Spinel oxides: Magnetocapacitance and multifunctional composites

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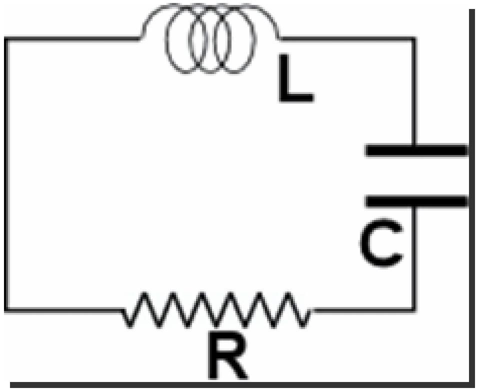
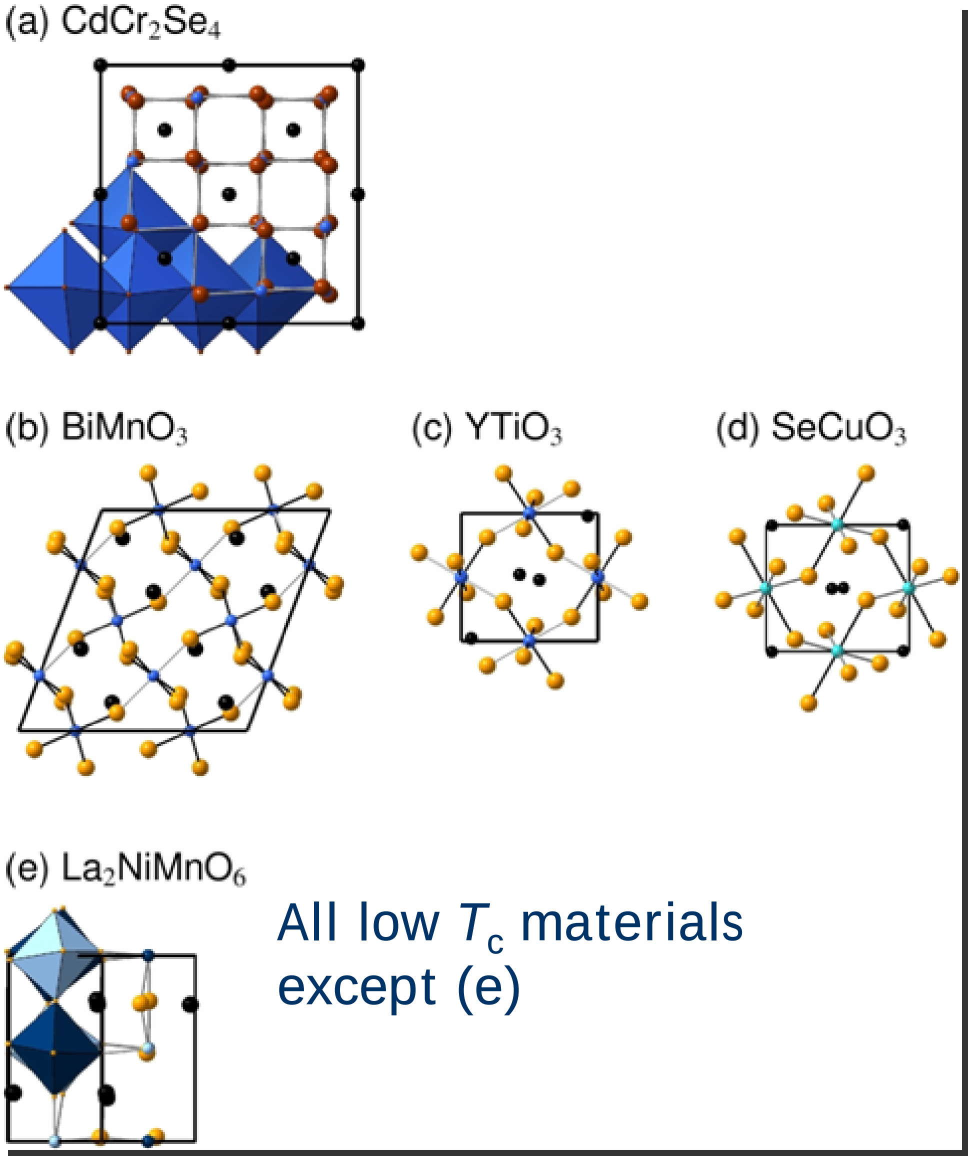
Motterials : Spin, Orbital, and Lattice Physics Near the Mott Transition, KITP, UCSB, 2007/9/10

Outline

- Magnetocapacitance in spinels:
    - The problem of insulating magnets
    - $CoCr_2O_4$
    - Mn_3O_4
- Tuning frustration in A-site magnetic spinels
- Jahn-Teller phenomena in spinels as a source of phase separation

Insulating magnets:





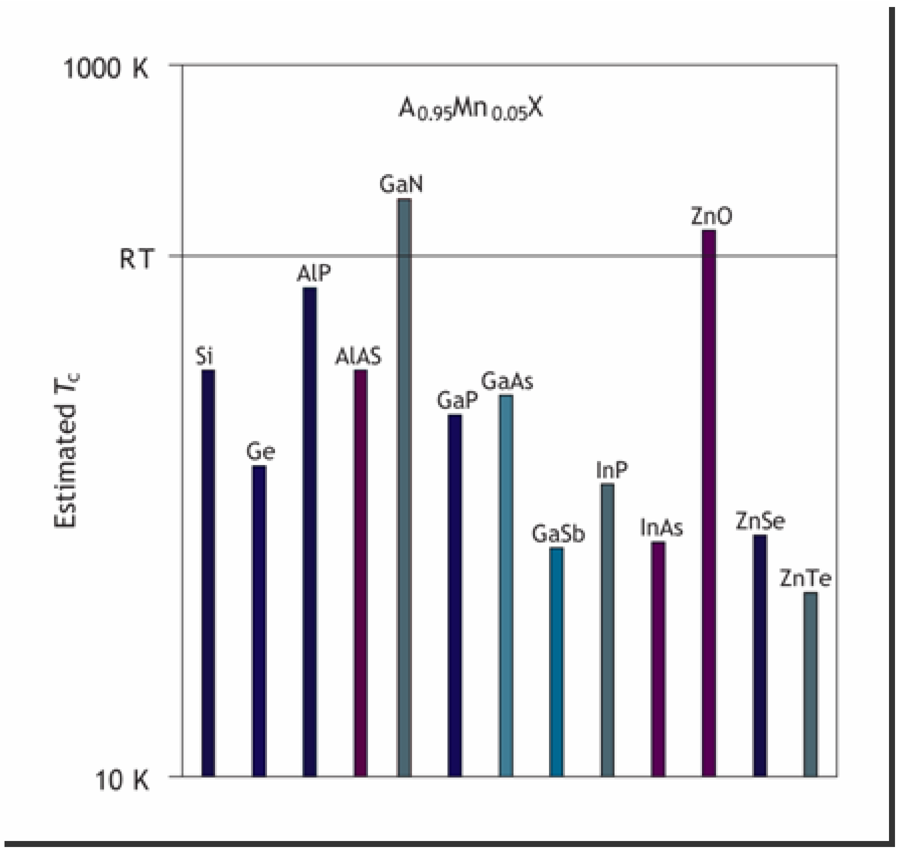
- High *k* and high μ materials
- Materials with magnetic field tunable capacitance
- Multiferroics

All require magnetic insulators !

All low T_c materials except (e)

Magnetism in substituted ZnO

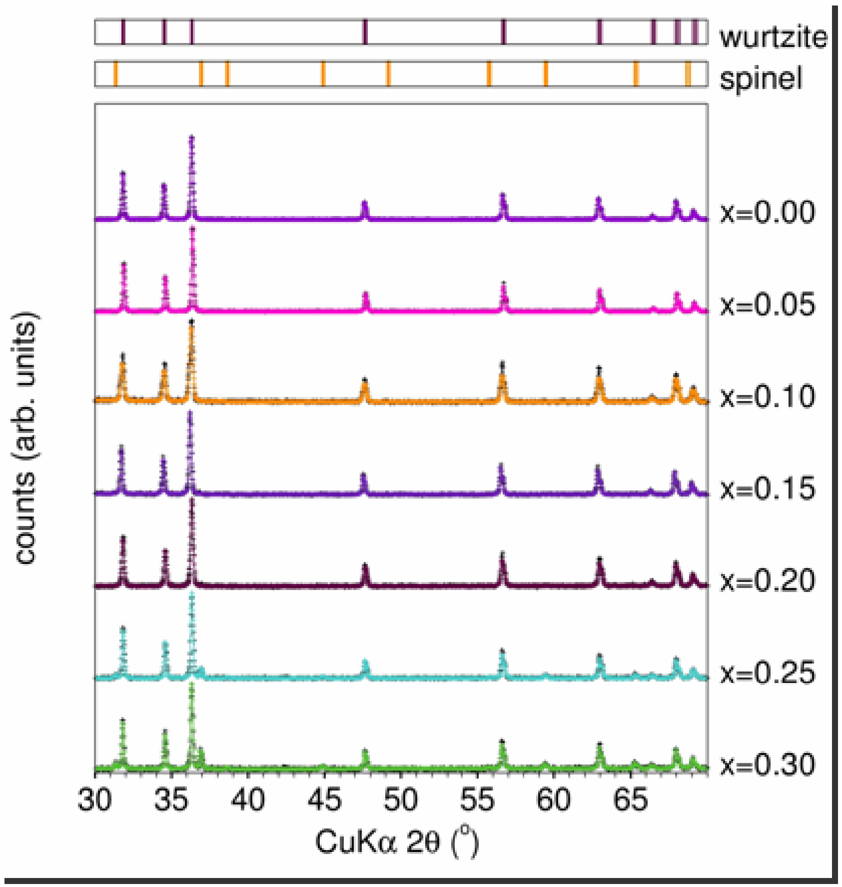
Dietl *et al*.: Hole doped (3.5×10^{20} cm^{-3}) wide band gap semiconductors can be rendered ferromagnetic. [Dietl, Ohno, Matsukura, Cibért and Ferrand, *Science* **287** (2000) 1019]



