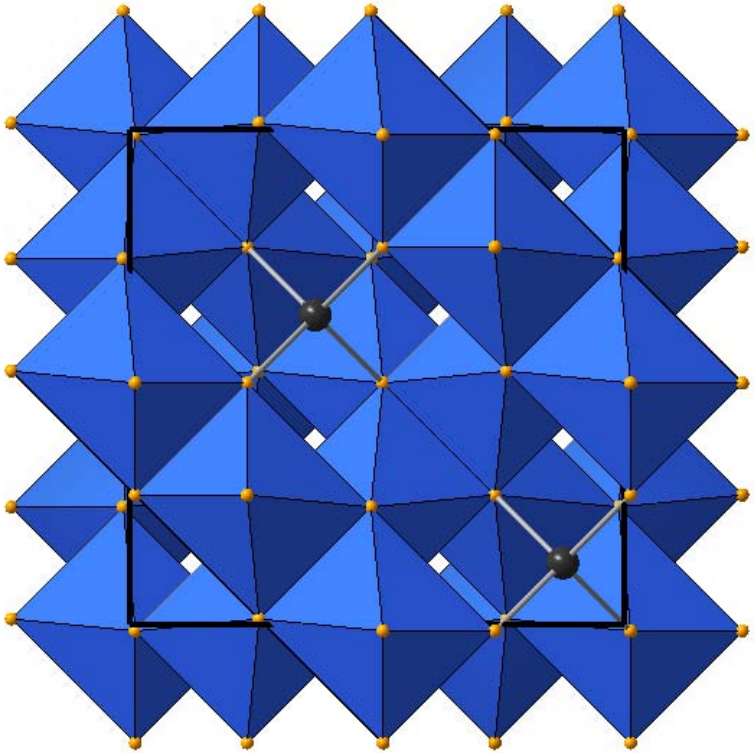
The spinel structure: $MgAl_2O_4$ *Fd-3m* (diamond) a ~ 8.5 Å



A	1/8	1/8	1/8
B	1/2	1/2	½
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, $CdCr_2S_4$, $HgCr_2S_4$, $CuTi_2S_4$, $CdCr_2Se_4$, $CuCr_2Te_4$

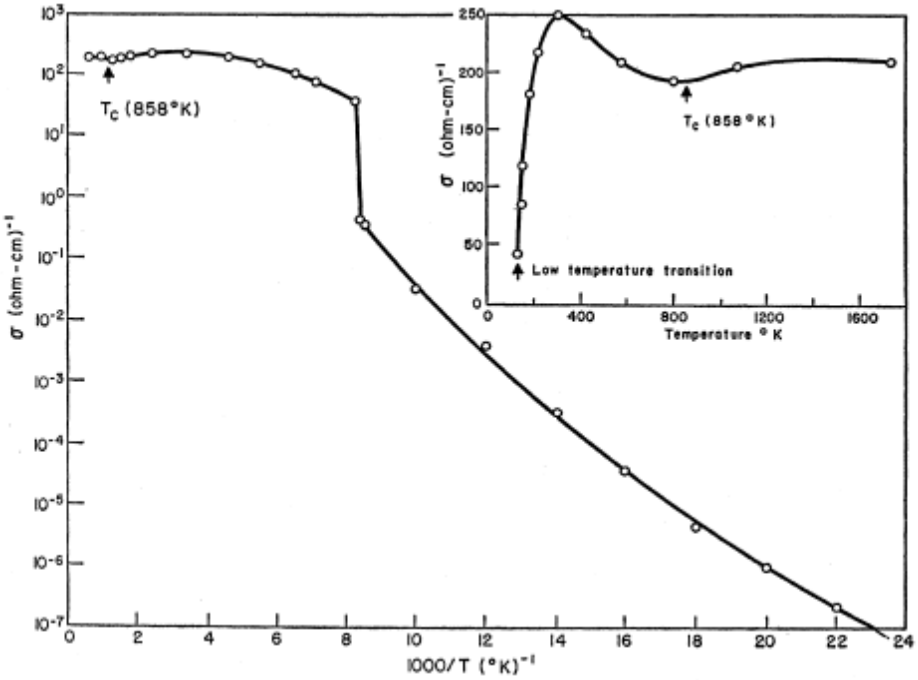
"Inverse: spinels:
$Fe(MgFe)O_4$, $Mn(NiMn)O_4$, $Zn(SnZn)O_4$, $Mg(Ti,Mg)O_4$, $Zn(Ti,Zn)O_4$, $In(Fe,In)S_4$, $Li(Ni,Li)O_4$, $Fe(Fe,Fe)O_4$

