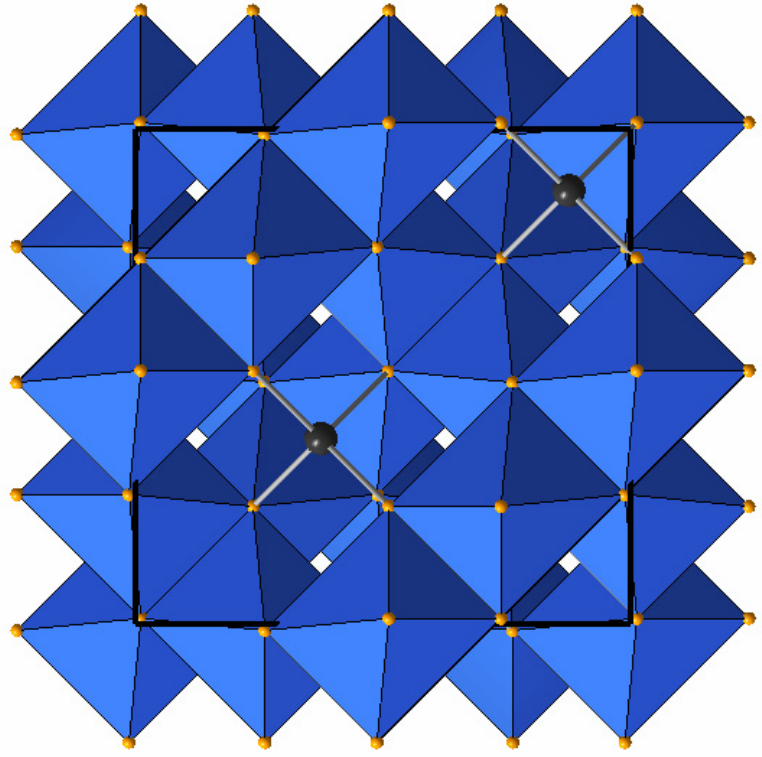


The spinel structure:  $MgAl_2O_4$   $Fd-3m$  (diamond)  $a \sim 8.5 \text{ \AA}$

A	1/8	1/8	1/8
B	1/2	1/2	1/2
X	0.264	0.264	0.264*

\* in  $MgAl_2O_4$



“Normal” spinels:

- $CoAl_2O_4$ ,  $GeCo_2O_4$ ,  $MgTi_2O_4$ ,  $MnV_2O_4$ ,
- $CdCr_2S_4$ ,  $HgCr_2S_4$ ,  $CuTi_2S_4$ ,  $CdCr_2Se_4$ ,
- $CuCr_2Te_4$

“Inverse” spinels:

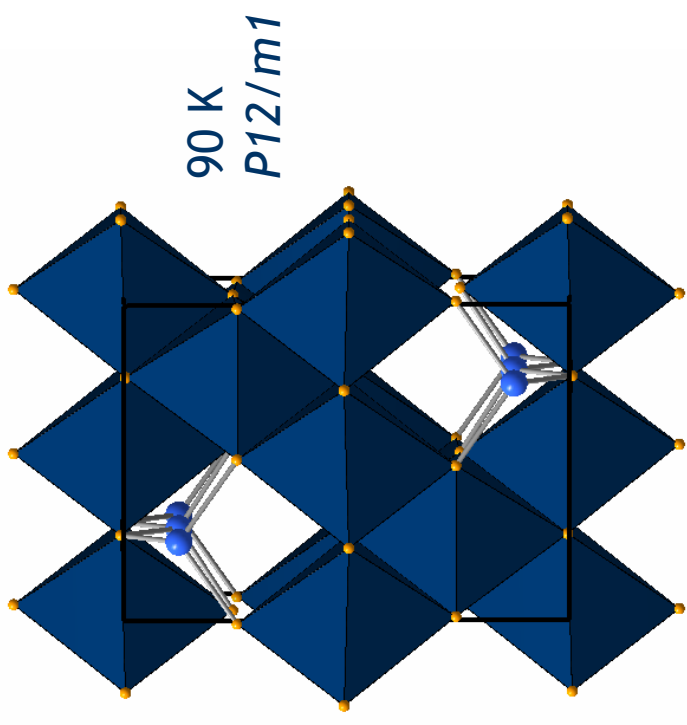
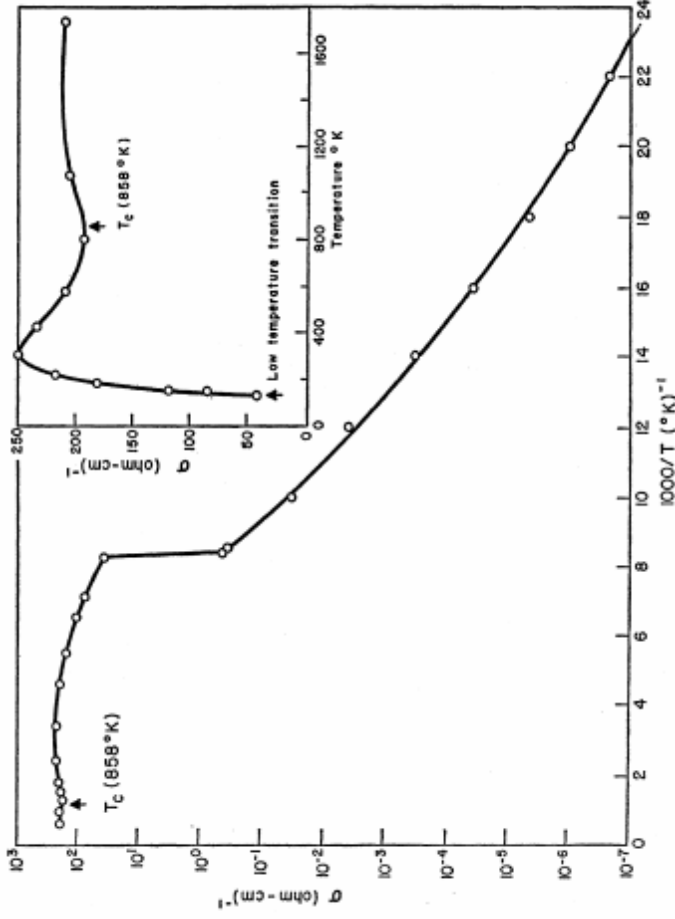
- $Fe(MgFe)O_4$ ,  $Mn(NiMn)O_4$ ,  $Zn(SnZn)O_4$ ,
- $Mg(Ti,Mg)O_4$ ,  $Zn(Ti,Zn)O_4$ ,  $In(Fe,In)S_4$ ,
- $Li(Ni,Li)O_4$ ,  $Fe(Fe,Fe)O_4$

What determines *site-selection*: Whether an ion will prefer to sit in the tetrahedral or octahedral site ?

1. Covalency and hybridization:  $\text{Cu}^{1+}$ ,  $\text{Zn}^{2+}$  like the tetrahedral site. Also  $\text{Cd}^{2+}$ ,  $\text{In}^{3+}$  ... (in chalcogenides)
2. Crystal field stabilization: Ions such as  $\text{V}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$  etc. have a strong preference for octahedral coordination because the crystal field stabilization is significantly larger.
3. When these effects are accounted for, size and charge kick in.

Site ordering can make a huge difference in property:  $\text{ZnFe}_2\text{O}_4$  is a soft ferrimagnet when Zn and Fe are distributed over the A and B sites. When it is well ordered (all Zn on the A site), it is a frustrated antiferromagnet.

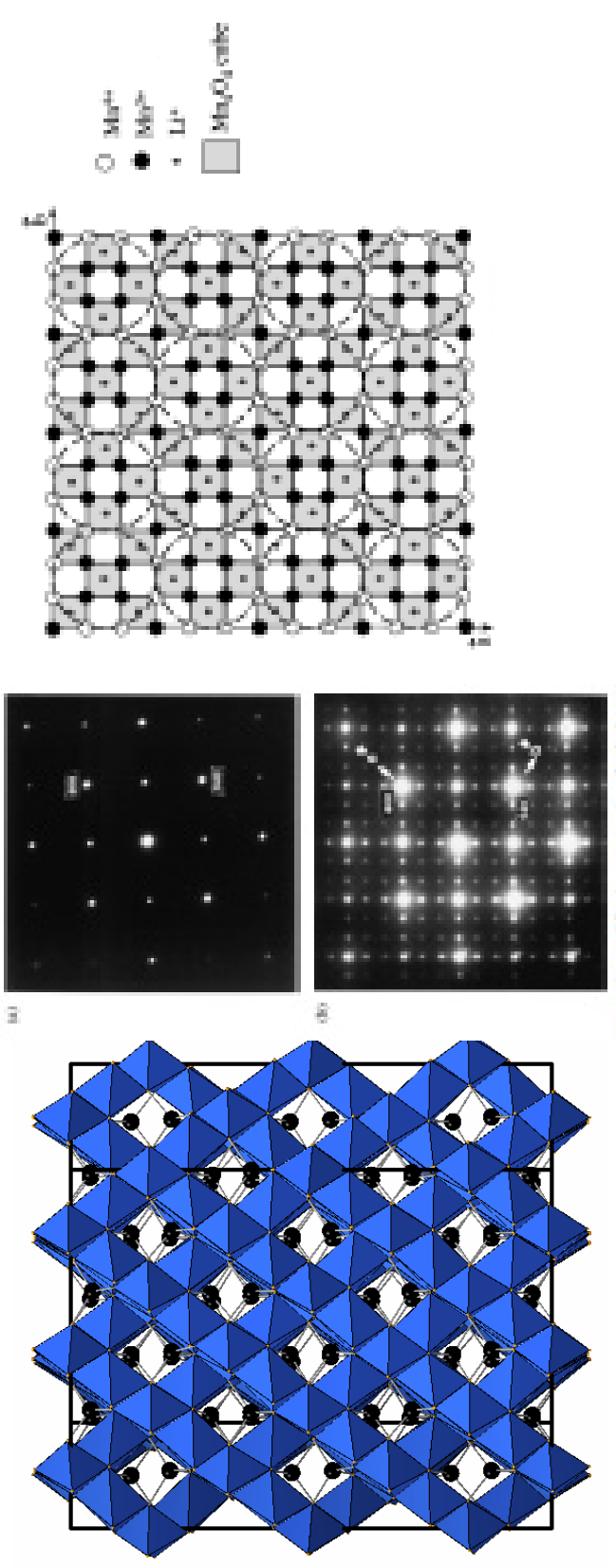
The Verweij transition in  $\text{Fe}_3\text{O}_4$ :  
E. J. W. Verwey and P. W. Haayman, *Physica* **8** (1941) 979.  
Also *Wigner Crystallization*.