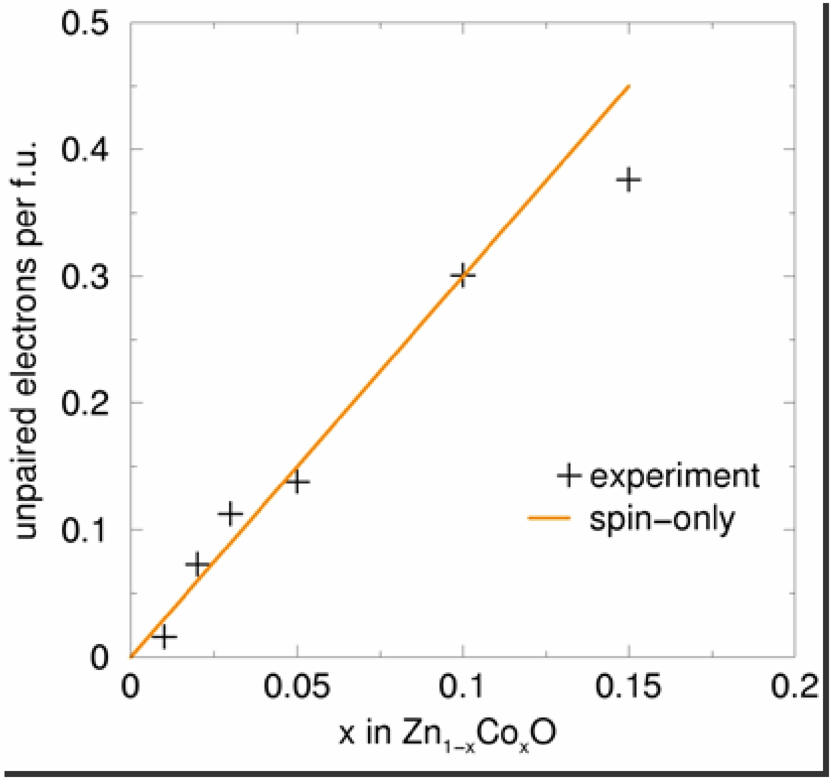
T_c's near room temperature in ZnO:*Mn* and GaN:*Mn*

Magnetism in substituted ZnO

Bulk Co-substituted ZnO made using a precursor route. Clean phases $Zn_{1-x}Co_xO$ till $x = 0.15$ typically

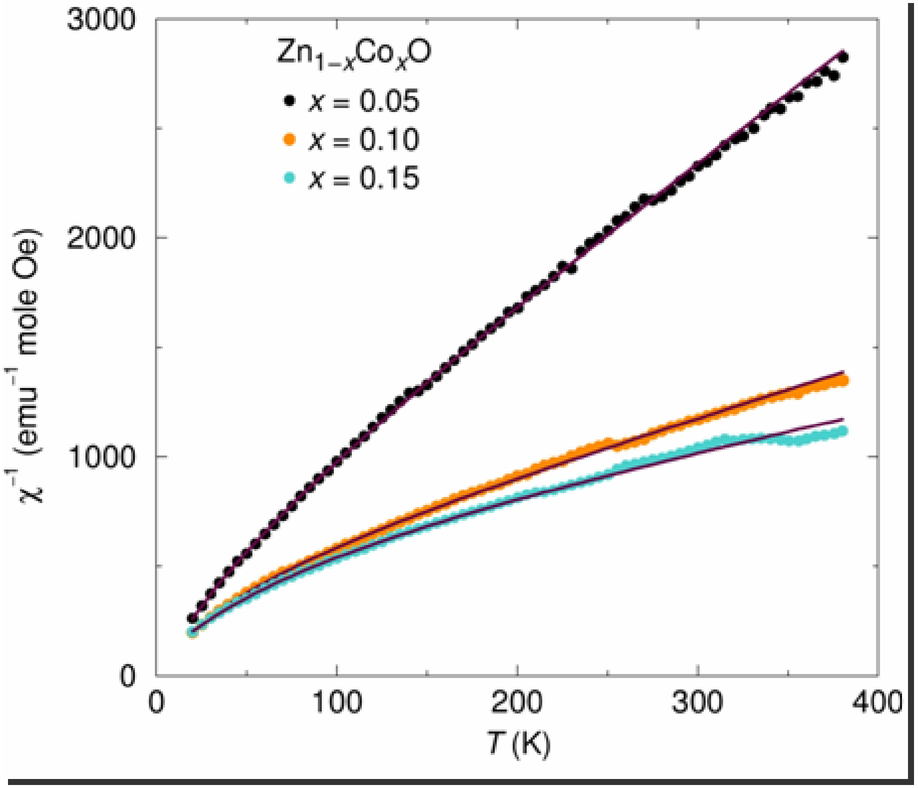


Characterized by X-ray, TEM/EDS, SQUID magnetometry



Magnetism in substituted ZnO

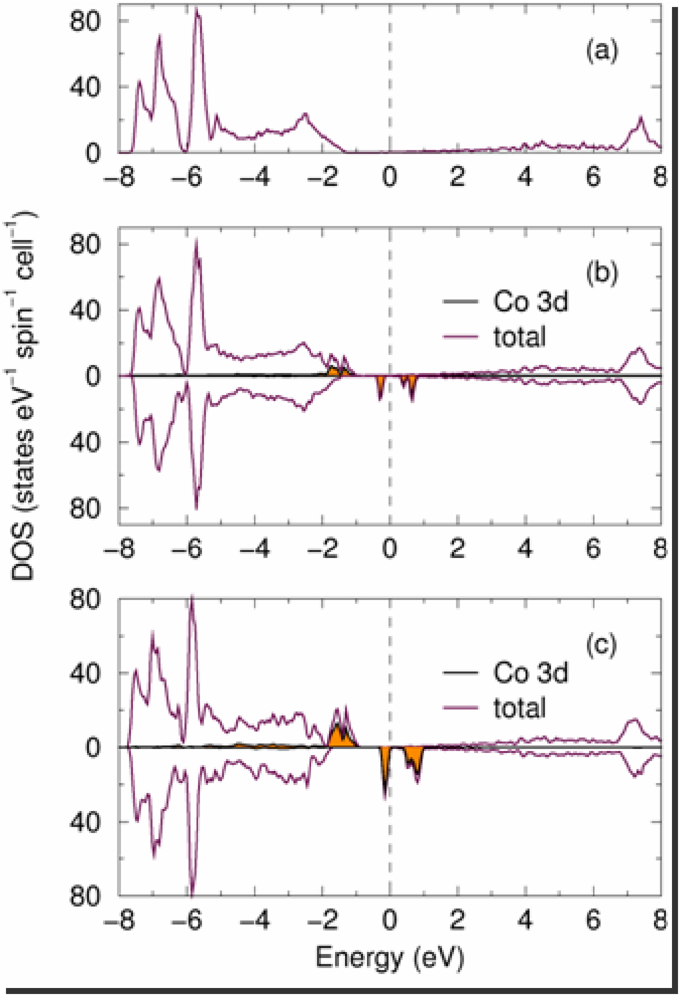
Experiments on clean bulk samples do not suggest ferromagnetism



Instead, $\chi = C_1/T + C_2/(T\text{-}\Theta)$ describes the magnetic susceptibility between 20 K and 400 K.