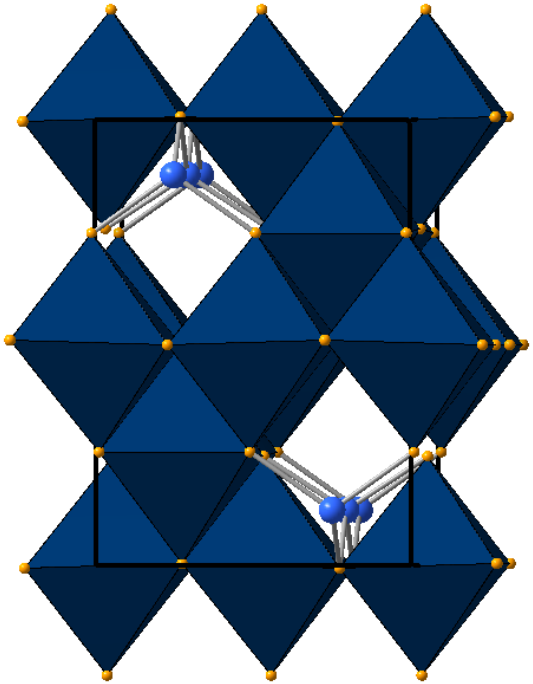
What determines *site-selection*: Whether an ion will prefer to sit in the tetahedral or octahedral site ?

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

Site ordering can make a huge difference in property: $ZnFe_2O_4$ 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 Verwey transition in Fe_3O_4:
E. J. W. Verwey and P. W. Haayman, Physica **8 (1941)** 979.
Also *Wigner Crystallization*.



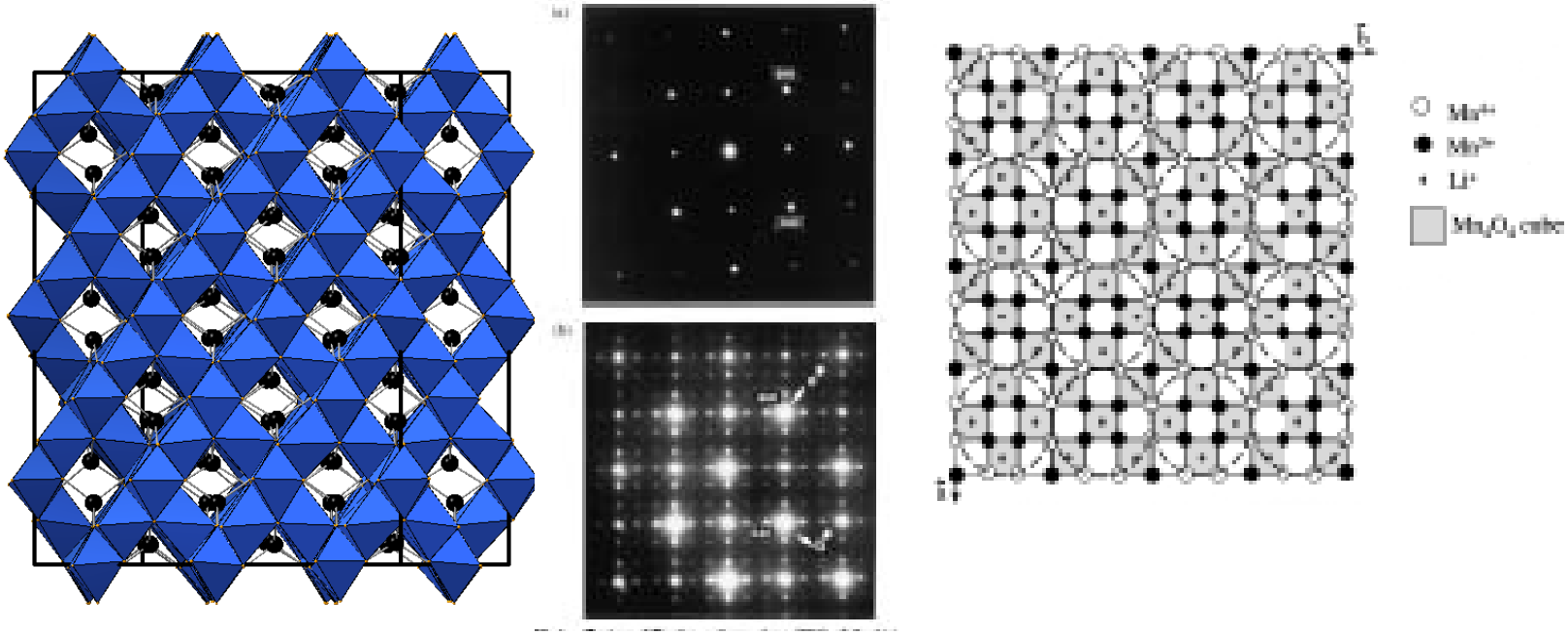


90 K
P12/m1

Charge ordered structure of magnetite Fe3 O4 below the Verwey transition, J. P. Wright, J. P. Attfield and P. G. Radaelli, Phys. Rev. B66 (2002), 214422(1): Fe^{2+} and Fe^{3+} are ordered on the octahedral site.

