The Abdus Salam
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Educational, Scientific and
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School and Workshop on Highly Frustrated Magnets and Strongly Correlated Systems: From Non-Perturbative Approaches to Experiments

30 July - 17 August, 2007

Highly Frustrated Magnets: Materials and Materials Preparation

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Abdus Salam ICTP August 30, 2007

Outline:

I. Families of geometrically frustrated materials.

A. Triangles, tetrahedra and magnetic frustration.

(Subversion of the 3rd Law by suppression of long range magnetic order)

1. The frustration index $f \sim |\theta|/T_{ord}$
2. Role of the spin quantum number.

B. Common frustrated lattices in 2 and 3 dimensions.

1. Triangular planar
2. Kagomé
3. Face-centred cubic
4. Pyrochlore

C. Real materials: transition metal compounds

1. Triangular planar
   a. "ordered rock salt"
      $NaNiO_2$, $LiNiO_2$
   b. anhydrous alums
      $AM(SO_4)_2$: ex A = Rb^+, M = Fe^{3+}
2. Kagomé
   a. Jarosites
      $AM_3(SO_4)_2(OH)_6$: ex A = K^+, M = Fe^{3+}
   b. Herbertsmithites
      $ZnCu_3(OH)_6Cl_2$

3. F.c.c.
   A. B-site ordered "double perovskites"
      $A_2BB'O_6$: ex A = Ba, B = Y, B' = Ru

4. Pyrochlore

a. pyrochlore oxides: $A_2M_2O_7$, ex $Y_2Mo_2O_7$

b. Spinel oxides: AB_2O_4. ex $ZnCr_2O_4$

5. Other frustrated 3D lattices.

a. "SCGO" $SrCr_{12-x}Ga_xO_{19}$

b. Garnet: $A_3M_5O_{12}$. ex $Gd_3Ga_5O_{12}$

c. "ordered rock salt" ex $Li_3Mg_2RuO_6$

d. $BaM_{10}O_{15}$: M = V^{3+}, Cr^{3+}

II. Materials preparation and crystal growth.

A. Control of transition metal oxidation state and oxygen stoichiometry.

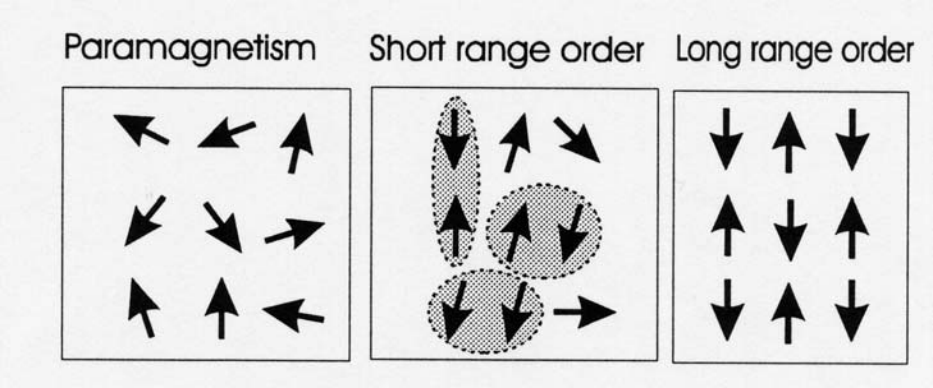
1. oxygen affinity, pO, buffer gases

B. Crystal growth methods.

1. Bridgeman
2. Czochralski
3. Floating zone
4. Flux
5. Hydrothermal

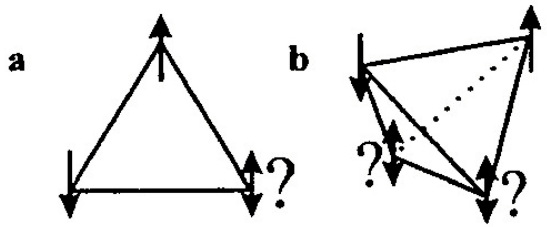
C. “Soft chemical” routes to metastable phases

A. Triangles, tetrahedra and magnetic frustration.



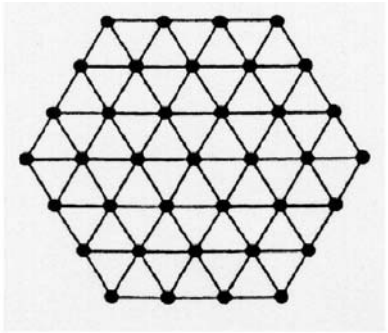
3rd Law: S → 0 as T → 0

triangular topology frustrates LRO

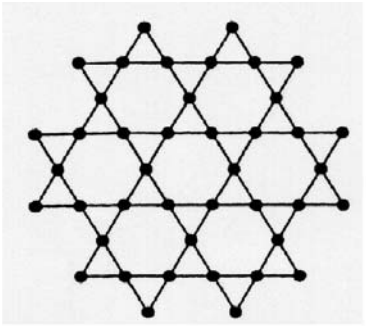


Subversion of the 3rd Law ?

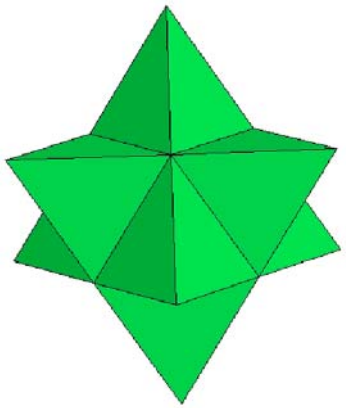
Realization of frustrated topology in real(common)lattices, 2D and 3D



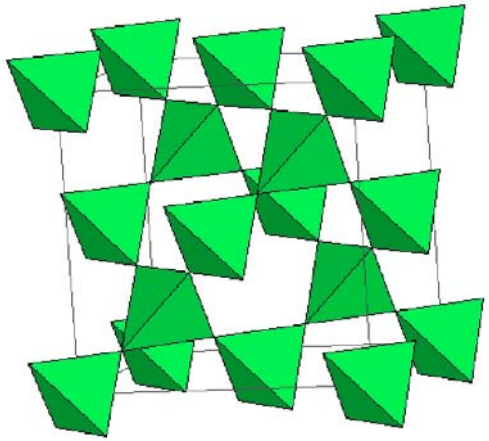
a. triangular



b , Kagome



c. face centered cubic



d. pyrochlore

The frustration index: $f \sim |\theta| / T_{ord}$

P. Schiffer, A.P. Ramirez, Comm. Cond. Matter Phys. 10 (1996) 21.

from mean field theory:

$$\theta = \frac{2S(S+1)}{3k} \sum_{m=1}^{N'} z_m J_m$$

algebraic, weighted, sum of all pairwise exchange interactions

$$H_{ex} = -2JS_n \cdot S_m$$

sets energy (temperature) scale for the magnetic exchange.