Charge ordered structure of magnetite  $\text{Fe}_3\text{O}_4$  below the Verweij transition, J. P. Wright, J. P. Attfield and P. G. Radaelli, *Phys. Rev. B* **66** (2002), 214422(1):  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are ordered on the octahedral site.

$\text{LiMn}_2\text{O}_4$ : A charge-ordered battery material:

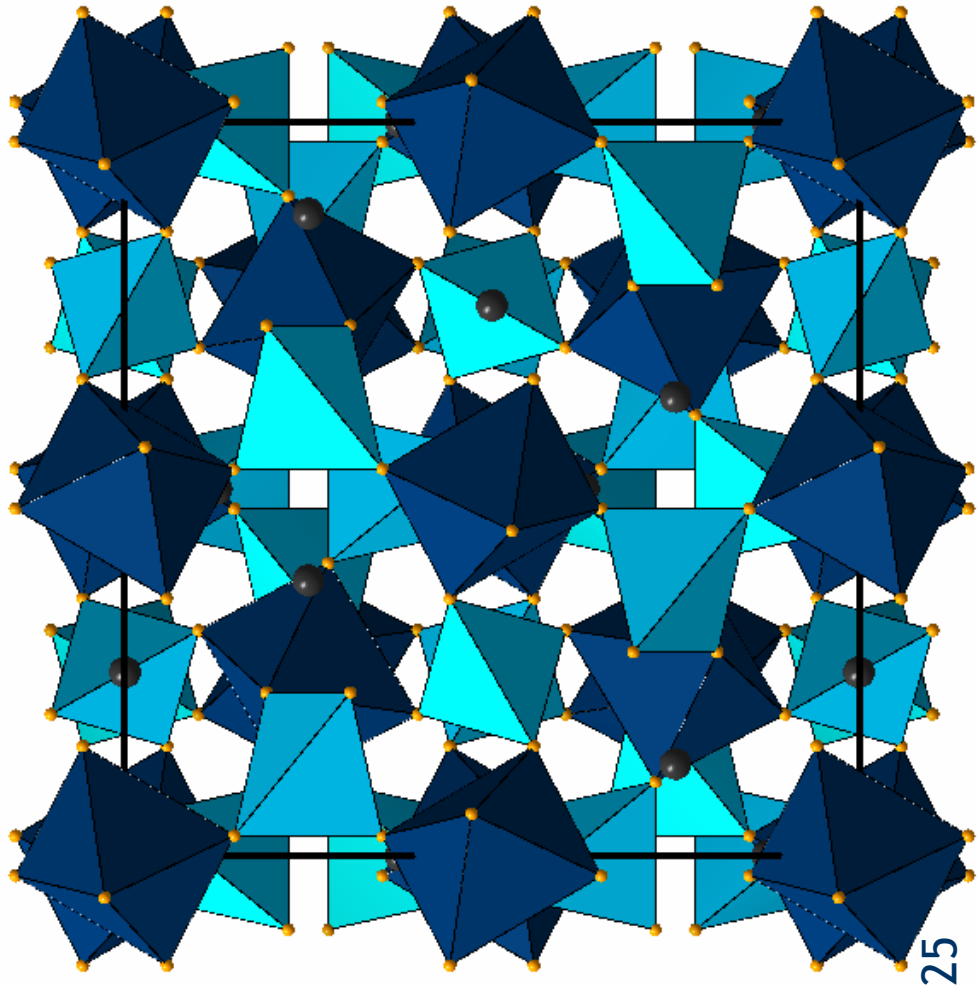
Complex ordering pattern at 297 K (this is a Jahn-Teller system).