Magnetism in substituted ZnO

DFT (SIESTA: PP + LO) calculations by Nicola Spaldin on model substituted ZnO supercells also discourage the search for ferromagnetism



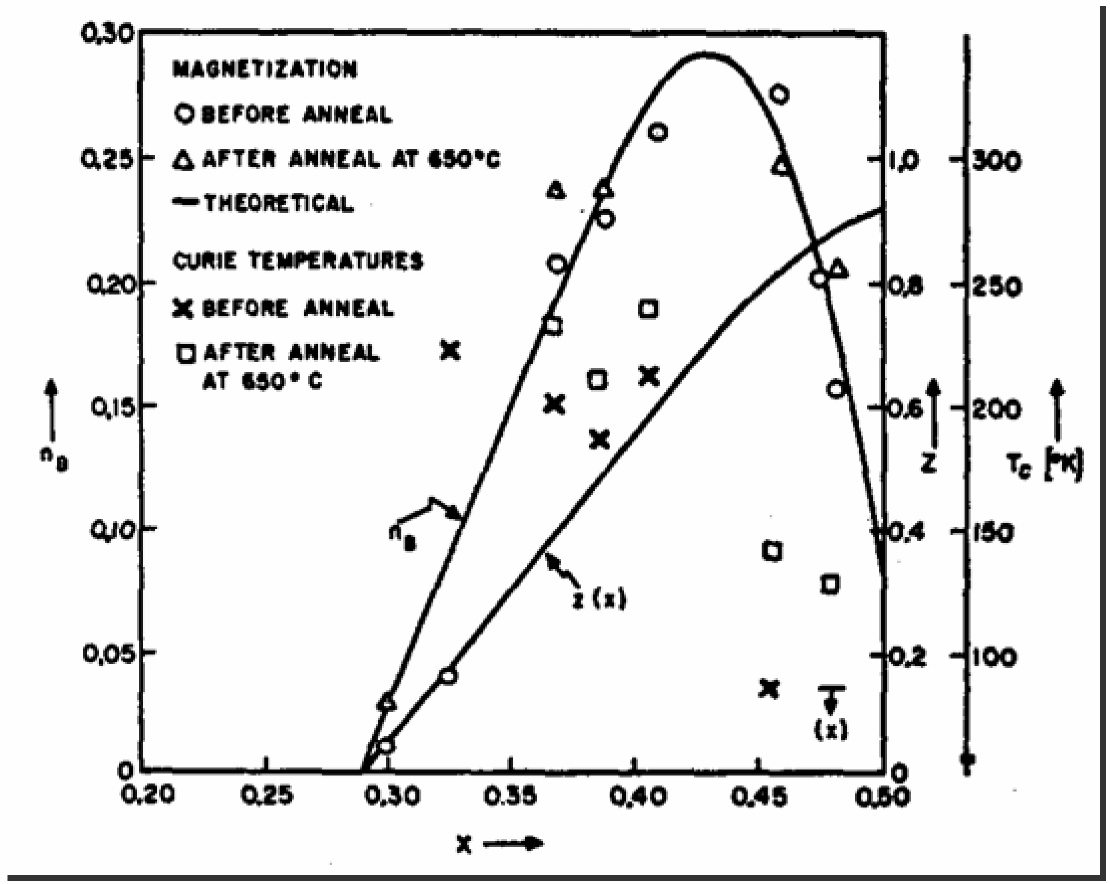
	FM	AFM
$Zn_{14}Co_2O_{16}$		
"near"	-1	0
"separated"	-4	0
$Zn_{13}\square Co_2O_{16}$		
"near"	-60	0
"separated"	-60	0
$Zn_{14}Co_2O_{15}\square$		
"near"	0	-1
"separated"	0	-4

{ FM only with high hole doping.

Risbud, Spaldin, Chen, Stemmer, Seshadri, *Phys. Rev. B.* **68** (2003) 205202; Spaldin, *Phys. Rev. B.* **69** (2004) 125201; Lawes, Risbud, Ramirez, Seshadri, *Phys. Rev. B* **71** (2005) 045201.

Are there any diluted magnetic oxide semiconductors ?

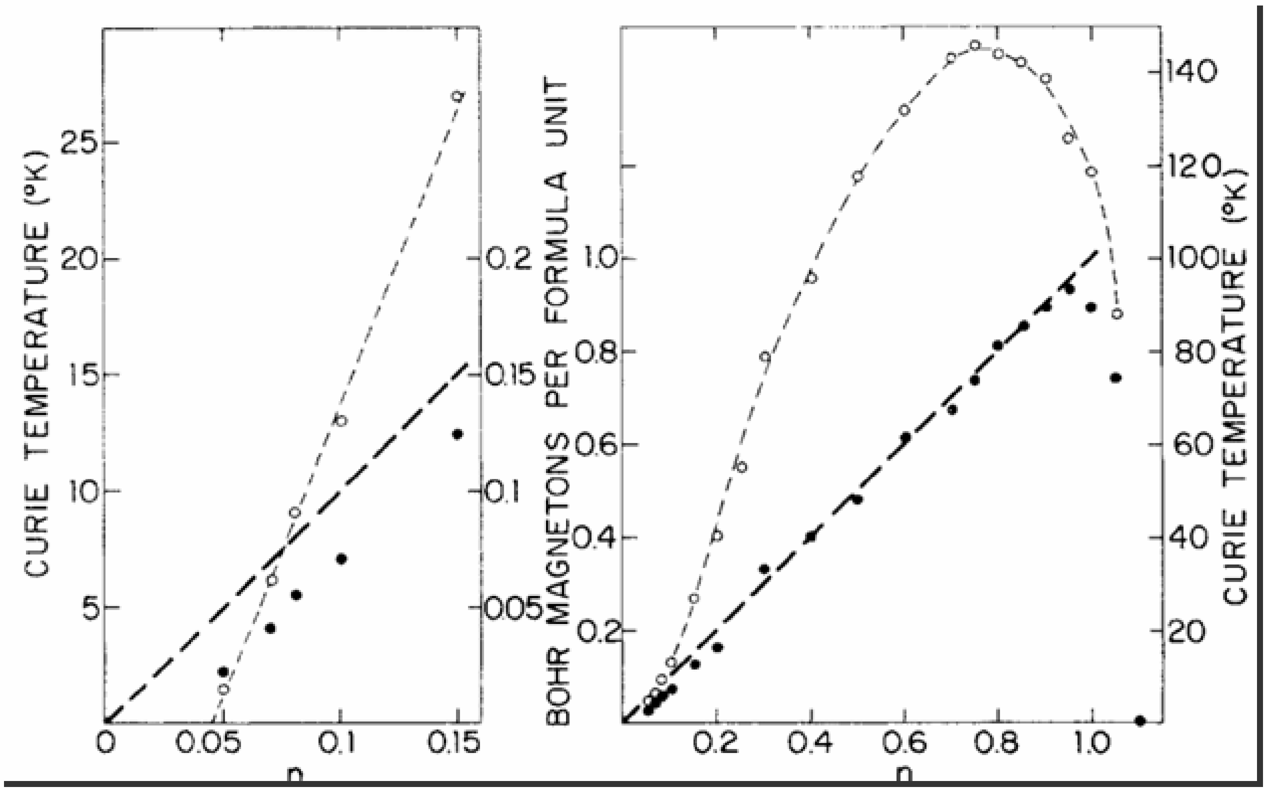
(La,Ca)MnO$_3$, and (Li,Ni)O are examples of oxide systames that start with an AFM parent compound and are hole-doped to achieve ferromagnetism; *percolative*, no dilute



Goodenough, Wickham and Croft, *J. Appl. Phys.* **29** (1958) 382.

Sulphides ?

$Fe_{1-x}Co_xS_2$ is an intinerant electron ferromagnet, and is conducting and magnetic for nearly $0.05 \leq x \leq 1$. For almost all x, M_{sat} (μ_B)/Co = 1 [Jarrett *et al. Phys. Rev. Lett.* **21** (1968) 617]



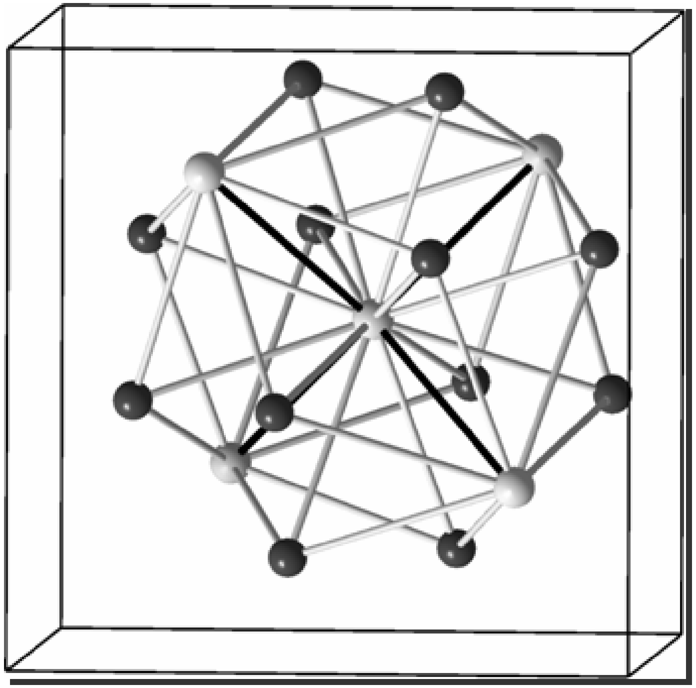
n-type DMS ?
Why isn’t it correlated ?

Diluted *ferri*Magnetism ?

Good oxide ferromagnets are also metals [CrO_2, (La/Sr)MnO_3, Sr_2FeMoO_6]

In the (insulating) oxide world antiferromagnetic interactions rule.