$T_{ord} = T_c, T_N, T_g$

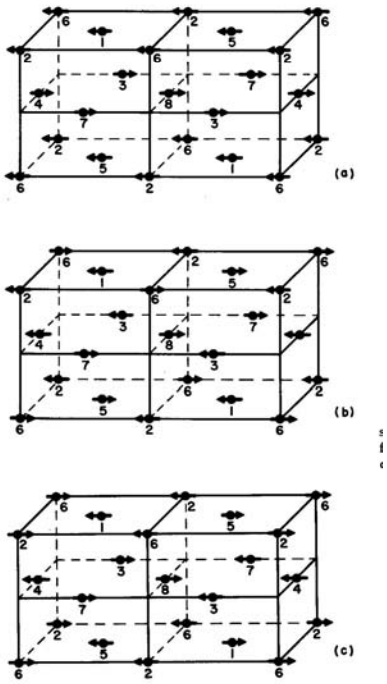
if f >> 5, evidence for frustration

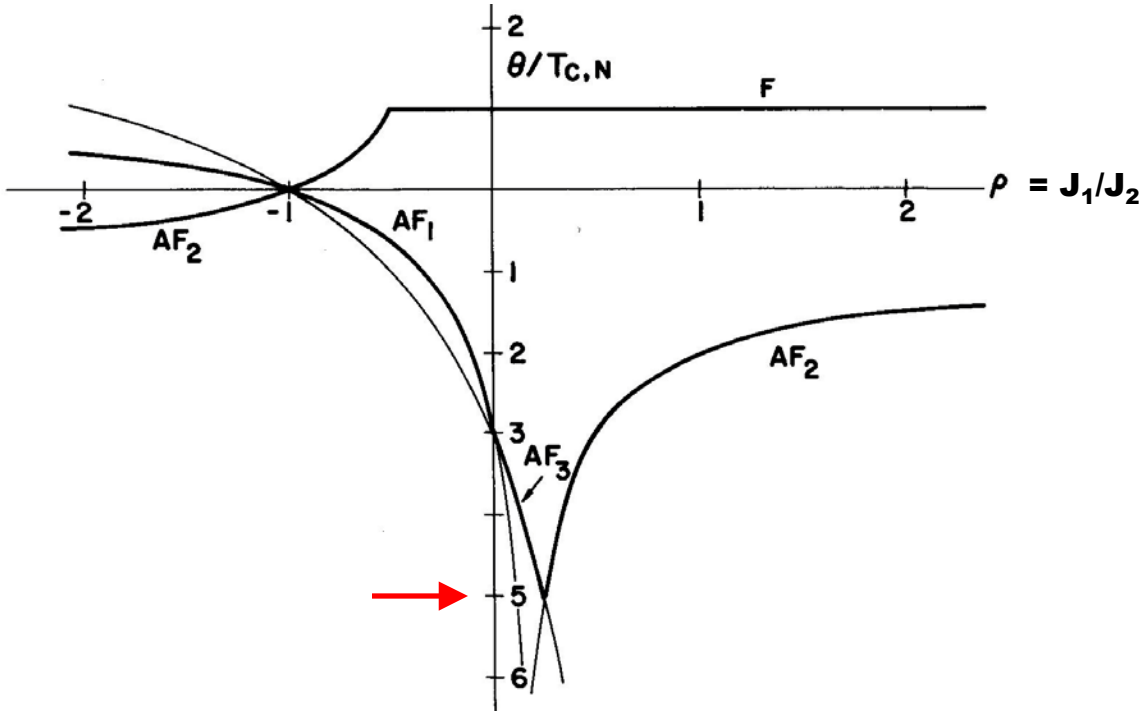
MFT phase diagram for f.c.c. lattice

AF_1

AF_2

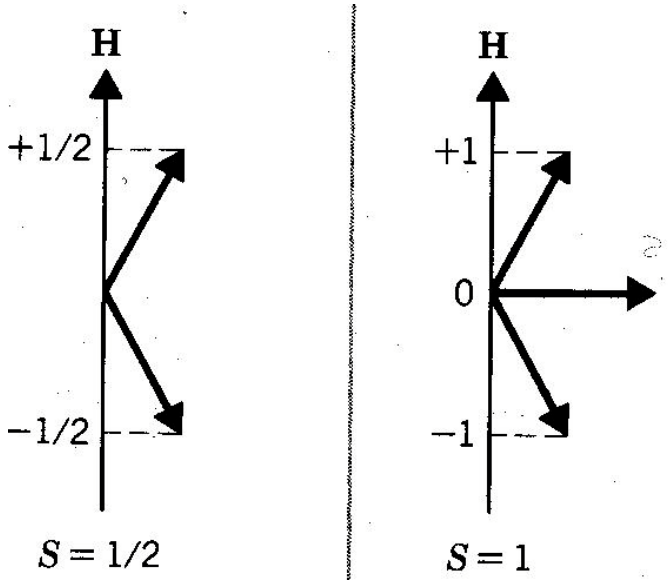
AF_3





J.S. Smart, "Effective field theories of magnetism"
W.B. Saunders 1966

Spin quantum number and quantum fluctuations:
As S↓, system becomes more quantum mechanical.



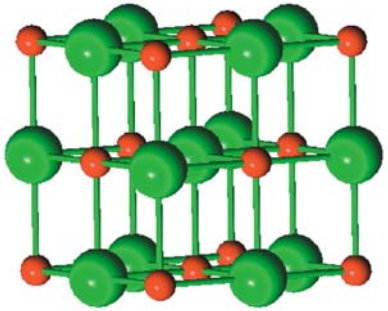
Spin state fluctuations have major effect on attempt to establish long range order.

C. Real materials: transition metal compounds

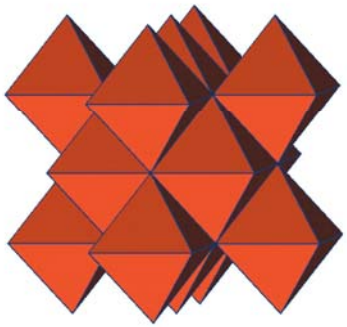
1. Triangular planar

a. “ordered rock salt”

$NaNiO_2$, $LiNiO_2$, $LiCrO_2$



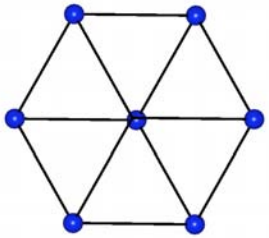
NaCl



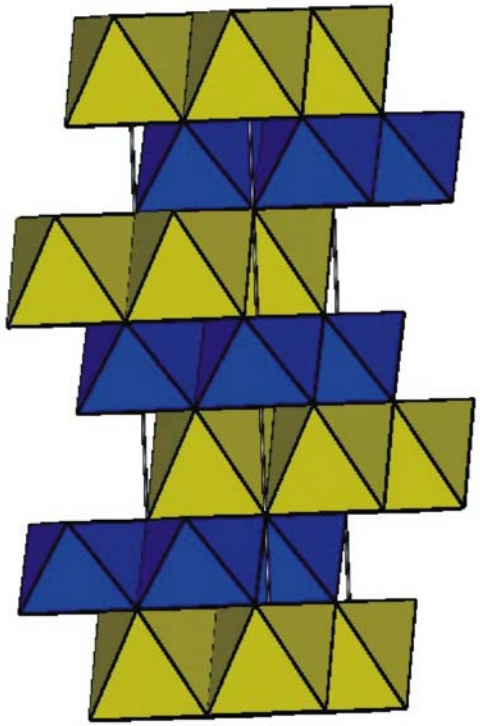
octahedra sharing all edges

$M^{2+}O^{2-} = M_2O_2 = M^{1+}M'^{3+}O_2$

M^{+} and M^{3+} order into layers normal to the body diagonal <111> of the NaCl cubic cell (Fm3m → R-3m)



M^{3+} layer



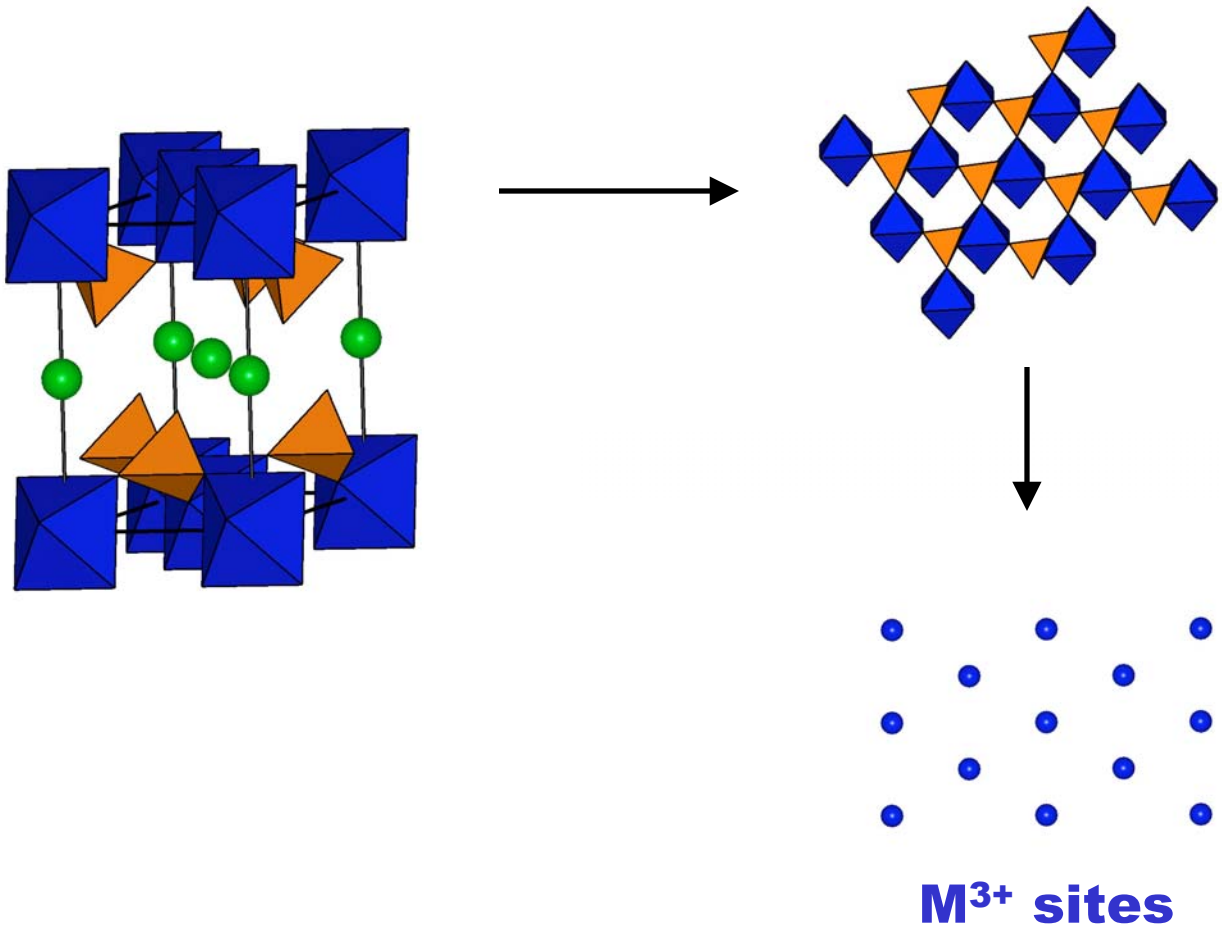
<111>

Compound	θ(K)	T_c(K)	θ/T_c	J_{intra}	J_{inter}	Grd.State
$NaNiO_2$	+100	23	4.4	F	AF	AF LRO
$LiNiO_2$	+ 20	9*	2.2	F?	AF?	spin glass
$LiCrO_2$	- 600	62	9.7	AF	AF	AF LRO