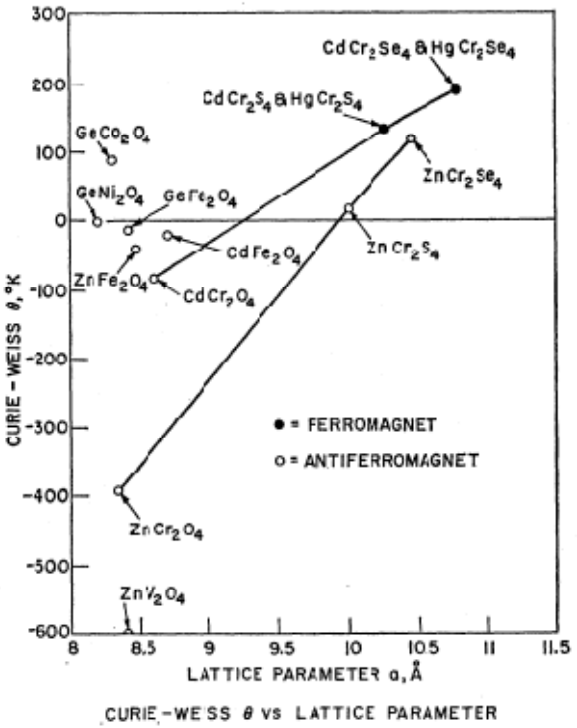
$LiMn_2O_4$: A charge-ordered battery material:

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



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

While most magnetic spinels are *ferrimagnetic*, there exist a select few (mostly Cr-based) ferromagnetic spinels: *Exchange Interactions in Ferromagnetic Chromium Chalcogenide Spinels*, P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, Phys. Rev. 151, 367–377 (1966).



CURIE–WEISS θ vs LATTICE PARAMETER

Table I. Summary of crystallographic and magnetic characteristics.

Composition	Lattice parameter (Å)	U parameter	Magnetic moment (4.2°K) (μ_B/molecule)	Curie temperature T_C(°K)	Curie Weiss θ(°K)	Curie constant C_M	$\frac{\theta}{T_c}$
$Cd[Cr_2]S_4$	10.244	0.390	5.2	97	+135	3.2	1.39
$Cd[Cr_2]Se_4$	10.755	0.390	5.4	142	+190	3.67	1.34
$Hg[Cr_2]S_4$	10.237	0.390	5.3	60	+137	3.62	2.28
$Hg[Cr_2]Se_4$	10.753	0.390	5.4	120	+192	3.34	1.60
$Zn[Cr_2]S_4$	9.988	0.385	···	T_N<20	+18[a]	3.34[a]	···
$Zn[Cr_2]Se_4$	10.443	0.384[b]	···	$T_N \simeq 20$[a]	+115[a]	3.54[a]	···

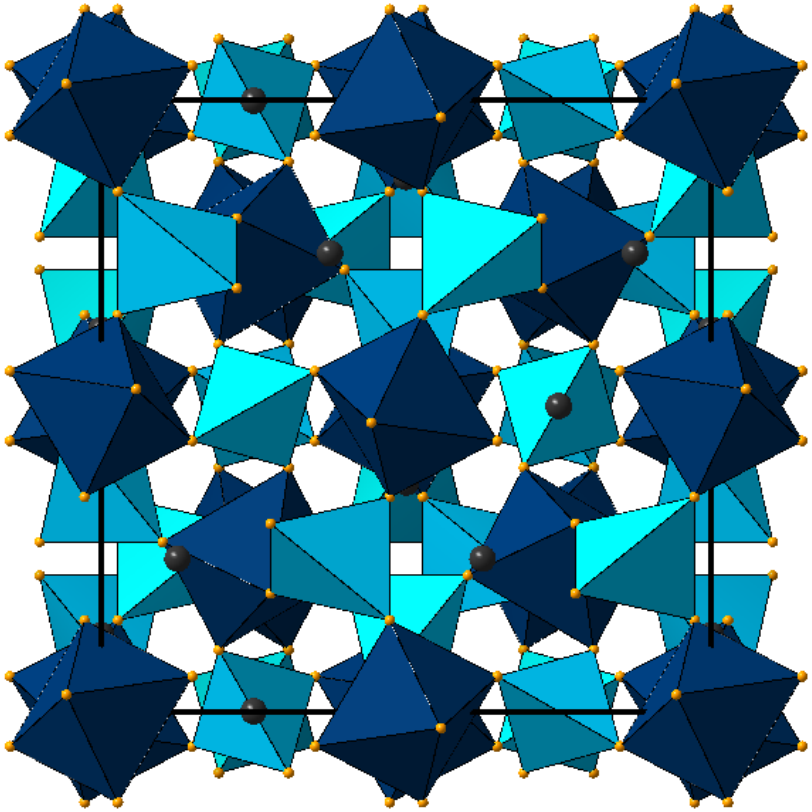
Phys. Rev. Lett. 15, 493–495 (1965)

Ferromagnetic 90° superexchange.