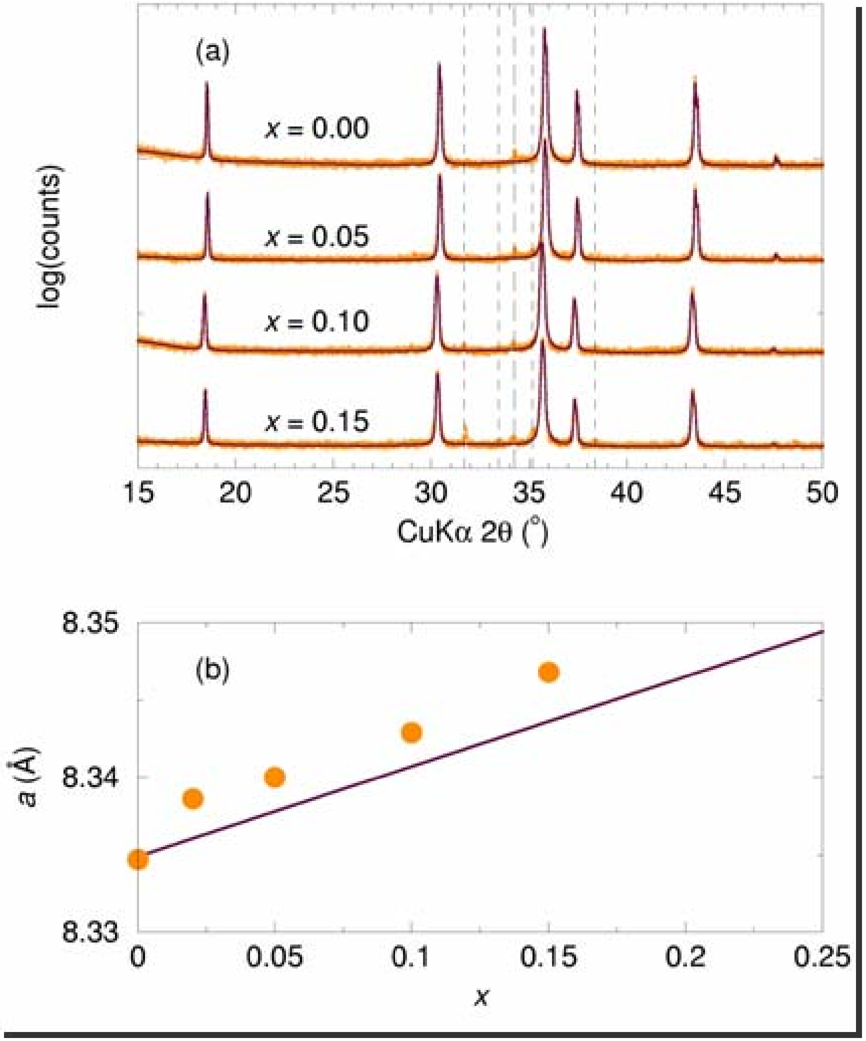
Can we put this to good use ? Use the spinel lattice as host. Hope for ferrimagnets.



cation connectivity in spinel

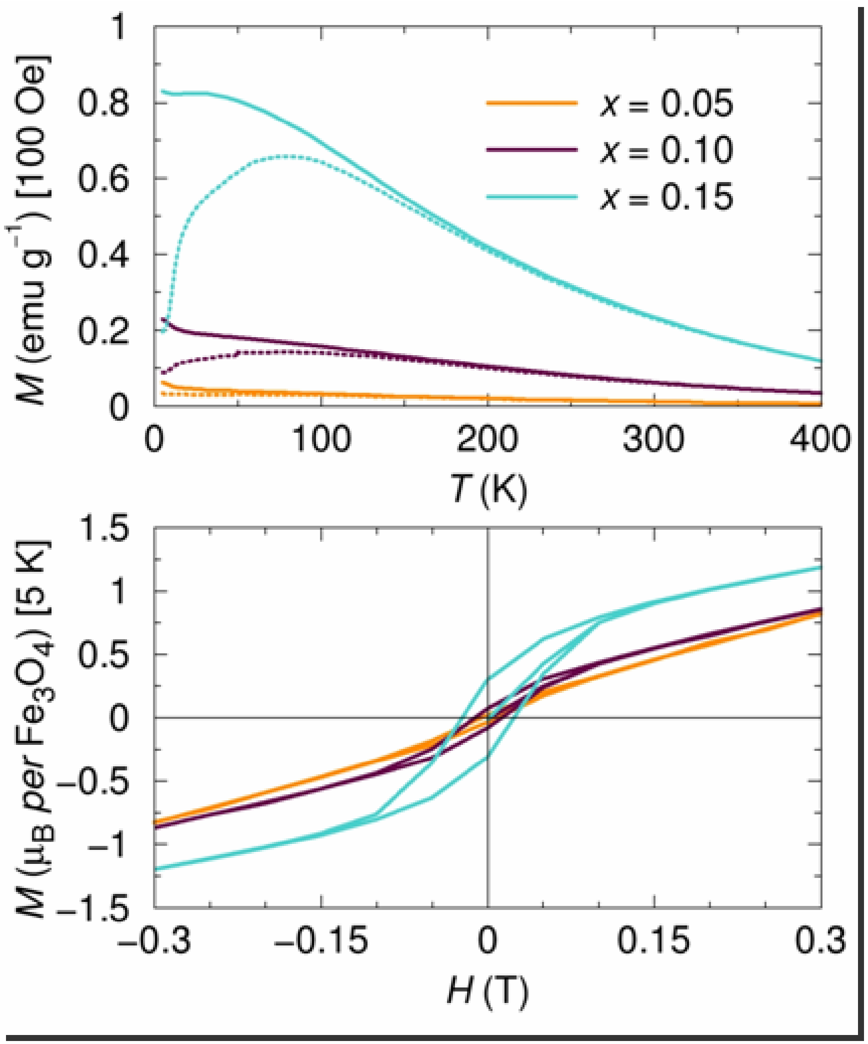
Diluted *ferri*Magnetism ?

"$[ZnGa_2O_4]_{1-x}[Fe_3O_4]_x$"



X-ray diffration indicates a solid solution, with some Ga_2O_3 impurity.

Diluted *ferri*Magnetism ?

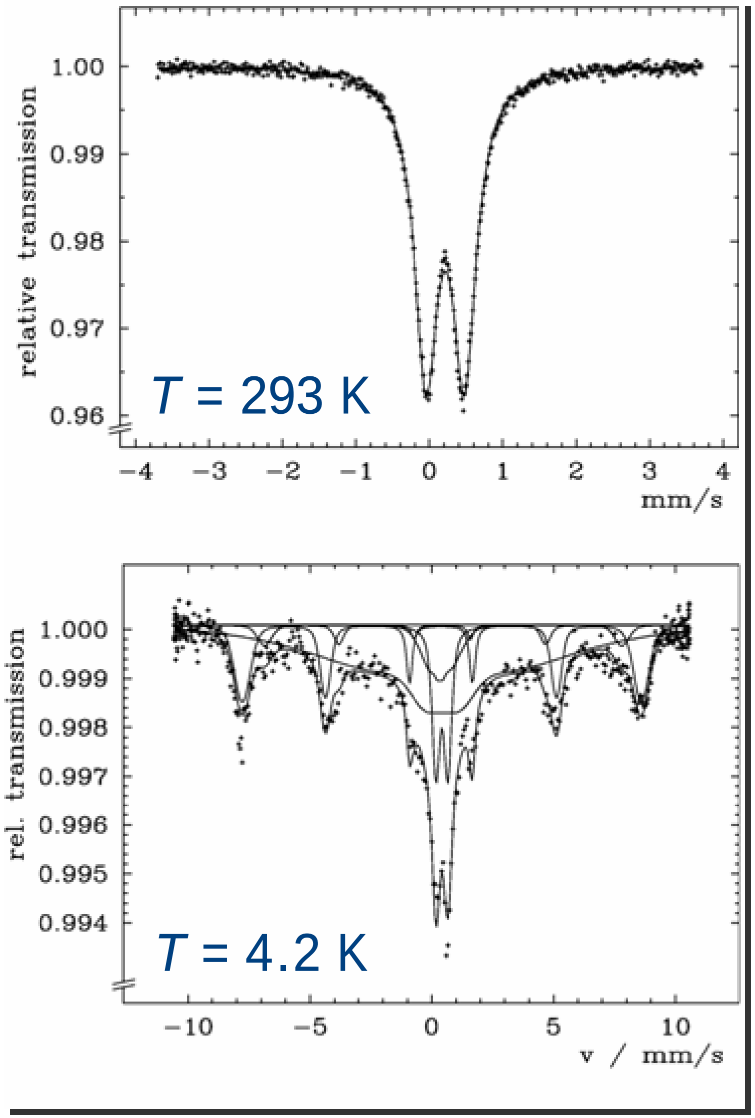


The $x = 0.15$ sample shows the onset of magnetic ordering at nearly 200 K. At 5 K, there is clear hysteresis, with approximately 25% of the Fe spins saturated.

“$[ZnGa_2O_4]_{1-x}[CoFe_2O_4]_x$” shows similar behavior.

“$[ZnGa_2O_4]_{1-x}[Cr_2O_3]_x$” does not.

Diluted *ferri*Magnetism ?