*spin freezing

b. anhydrous alums : $AM(SO_4)_2$

A^{+1} = K,Rb,Cs M^{3+} = Fe,Ti



Selected data for some anhydrous alums

Compound	S	θ_c/K	T_c/K	$\lvert\theta_c\rvert/T_c$
$CsFe(SO_4)_2$	5/2	−34.17	4.4	7.8
$RbFe(SO_4)_2$	5/2	−29.12	4.2	6.9
$KFe(SO_4)_2$	5/2	−55.5	8.3	6.7
$KTi(SO_4)_2$	1/2	−10.2	<1.2	>10

- **relatively large f values**
- **Ti phase does not order to 1.2K**

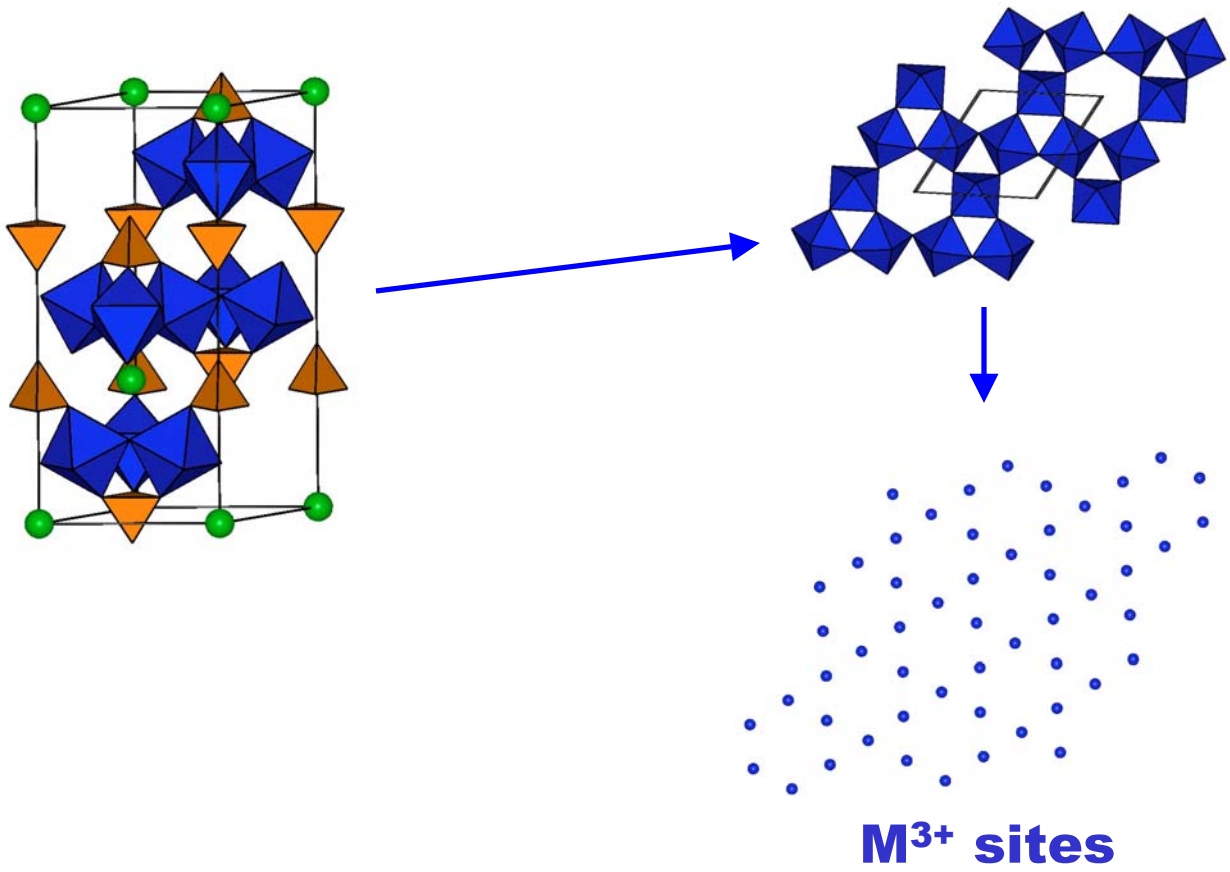
2. Kagomé

a. Jarosites

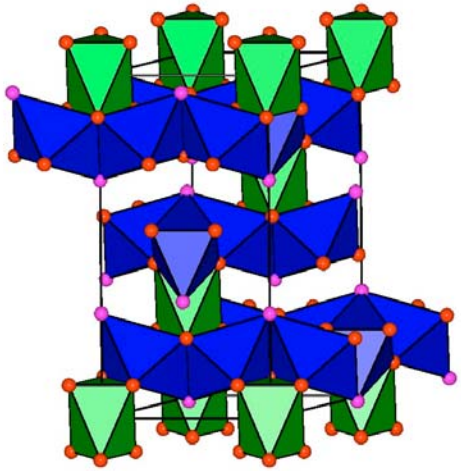
$AM_3(SO_4)_2(OH)_6$: ex

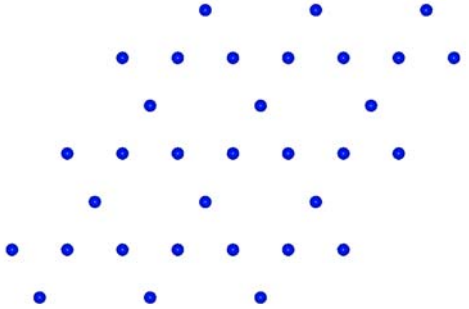
A^+ = Na, K, Rb, NH_4, H_3O, Ag, Tl • • •

M^{3+} = Fe, Cr, V



b. Herbertsmithite $ZnCu_3(OH)_6Cl_2$





Cu^{2+} sites

$AFe_3(SO_4)_2(OH)_6$

[PRB 67 (2003) 064401]

[NatureMater. 4 (2004) 323]

A^+	C^a	Θ_{CW}/K^a	T_N/K	T_D/K^b	f^c	$\frac{c}{3}(=d)/Å$
Na^+	5.91	−825	61.7	~58	13.5	5.535
K^+	5.77	−828	65.4	~53	12.7	5.728
Rb^+	5.82	−829	64.4	~53	12.9	5.856
NH_4^+	5.84	−812	61.8	~53	13.1	5.767[d]

$(H_3O)Fe_3(SO_4)_2(OH)_6$

No LRO to 1.4K

spin glassy ground state.

disorder due to H_3O^+ - OH^- proton exchange.

Herbertsmithite $ZnCu_3(OH)_6Cl_2$

Θ ~ -300 K but

- **no LRO from neutrons to 1.4K !**
- **no LRO specific heat to 50 mK !**
- **spin liquid ground state?**

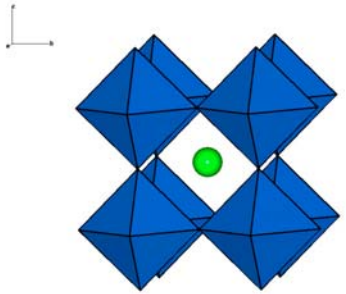
PRL 98 (2007) 107204

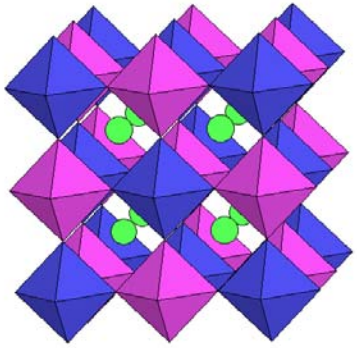
3. F.c.c. B-site ordered "double perovskites"

