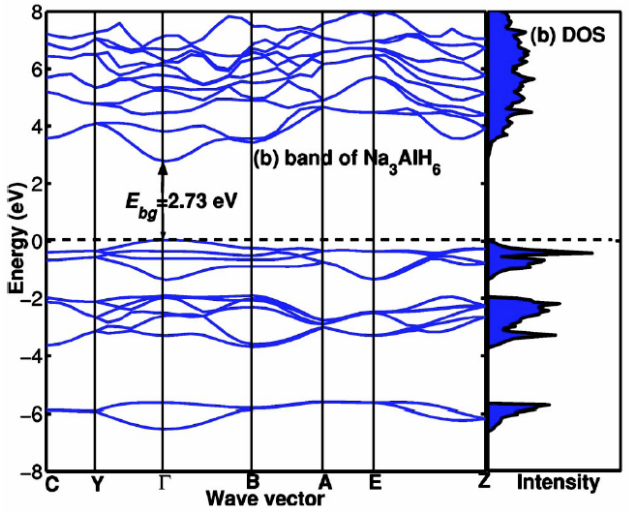


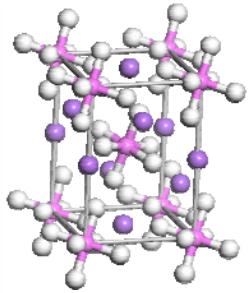


Al-H
=1.63 Å

Xuezhi Ke and Isao Tanaka, PRB 71 (2005) 024117

Bandstructure of Na_3AlH_6



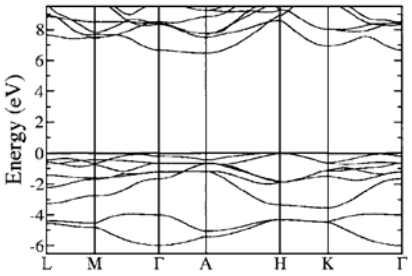


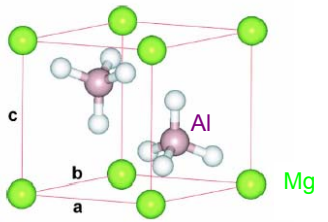
Al-H
=1.78 Å

Hydrogen content of complex metal-hydrides

		M	H / M
		[g mol^{-1}]	[wt%]
Lithiumboro-hydride	$LiBH_4$	21.784	18.4
Sodiumboro-hydride	$NaBH_4$	37.83	10.6
Potassiumboro-hydride	KBH_4	53.94	7.4
Lithiumaluminum-hydride	$LiAlH_4$	37.95	9.5
Sodiumaluminum-hydride	$NaAlH_4$	54.0	7.4
Sodiumaluminum-hydride	Na_3AlH_6	102.0	5.9
Sodiumlithiumaluminum-hydride	Na_2LiAlH_6	85.9	7.0
Magnesiumnickel-hydride	Mg_2NiH_4	111.3	3.6
Magnesiumiron-hydride	Mg_2FeH_6	110.5	5.4
Magnesiummanganese-hydride	Mg_3MnH_7	134.9	5.2

$Mg(AlH_4)_2$





PHYSICAL REVIEW B 72, 073107 (2005)

Ab initio study of $Mg(AlH_4)_2$

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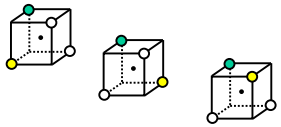
(Received 20 May 2005; published 17 August 2005)

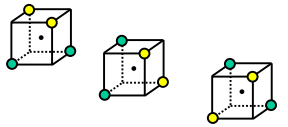
Determinant for the 4 H only

$$\begin{vmatrix} E_H-3V-E & -w & -w & -w \\ -w & E_H-3V-E & -w & -w \\ -w & -w & E_H-3V-E & -w \\ -w & -w & -w & E_H-3V-E \end{vmatrix} = 0$$