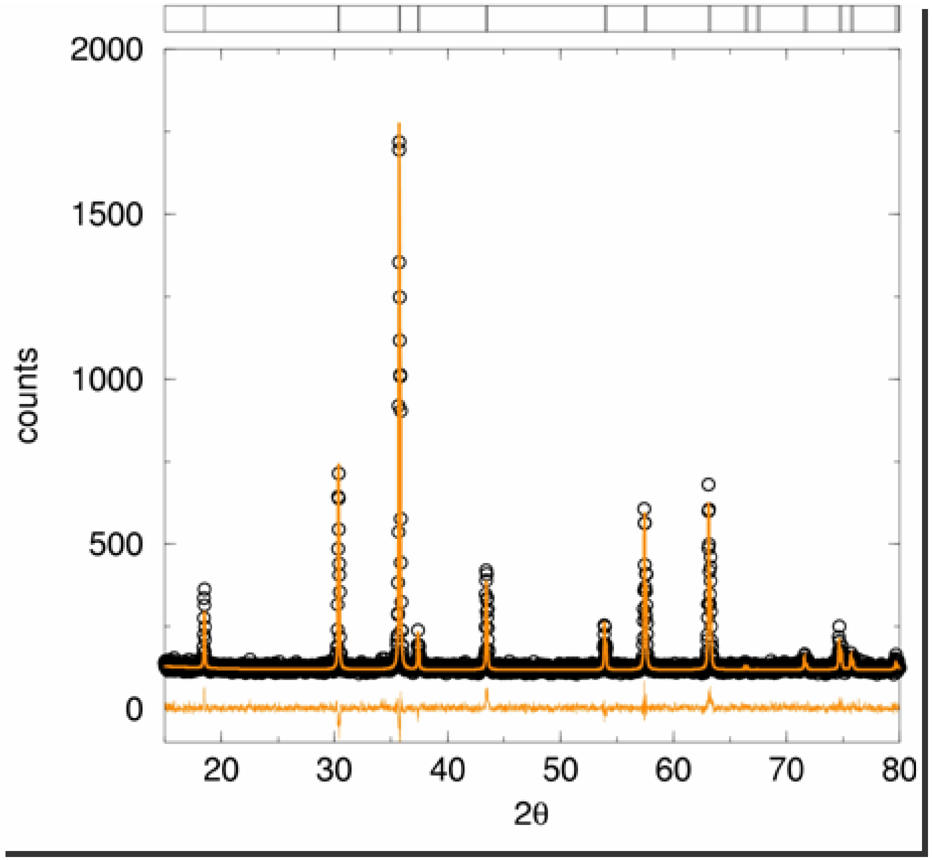


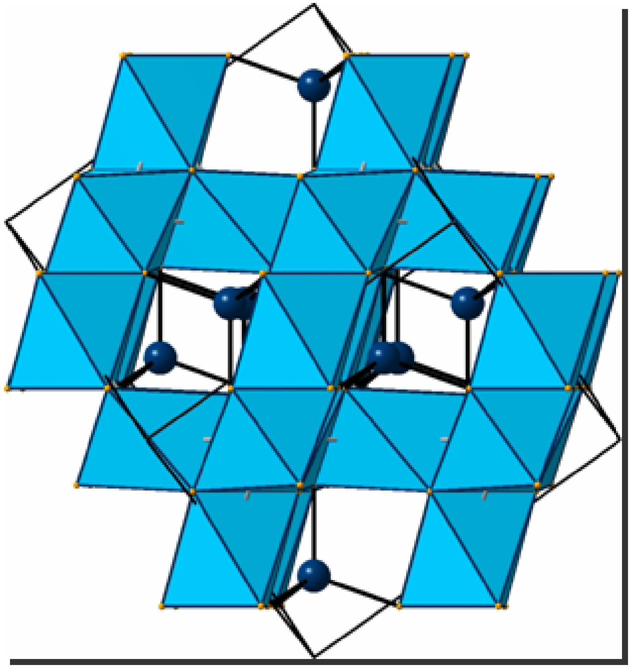
Mössbauer, $x = 0.15$: Significant fraction of the sample is magnetic at 4.2 K. The sample has only Fe^{3+}

Risbud, Seshadri, Ensling, and Felser, *J. Phys. Condens. Matter* **17** (2005) 1003-1010.

Ferrimagnets: $CoCr_2O_4$

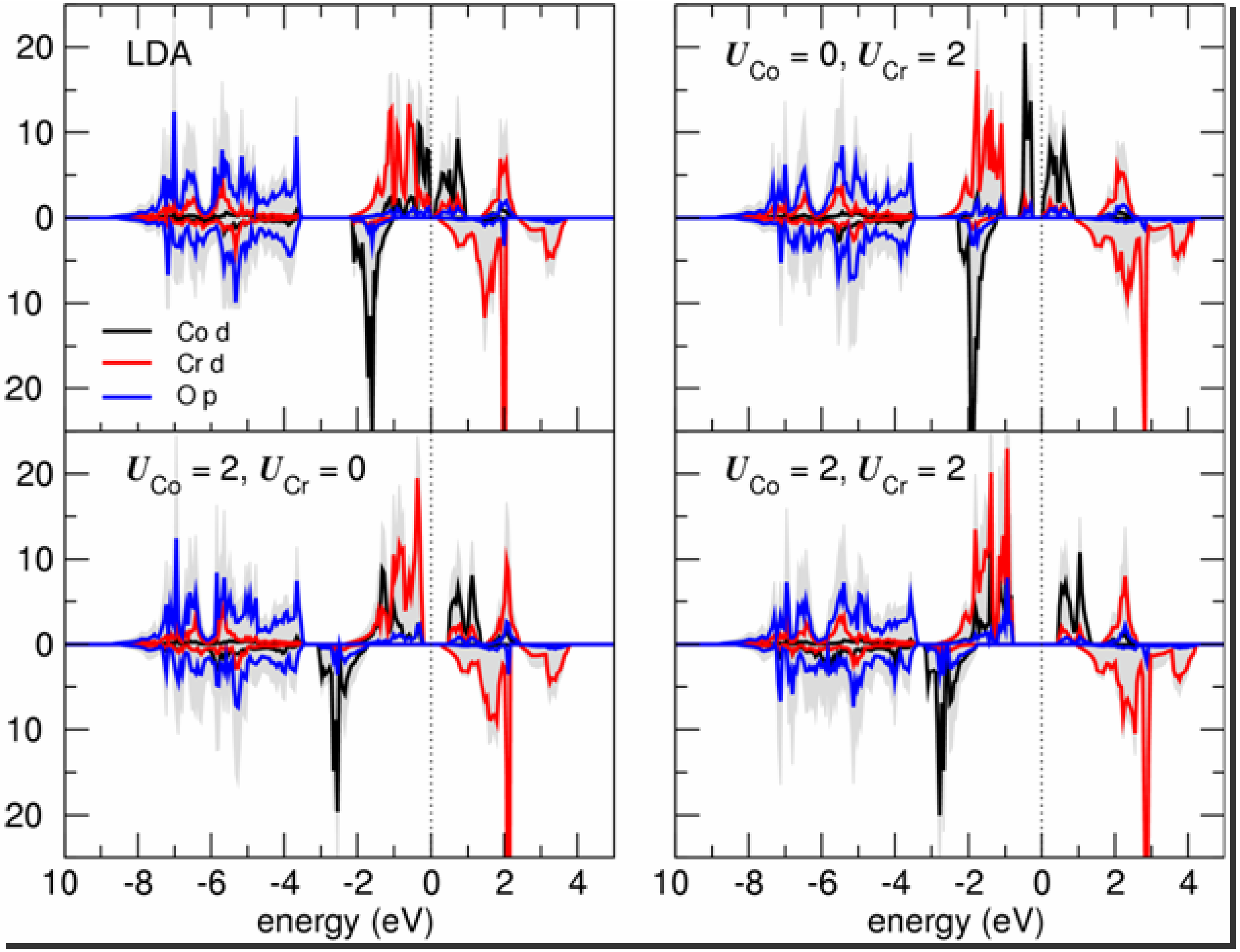
Tetrahedral Co^{2+} (d^7) and octahedral Cr^{3+} (d^3): Stable (closed magnetic shell) configurations: *Ferri*magnetic semiconductors ?





Ferrimagnets: $CoCr_2O_4$

LDA + *U*: Full moment collinear ferrimagnet/semiconductor

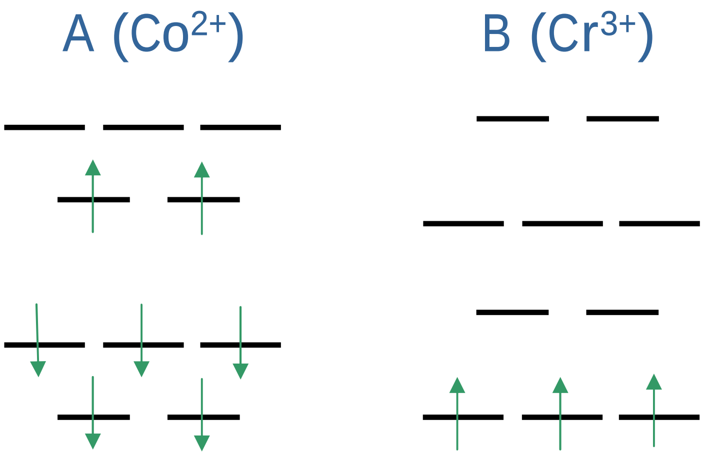


VASP calculations by Claude Ederer

Pellets are green.