A_2BBO_6 : A = Ca,Sr,Ba, La

B = Y, Mg, Ca, Li

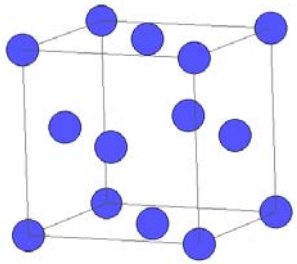
B = Mo, Re, Ru

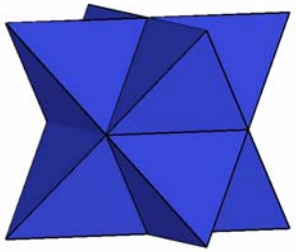




ABO_3 - simple perovskite

A_2BBO_6 - ordered double perovskite

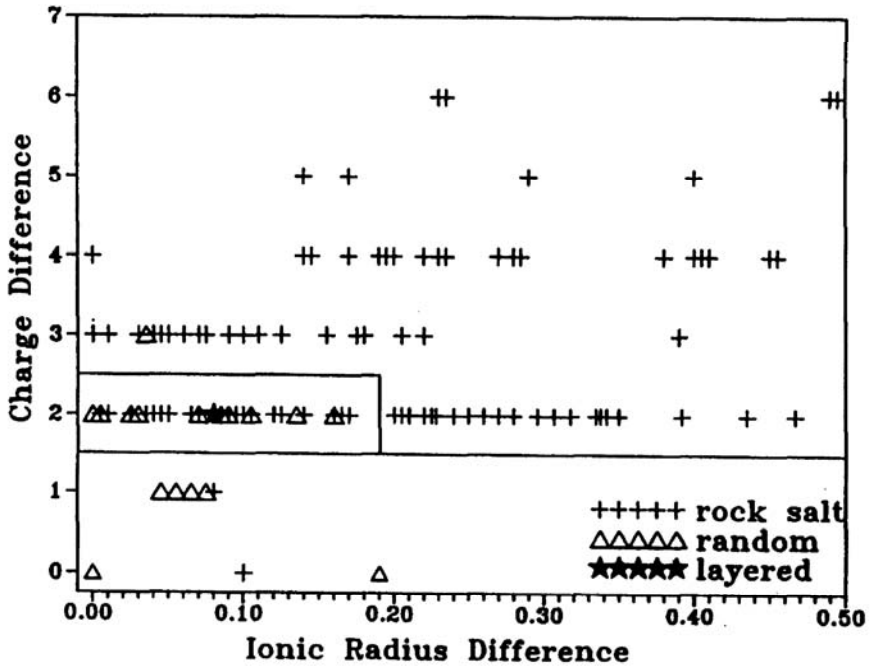




B (magnetic) sublattice f.c.c.

edge-sharing tetrahedra: unfashionable but still frustrated lattice

Factors controlling B-site (BB) ordering



- BB radius difference
- BB formal charge difference

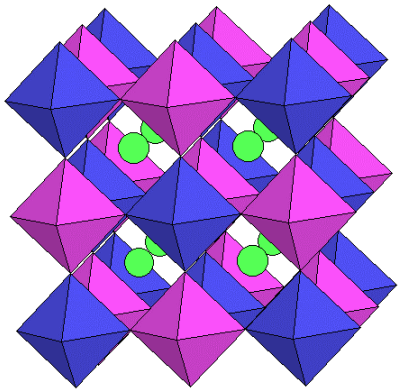
M.T. Anderson et al Prog. Sol. State Chem. 22 (1993) 197

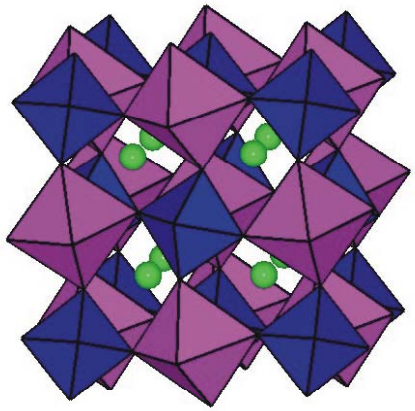
- **Ordered double perovskites - flexibility in crystal engineering.**

- **Control of crystal structure symmetry - cubic vs monoclinic**

Goldschmidt tolerance factor, $t = (A - O) / 2^{1/2} (\langle B - O \rangle)$

$t \sim 1$ ($Fm3m$) **$t \sim 0.9$ ($P2_1/n$)**

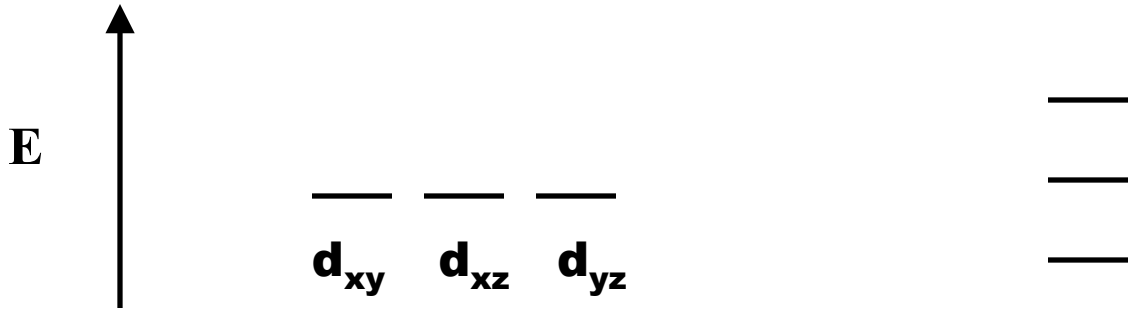




- **Control of site symmetry of magnetic ion/orbital degrees of freedom**

Fm3m (m3m or O_h)
(t_{2g}^n) retain orbital degeneracy

$P2_1/n$ (-1)
(t_{2g}^n) degeneracy lifted
"orbital ordering"



- **Control of spin state of magnetic ion within same crystal symmetry**

Ba_2BBO_6 (Fm3m)

B = Ca^{2+}

B^{6+} = Re^{6+} (S = 1/2)

= Os^{6+} (S = 1)

B = Y^{3+}, Lu^{3+}

B^{5+} = Mo^{5+} (S = 1/2)

= Re^{5+} (S = 1)

= Ru^{5+} (S = 3/2)

La_2BBO_6 ($P2_1/n$)

B = Li^{+}

B^{5+} = Mo^{5+} (S = 1/2)

= Re^{5+} (S = 1)

= Ru^{5+} (S = 3/2)

Sr_2BBO_6 ($P2_1/n$)

B = Ca^{2+}

B^{6+} = Re^{6+} (S = 1/2)

B = $Y^{3+}Lu^{3+}$

B^{5+} = Ru^{5+} (S = 3/2)

Compound	S	θ(K)	T_c(K)	f	Ground State
Ba_2YRuO_6	3/2	-571	36	16	AF LRO
La_2LiRuO_6	3/2	-207	23.8	9	AF LRO
Ba_2YReO_6	1	-480	40*	12	?
La_2LiReO_6	1	-204	33*	6	?
Ba_2YMoO_6	1/2	-91	< 2	> 45	?
Sr_2CaReO_6	1/2	-443	14	32	spin glass