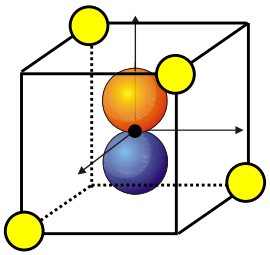
Eigenvalues	Eigenvectors	
E= E_H -3V+w	(1/√2) (-1, 1, 0, 0) (1/√2) (-1, 0, 1, 0) (1/√2) (-1, 0, 0, 1)	
E= E_H -3V –3w	(1/2) (1, 1, 1, 1)	

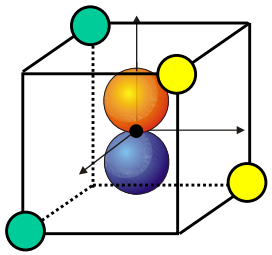
Better eigenvectors for the 4 H only

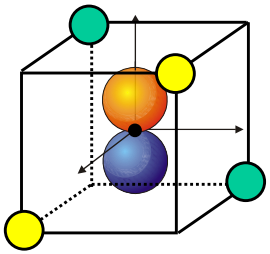
$$\begin{vmatrix} E_H-3V-E & -w & -w & -w \\ -w & E_H-3V-E & -w & -w \\ -w & -w & E_H-3V-E & -w \\ -w & -w & -w & E_H-3V-E \end{vmatrix} = 0$$

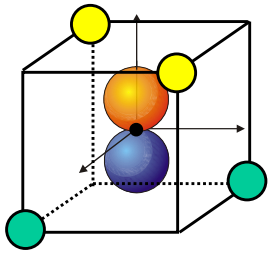
Eigenvalues	Eigenvectors	
E= E_H -3V+w	(1/2) (-1, 1, 1,-1) (1/2) (-1, -1, 1, 1) (1/2) (1, -1, 1, -1)	
E= E_H -3V –3w	(1/2) (1, 1, 1, 1)	

Alkali metal and 4H on a tetrahedral

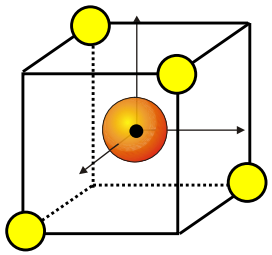
0 

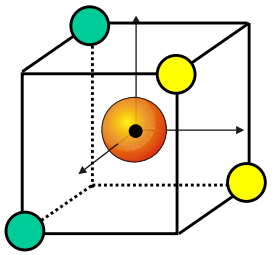
0 

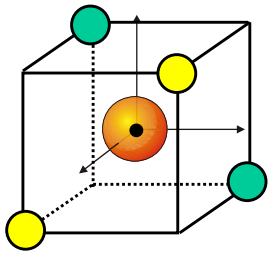
0 

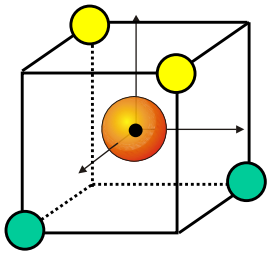
u 

Alkali metal and 4H on a tetrahedral

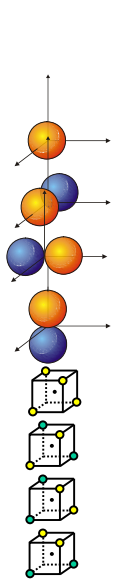
v 

0 

0 

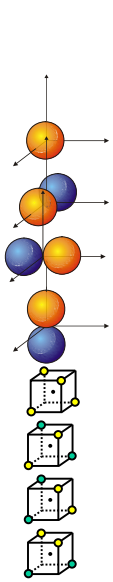
0 

Aluminium and 4H on a tetrahedral



E_s-E	0	0	0	-v	0	0	0
0	E_p-E	0	0	0	-u	0	0
0	0	E_p-E	0	0	0	-u	0
0	0	0	E_p-E	0	0	0	-u
-v	0	0	0	E_H-3w-E	0	0	0
0	-u	0	0	0	E_H+w-E	0	0
0	0	-u	0	0	0	E_H+w-E	0
0	0	0	-u	0	0	0	E_H+w-E