Ferrimagnets: $CoCr_2O_4$

LDA + U: Full moment collinear ferrimagnet/semiconductor



Kaplan, *Phys. Rev. B.* **119** (1960) 1460:

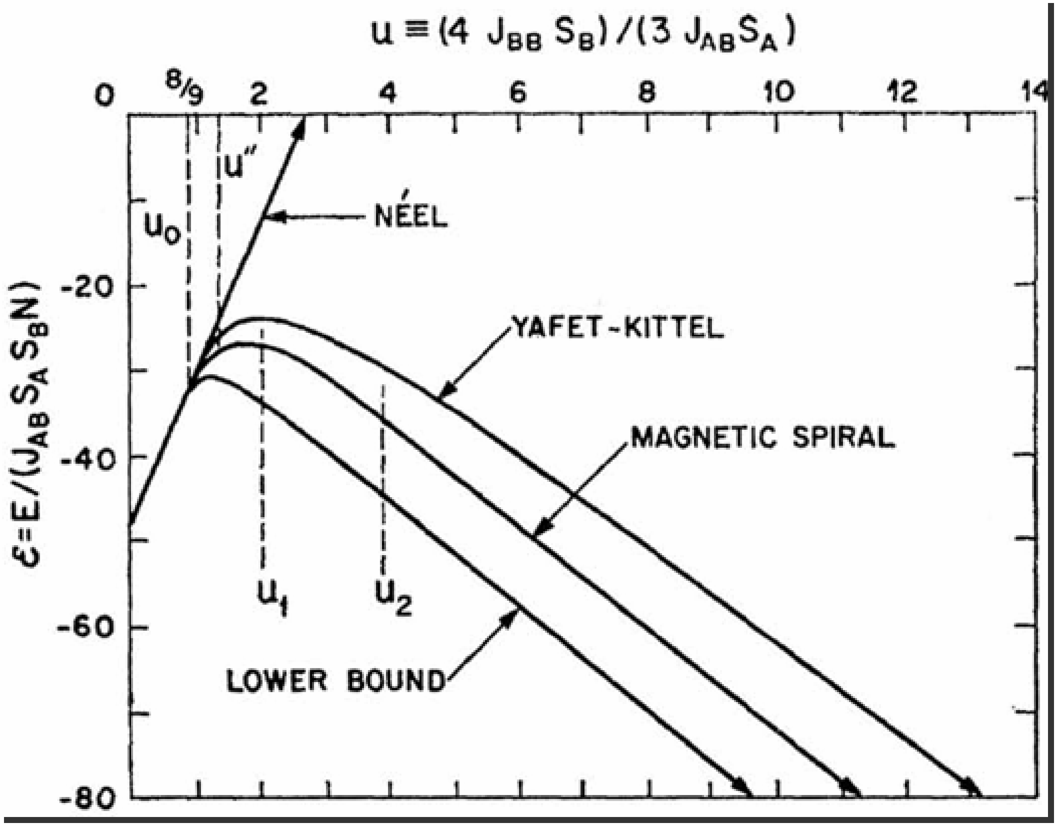
$$u = \frac{4J_{BB}S_B}{3J_{AB}S_A}$$

$$u < \frac{8}{9}$$ Implies a collinear (Néel) ground state

$$U_{\mathrm{Co}} = 4\,\mathrm{eV};\ U_{\mathrm{Cr}} = 2\,\mathrm{eV};\ u = 0.65$$

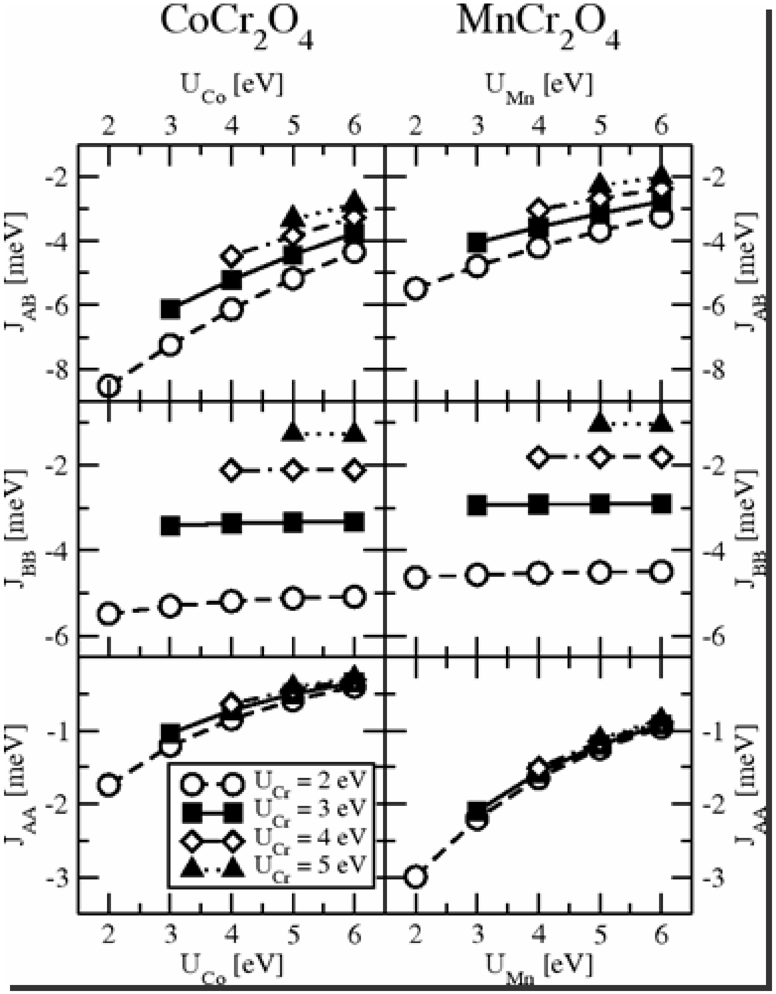
VASP calculations by Claude Ederer

Ferrimagnets: $CoCr_2O_4$



The LKDM spin-ordering diagram, from Kaplan and Menyuk, *Philos. Mag.* (2007) 1-75.

Ferrimagnets: $CoCr_2O_4$

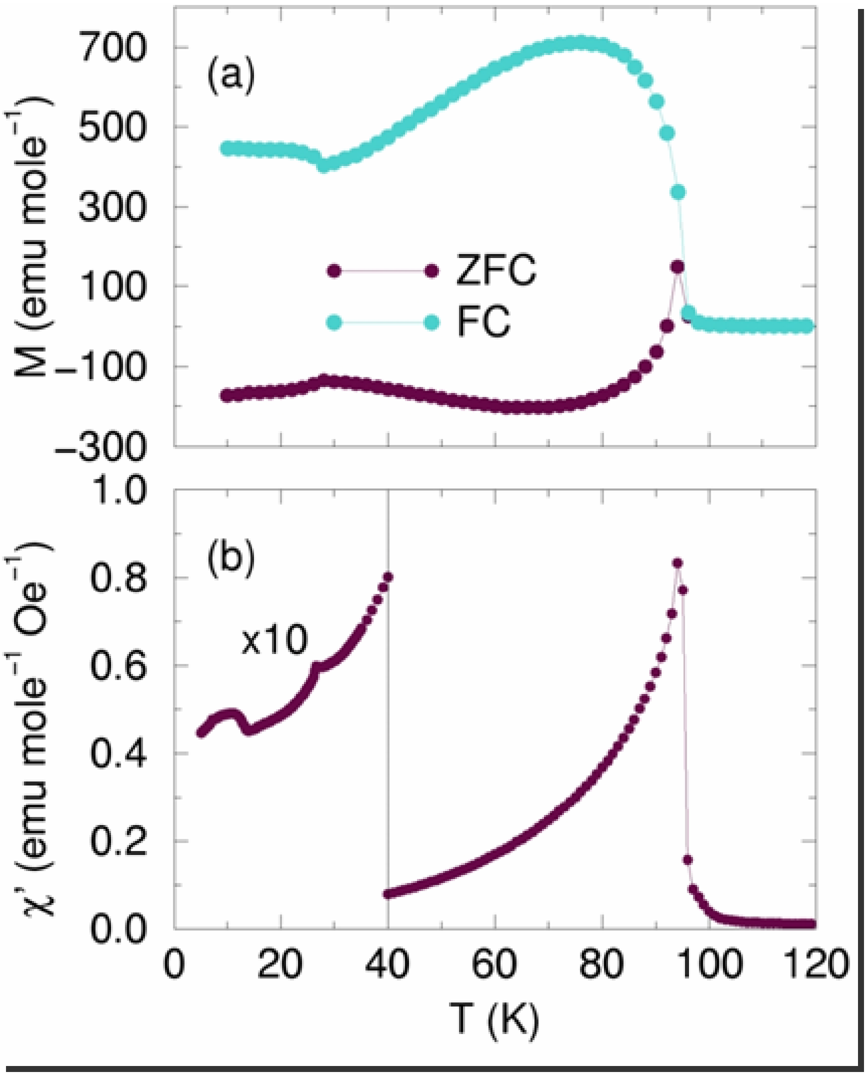


The different *J*s are hard to determine from *ab-initio* calculations.