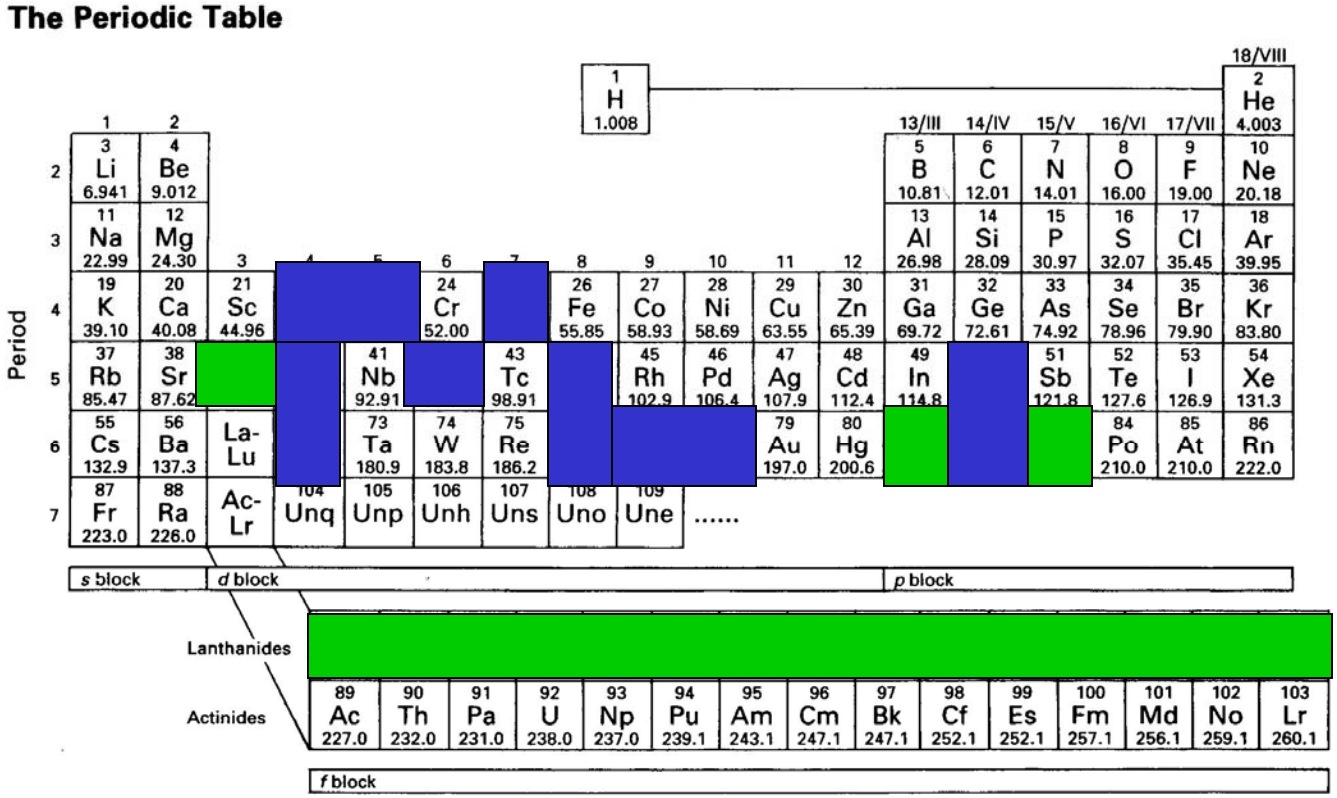
* broad χ(max), ZFC/FC divergence

4. Pyrochlore

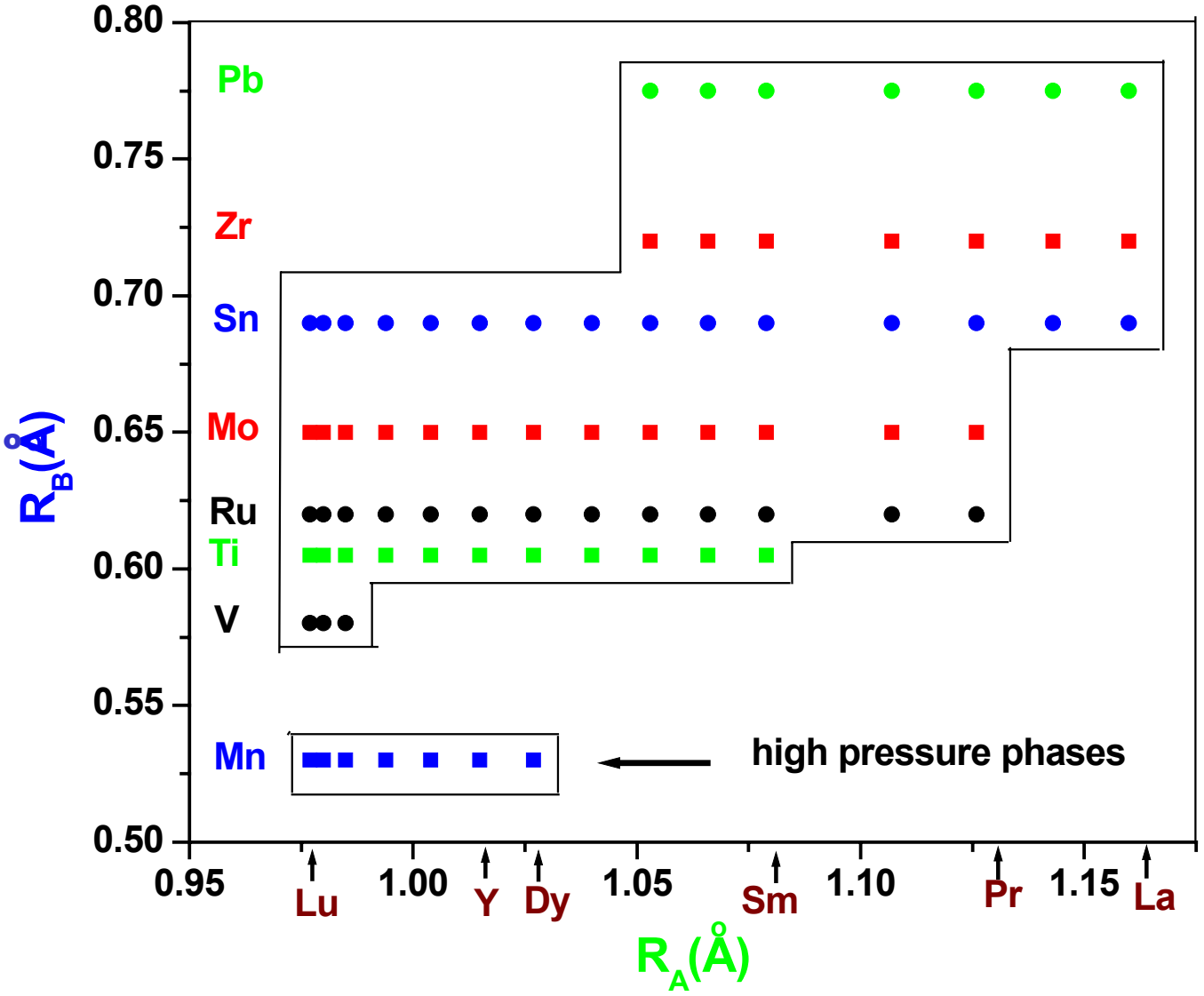
a. pyrochlore oxides: $A_2B_2O_7$ or $A_2B_2O_6O$

A^{3+} = Ln^{3+}(La-Lu,Y), Tl, Bi

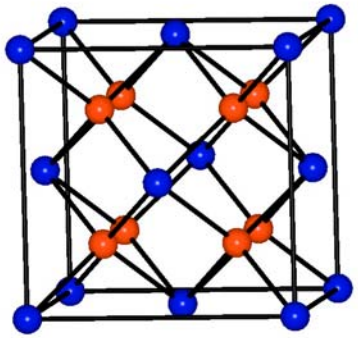
B^{4+} = 3d, 4d, 5d transition metals, Sn, Pb

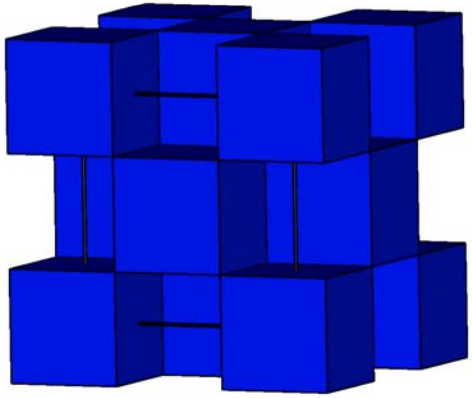


Pyrochlore “structure - field map”



Pyrochlore as an ordered defect CaF_2(fluorite)





$M^{4+}O_2 = M_4O_8$

M^{4+} coordinated
by 8 O^{2-}, perfect cube

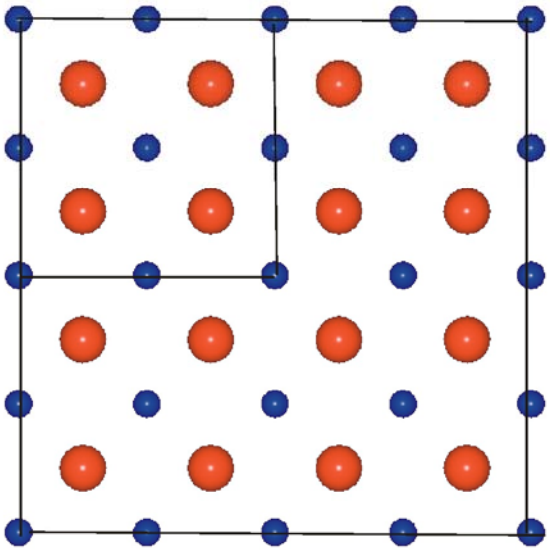
M_4O_8 → $A_2B_2O_7$

a ~ 5Å → a ~ 10 Å

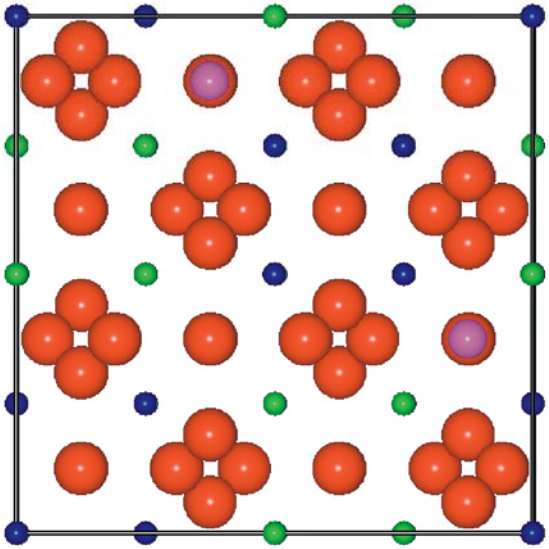
M_4O_8 x 8 = $M_{32}O_{64}$

$2M^{4+} \rightarrow A^{3+} + B^{4+}$

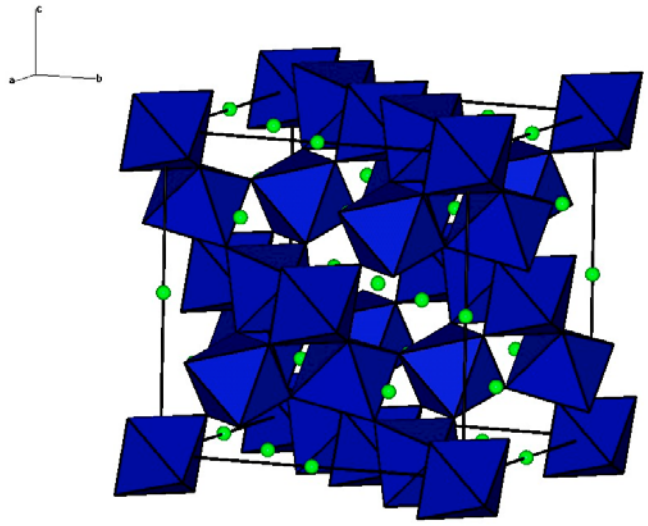
$A_{16}B_{16}O_{56}\square_8 = A_2B_2O_7$