Aluminium and 4H on a tetrahedral



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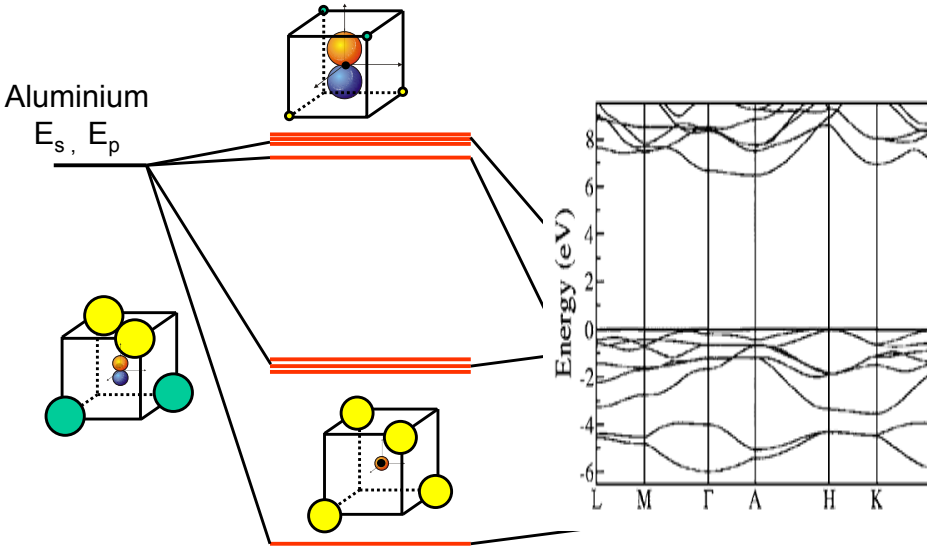
Eigenvalues and eigenvetors for u=v=w=1 eV and $E_s = E_p = 0$ and $E_H = -5$ eV

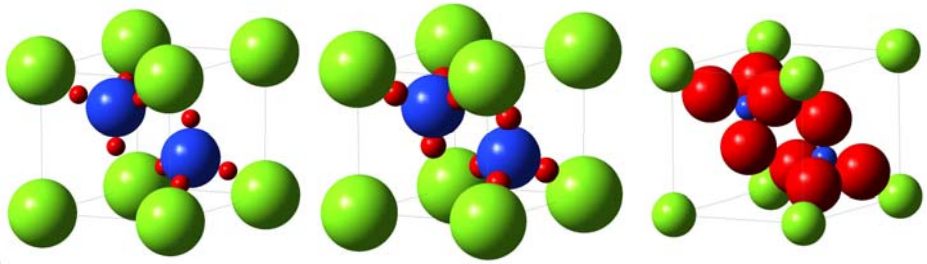
Eigenvalues	Eigenvectors							
0.236	0	0.973	0	0	0	-0.230	0	0
0.236	0	0	0.973	0	0	0	-0.230	0
0.236	0	0	0	0.973	0	0	0	-0.230
0.123	0.993	0	0	0	-0.122	0	0	0
-4.236	0	0.230	0	0	0	0.973	0	0
-4.236	0	0	0.230	0	0	0	0.973	0
-4.236	0	0	0	0.230	0	0	0	0.973
-8.1231	0.122	0	0	0	0.993	0	0	0

Energy level scheme



Crystal structure of $Mg(AlH_4)_2$

Covalent radii		Atomic radii		Ionic radii	
Mg	1.36 Å	Mg	1.50 Å	Mg	0.86 Å
Al	1.18 Å	Al	1.25 Å	Al	0.50 Å
H	0.37 Å	H	0.50 Å	H	1.10 Å



$P\bar{3}m1$ with a=b=5.2084 Å, c=5.8392 Å