See also: *Colossal magnetoresistance in Cr-based chalcogenide spinels,* A. P. Ramirez, R. J. Cava and J. Krajewski, Nature 386 (1997) 156.

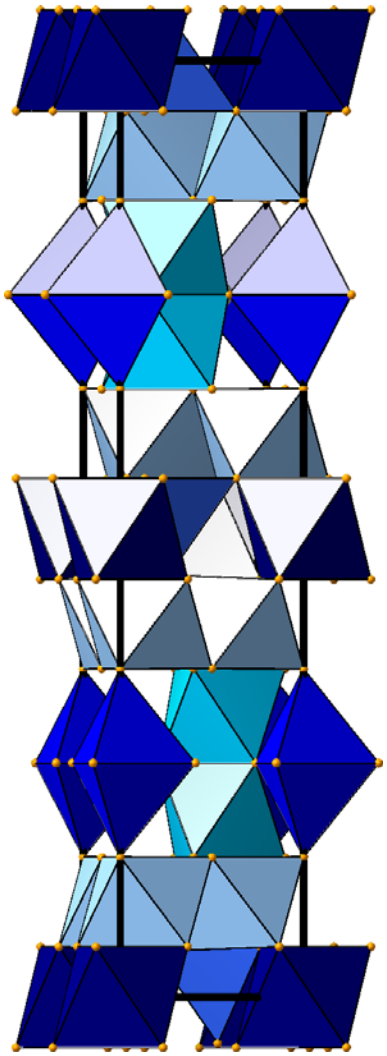
Garnet ferrimagnets: $Y_3Fe_5O_{12}$

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



a = 12.376 Å *Ia-3d*

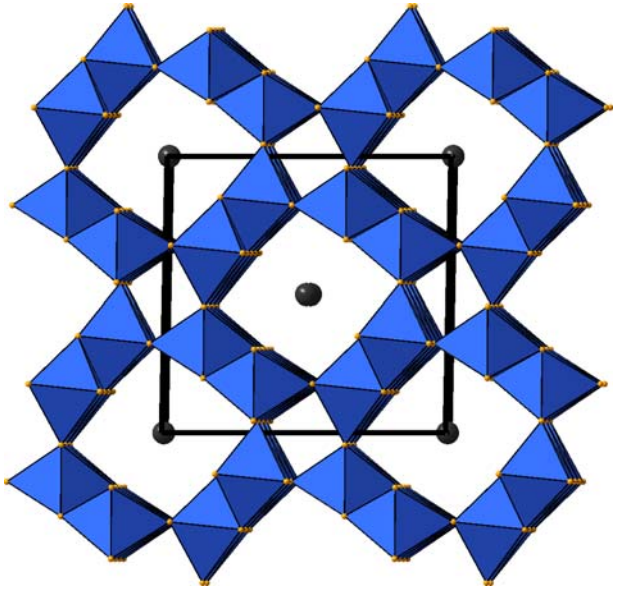
Y	24c	0	0.25	0.125
Fe	16a	0	0	0
Fe	24d	0	0.25	0.375
O	96h	-.0274	0.0572	0.1492



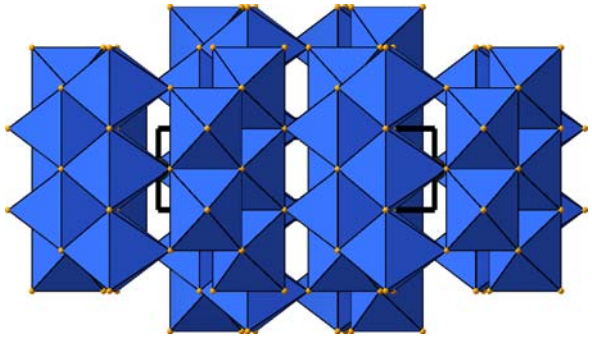
Magnetoplumbite ($SrFe_{12}O_{19}$) with five different Fe sites in 3 different kinds of coordination: octahedral, tetrahedral and and trigonal bipyramid.

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)