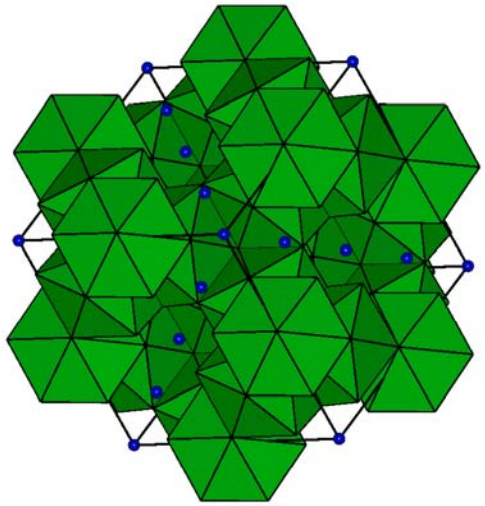


M_4O_8 face projection



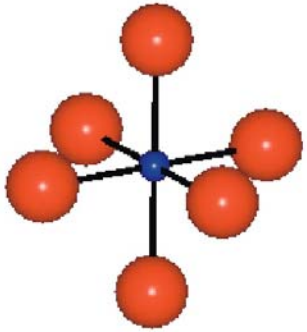
pyrochlore face projection



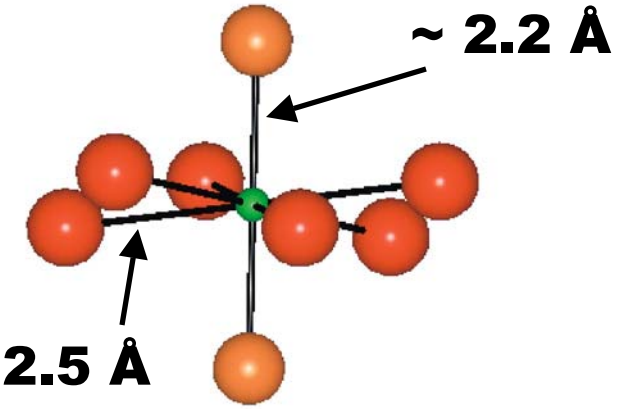


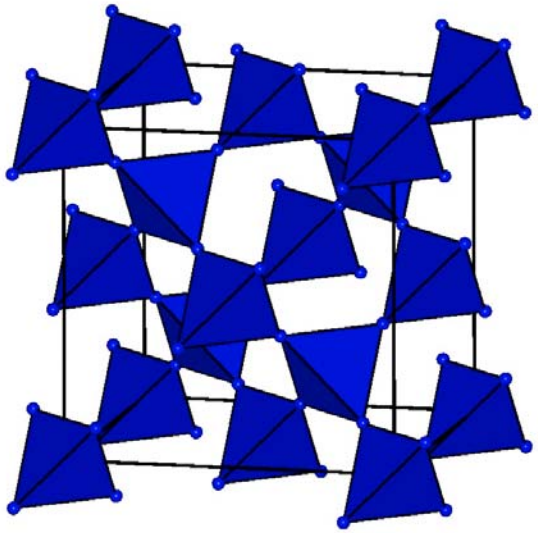
B - site octahedra

A - site hexagonal bipyramids



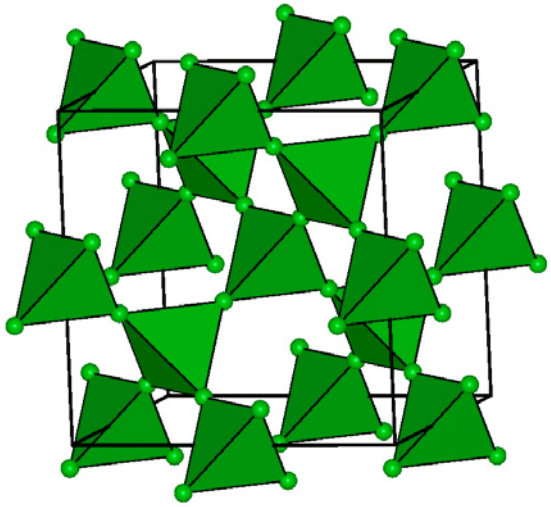
6 equiv B - O ~ 2.0 Å





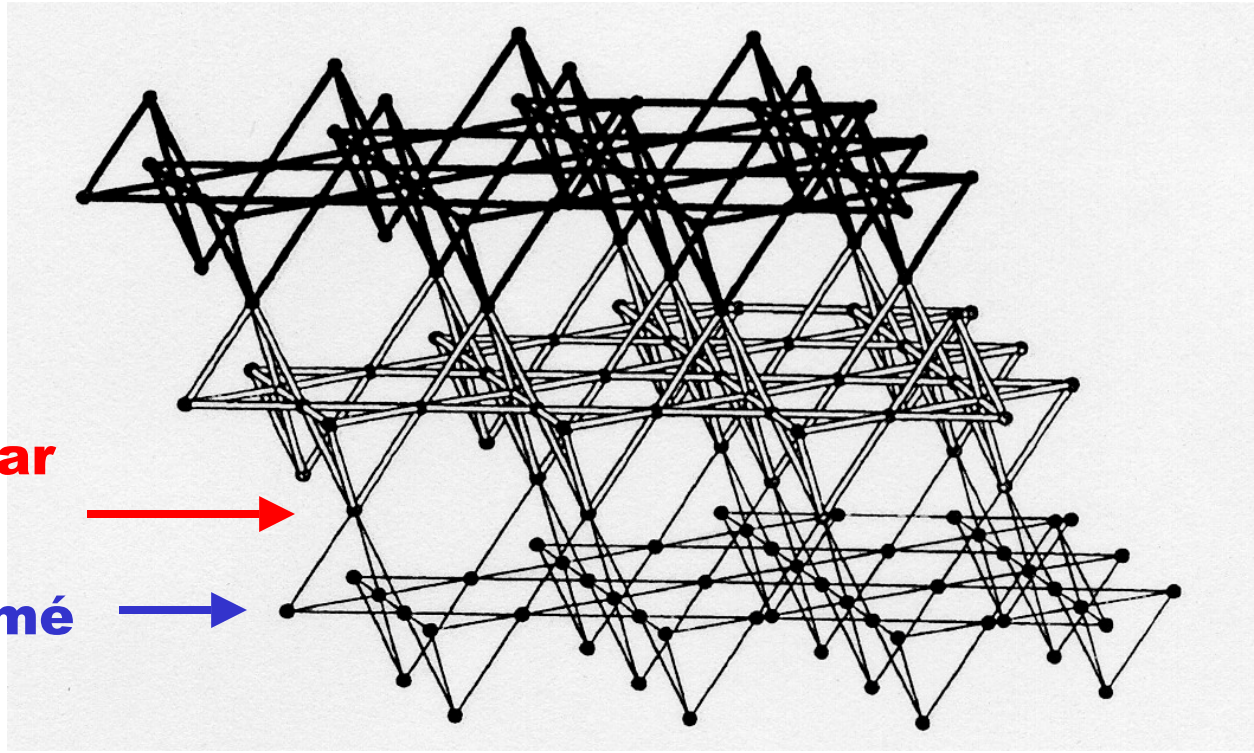
B-sites

A-sites



Both A and B sites pyrochlore lattices !!

Another view: pyro lattice as alternating stacking of Kagomé and triangular planar layers



Possibilities:

- **A-site only magnetic**

  A = Ln^{3+} ($\neq$ La, Y,Lu) , B = Ti^{4+}, Sn^{4+}, Zr^{4+} . . .

- **B - site only magnetic**

  A = Y, Lu, B = V^{4+}, Mn^{4+}, Mo^{4+}, Ir^{4+} . . .

- **both A and B sites magnetic**

A = Ln^{3+} ($\neq$ La, Y,Lu) , B = V^{4+}, Mn^{4+}, Mo^{4+}, Ir^{4+} . . .