J_{AA} is strong and can't be neglected (as is done by LKDM).

Ederer and Komelj, *Phys. Rev. B* **76** (2007) 064409(1-9).

Ferrimagnets: $CoCr_2O_4$



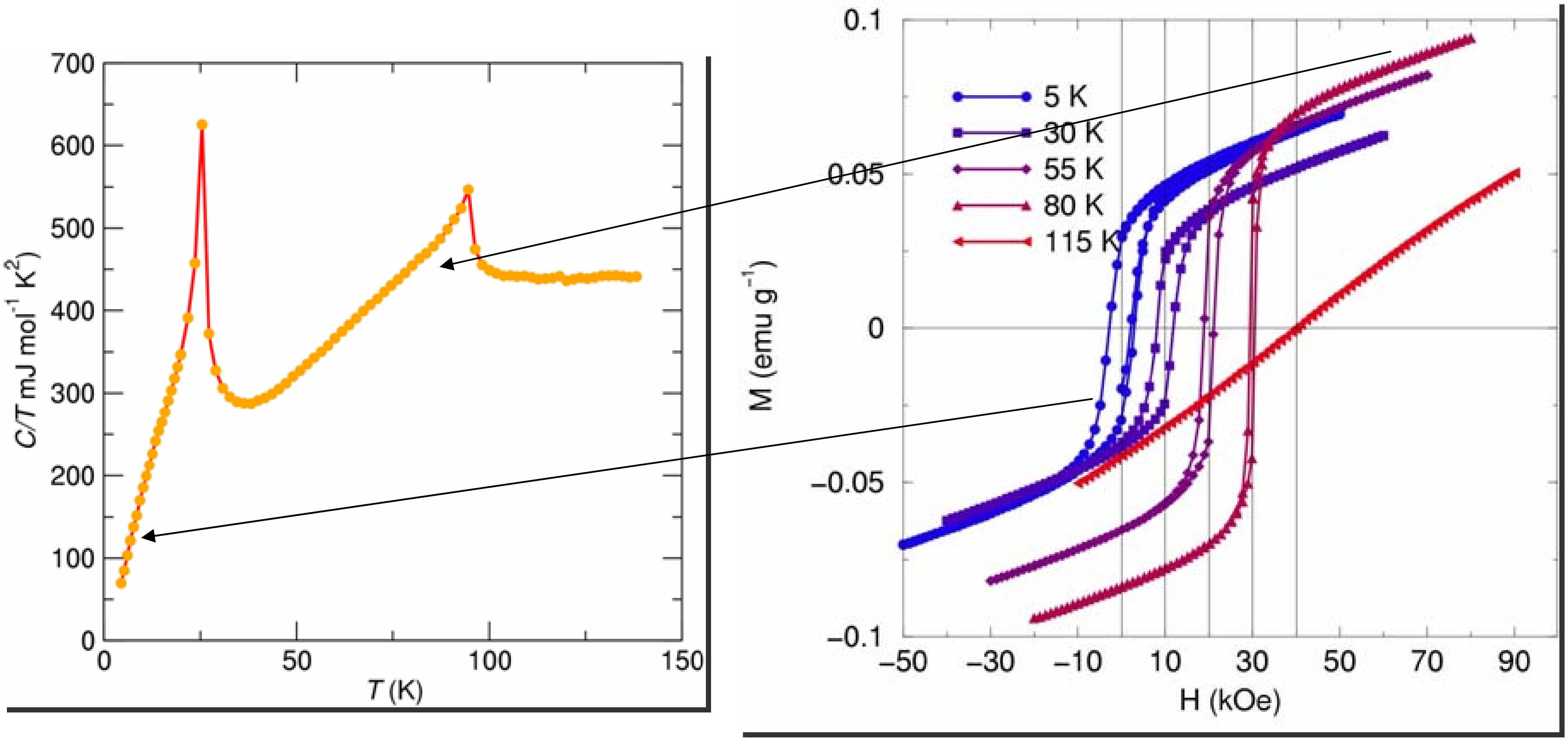
AC and DC magnetization measurements suggest that the Néel transition near 94 K is followed by further transitions near 27 K and lower:

Menyuk, Dwight, Wold, *J. Phys. (Paris)* **25** (1964) 528.

Tomiyasu, Fukunaga, Suzuki, *Phys. Rev. B.* **70** (2004) 214434.

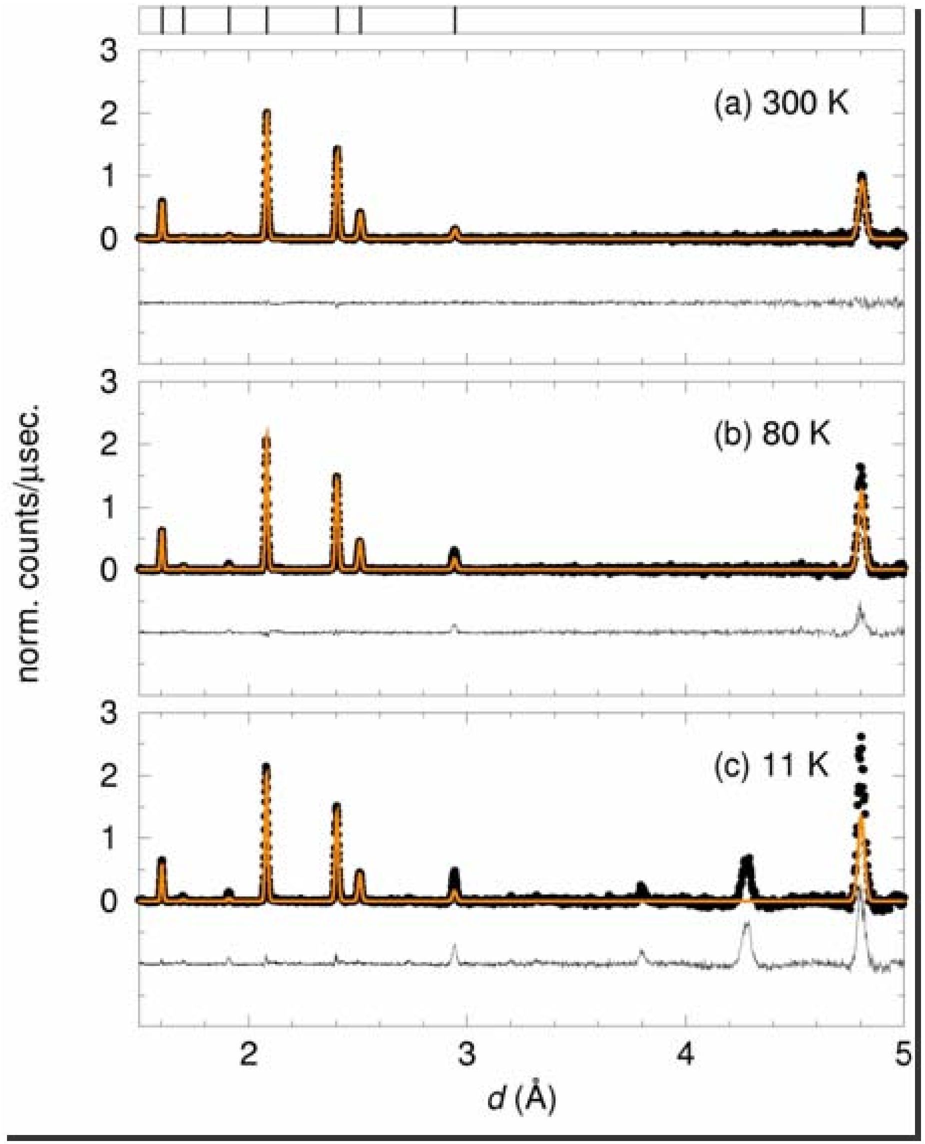
Ferrimagnets: $CoCr_2O_4$

Experiment: Spin canting/non-collinear



Specific heat changes much smaller than expected.