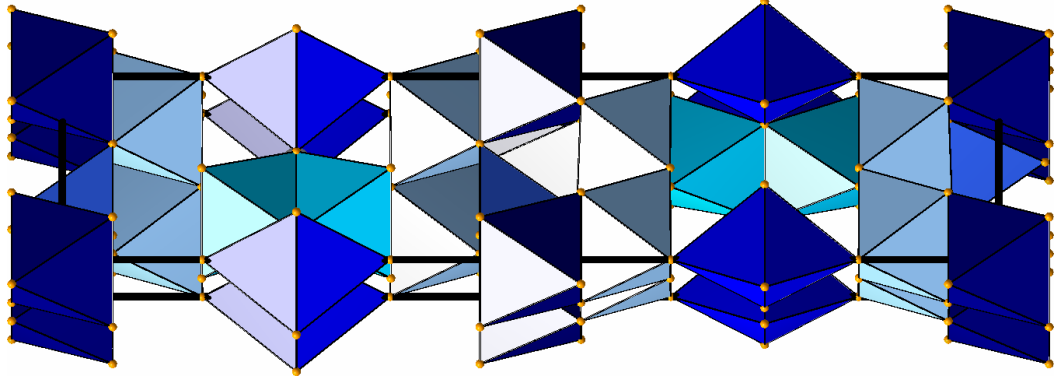
Rodriguez-Carvajal *et al.* Phys. Rev. Lett.  
81 (1998) 4660-4663.

Garnet ferrimagnets:  $Y_3Fe_5O_{12}$

Tetrahedral and octahedral B sites  
in a 2:1 ratio.



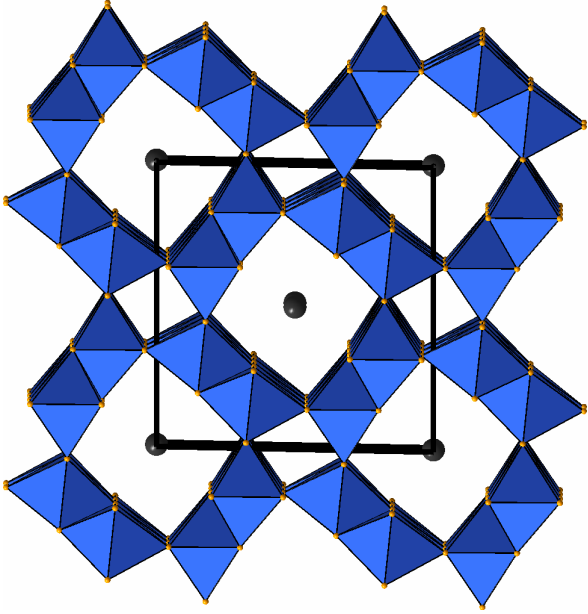
$a = 12.376 \text{ \AA}$	$1a-3d$				
Y	24c	0	0.25	0.125	
Fe	16a	0	0	0	
Fe	24d	0	0.25	0.375	
O	96h	-0.0274	0.0572	0.1492	



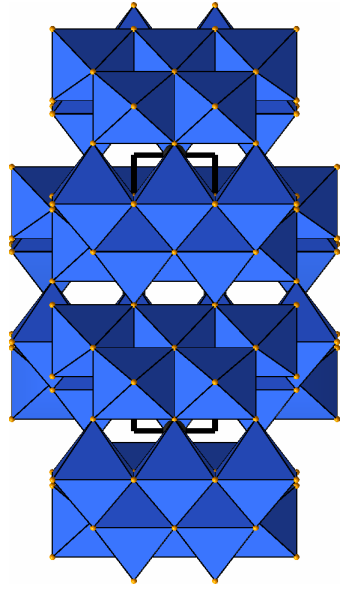
Magnetoplumbite (SrFe<sub>12</sub>O<sub>19</sub>) with five different Fe sites in 3 different kinds of coordination: octahedral, tetrahedral and trigonal bipyramid.

The structure is hexagonal ( $P6_3/mmc$ )

Hollandite ( $I12/m1$ ):  $Ba_2Mn_8O_{16}$



Down the  $c$  axis



From the side (down the  $a$  axis)