A-site only

- $Tb_2Ti_2O_7$ - spin liquid
- $Dy_2Ti_2O_7$ - spin ice
- $Gd_2Ti_2O_7$ - two AF orderings

B-site only

- $Y_2Mo_2O_7$ - spin glass, subtle disorder
- $Y_2Mn_2O_7$ - F - SRO, complex ground state
- $Lu_2V_2O_7$ - F insulator

A and B site

- $Ln_2Mo_2O_7$ and $Ln_2Ir_2O_7$ - metal insulator transitions (ferromagnetic metal to insulating spin glass)
- $Nd_2Mo_2O_7$ - anomalous Hall effect

Disorder Levels in Pyrochlores?
"antisite" A ⇔ B and O vacancies

Predictions: Phil. Mag. 82 (2002) 123

% antisite

A	Ti	Ru	Mo	Sn	Zr	Pb
Lu	.71	.94	1.7	4.4		
Yb	.66	.87	1.5	3.9		
Er	.58	.74	1.2	3.0		
Y	.54	.68	1.1	2.6		
Gd	.50	.58	.83	1.8	3.1	8.3
Sm	.52	.57	.76	1.6	2.7	6.4
Nd		.59		1.4	2.2	4.9
La				1.3	1.8	2.8

% O vacancies

Ti	Ru	Mo	Sn	Zr	Pb
.24	.31	.57	1.5		
.22	.29	.51	1.3		
.19	.25	.41	1.0		
.18	.23	.36	.87		
.17	.19	.28	.61	1.0	2.8
.17	.19	.25	.53	.88	2.1
	.20		.47	.75	1.6
			.43	.60	.94

b. Spinel oxides: AB_2O_4.

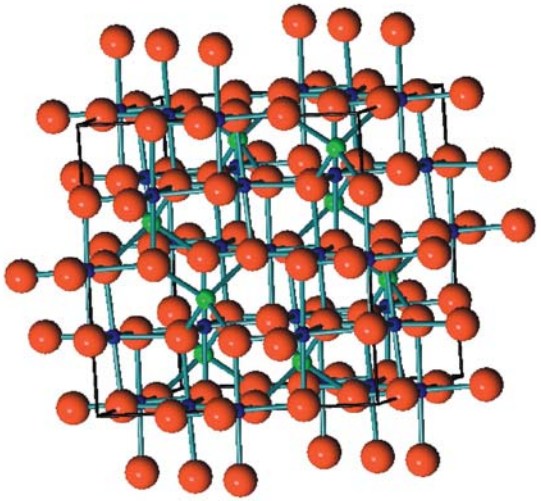
- The O^{2-} lattice is cubic close packed (f.c.c.)
- Typically, A^{2+} and B^{3+} but others are possible
  e.g. A^{1+}, B^{3+}, B^{4+} or A^{3+}, B^{2+}, B^{3+}
- A occupies a tetrahedral site (T_d) and B an octahedral site (O_h)
- In a close-packed lattice, there are
  per close-packed ion
  2 T_d sites and 1 O_h site
- Thus, the occupation rates are:

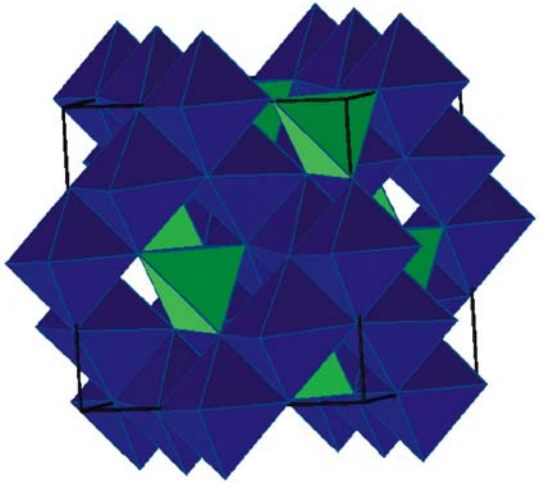
  1/8 T_d by A^{2+} 1/2 O_h by B^{3+}

Spinel $MgAl_2O_4$

Mg T_d

Al O_h





Edge-shared octahedra

Factors determining site occupation in spinels?

- **Unlike perovskites and pyrochlores, A^{2+} and B^{3+} have similar ionic radii**

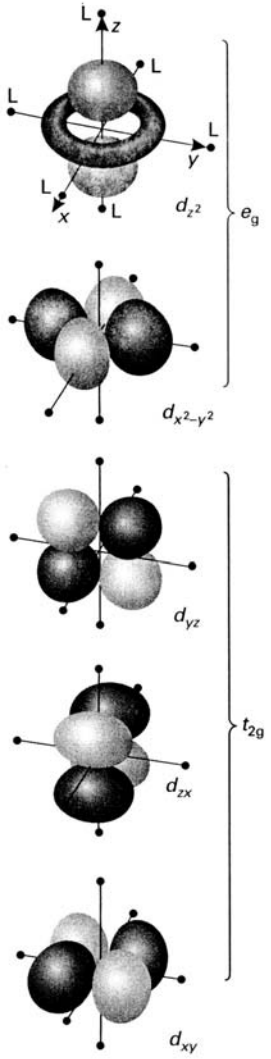
- **size differences not usually critical**

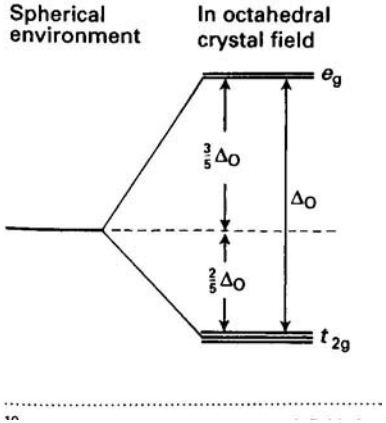
- **major factor is "O_h site preference energy"**

O.S.P.E.

derived from simple crystal field theory

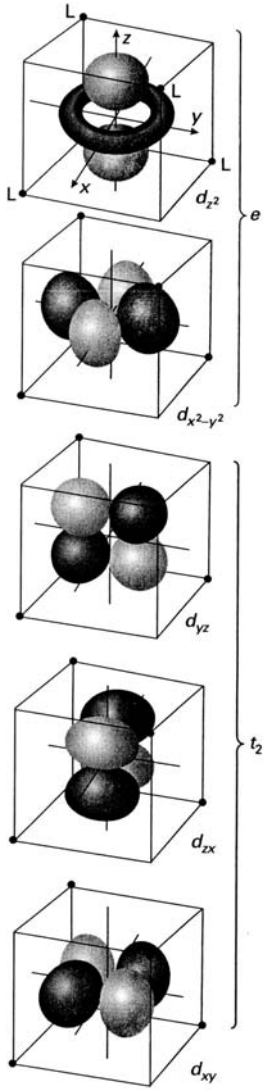
O_h xtal field

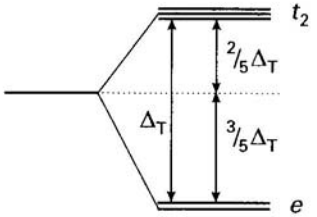




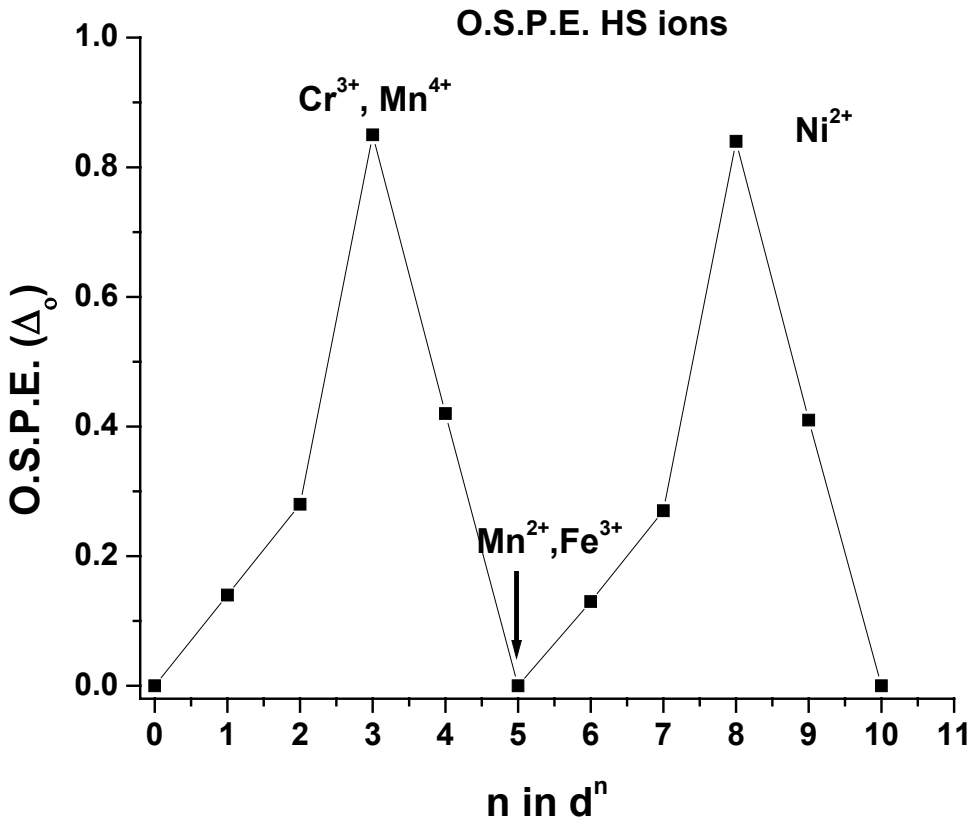
$\Delta_0 \sim 2\,\Delta_T$

T_d xtal field





"Inorganic Chemistry" Shriver and Atkins (Freeman 3rd Ed.)



Note:

large OSPE

$Cr^{3+}(t_{2g}^3)$ $Ni^{2+}(t_{2g}^6e_g^2)$

OSPE = 0

Mn^{2+}, $Fe^{3+}(t_{2g}^3e_g^2)$

OSPE even larger for 4d and 5d metal ions which are LS

Classification of spinels:

- **normal** $A^{2+}(T_d)$, $B^{3+}(O_h)$
  ex $ZnCr_2O_4$, $LiMn_2O_4$

- **inverted** $B^{3+}(T_d)$ A^{2+}, $B^{3+}(O_h)$
  ex Fe_3O_4 - $Fe^{3+}Fe^{2+}Fe^{3+}O_4$

- **mixed**

Spinels of interest:

$ZnCr_2O_4$ **- frustration driven cubic to tetragonal phase transition**

$LiMn_2O_4$ **- co-existence AF SRO/LRO**

$Li_2Mn_2O_4$, $MgMn_2O_4$ **- only 2D magnetic correlations**

5. Other frustrated 3D lattices.

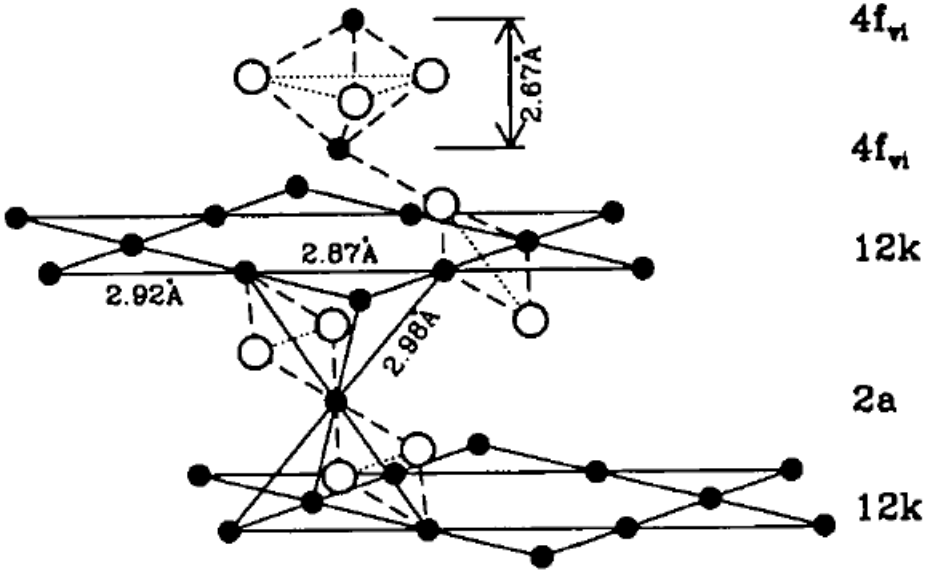
a. "SCGO" $SrCr_{12-x}Ga_xO_{19}$
b. Garnet: $A_3M_5O_{12}$. ex $Gd_3Ga_5O_{12}$
c. $BaM_{10}O_{15}$: M = V^{3+}, Cr^{3+}
d. "ordered rock salt" ex $Li_3Mg_2RuO_6$

a. SCGO decoupled "pyrochlore slabs"

Kagome

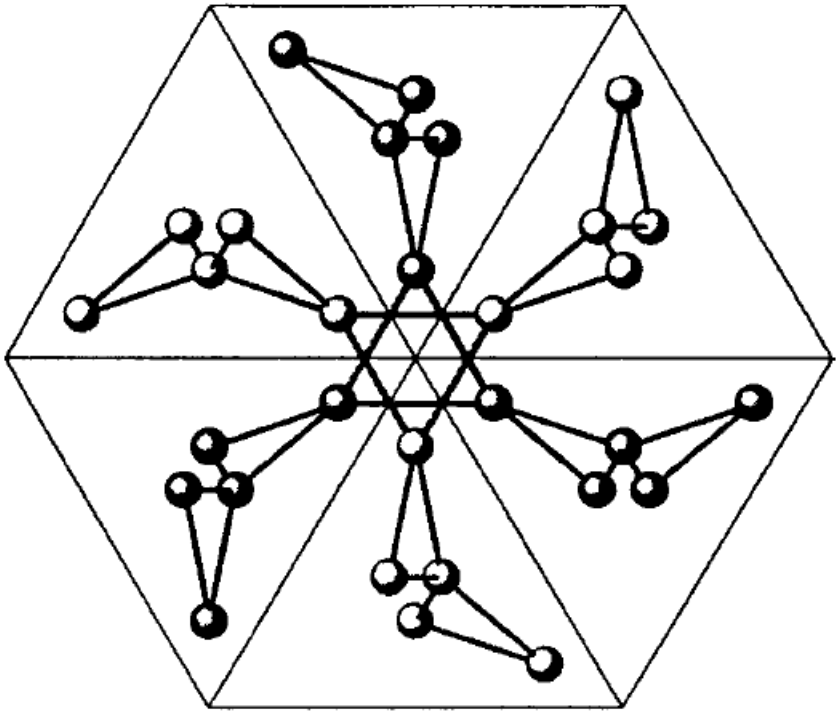
trig. planar

Kagome



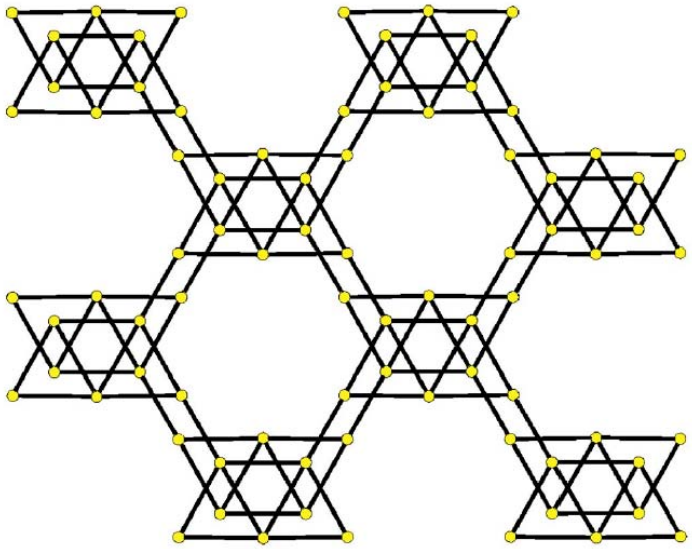
b. “GGG” Gd^{3+} lattice in $Gd_3Ga_5O_{12}$

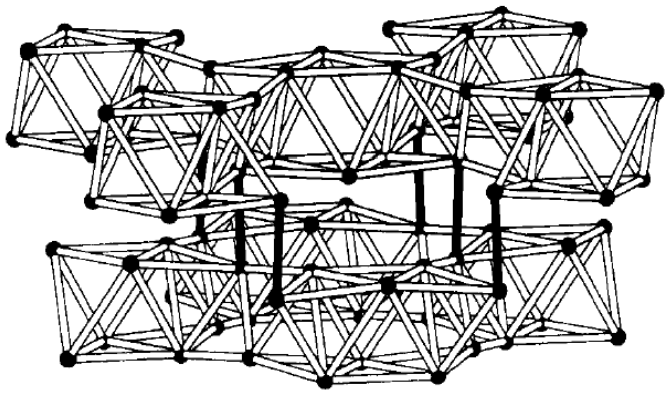
corner sharing triangles



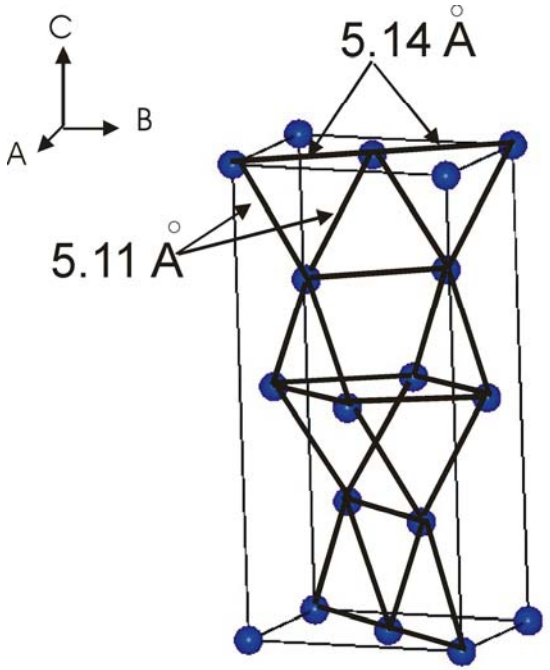
c. $BaM_{10}O_{15}$ - M = V,Cr

M_{10} clusters of edge-sharing tetrahedra





d. “ordered NaCl” $Li_3Mg_2RuO_6$



Ru-Ru-Ru = 59.81° x2, 60.39°

Ru-Ru distances and angles in $Li_3Mg_2RuO_6$

- **ribbons of edge-sharing triangles linked by corners**