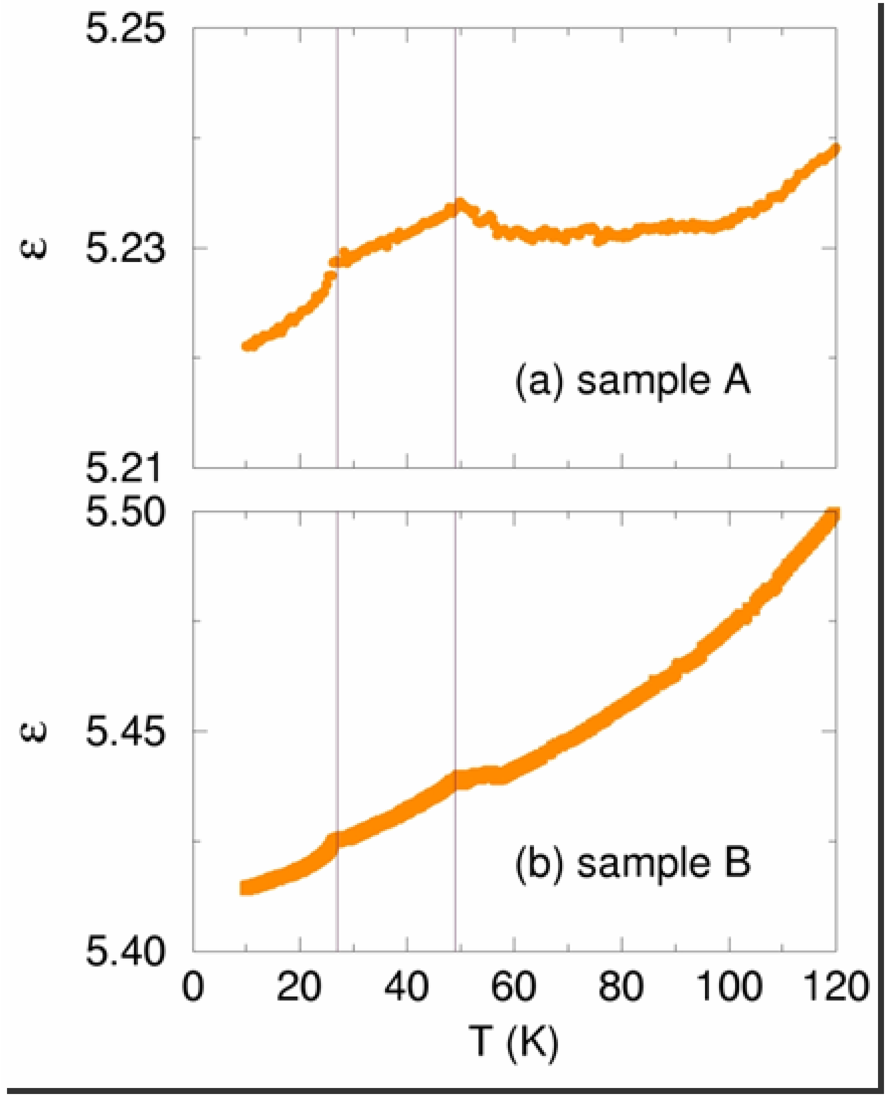
Ferrimagnets: $CoCr_2O_4$



Time-of-flight neutron studies on powders (NPDF, Los Alamos) suggest no change in structure, but do support the idea of complex magnetic ordering at low temperatures.

Fits to nuclear structure shown.

Ferrimagnets: $CoCr_2O_4$



Sharp changes in the capacitance at temperatures well below Néel ordering: Near 49 K and at the second magnetic transition at 27 K. Data were acquired at 30 kHz. Changes associated with noncollinear spins ? [Katsura, Nagaosa, and Balatsky, *Phys. Rev. Lett*. **95** (2005) 057205.]

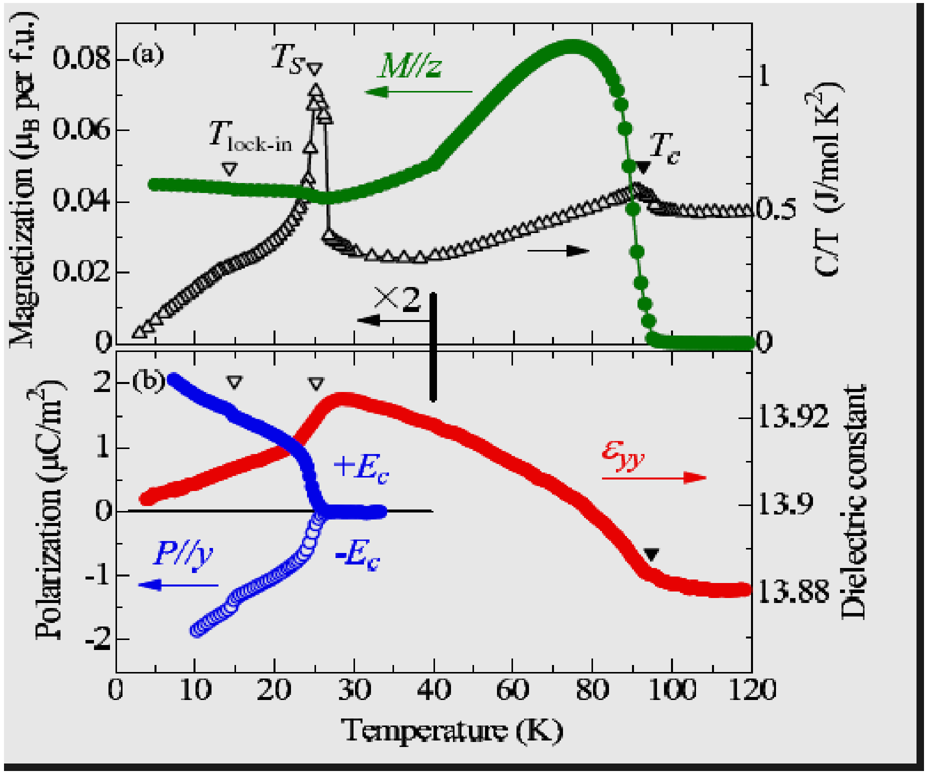
Lawes, Melot, Page, Ederer, Proffen, Hayward, Seshadri, *Phys. Rev. B* **74** (2006) 024413(1-6).

Ferrimagnets: $CoCr_2O_4$

Addendum:

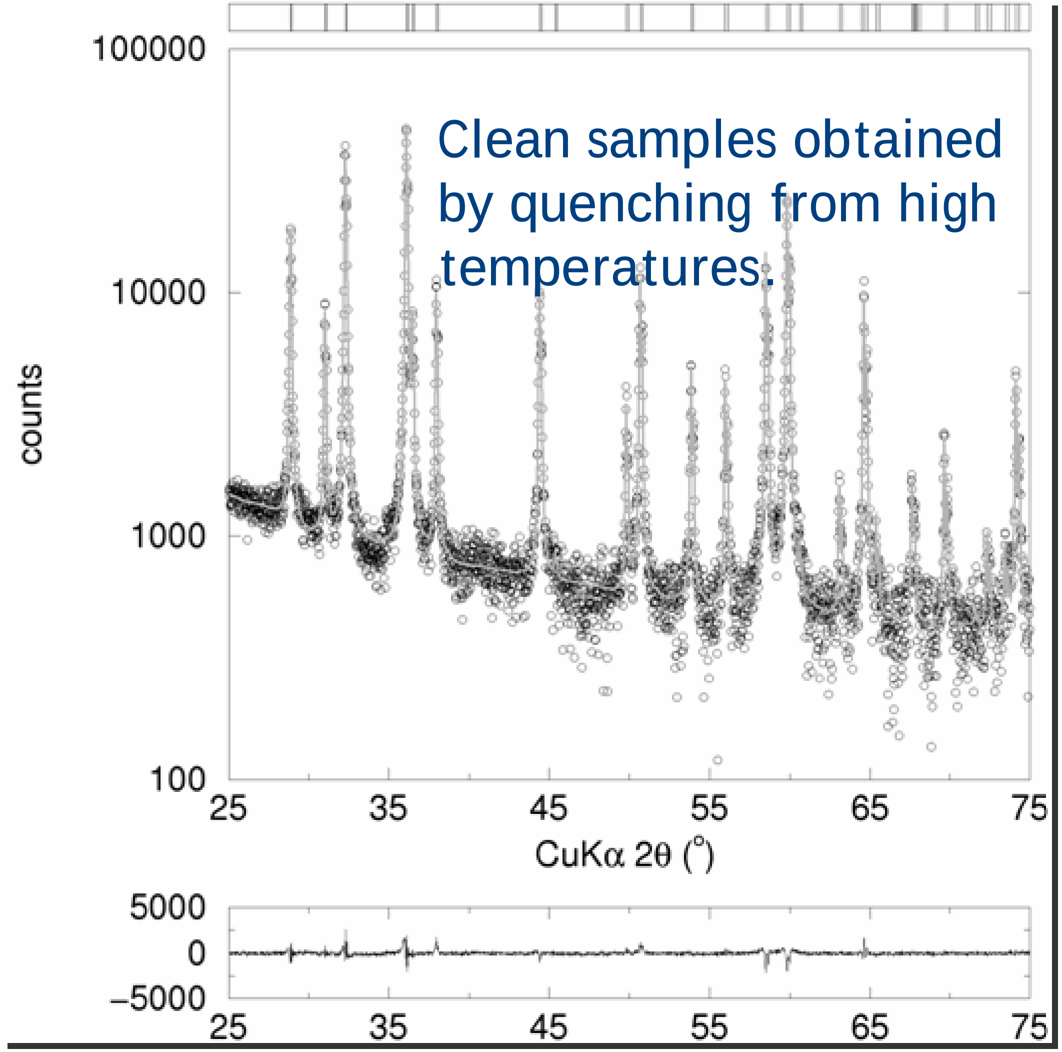
Yamasaki, Miyasaka, Kaneko, He, Arima, and Tokura, *Phys. Rev. Lett.* **96** (2006) 207204.

“Ferroelectric transition has been detected in a ferrimagnetic spinel oxide of $CoCr_2O_4$ upon the transition to the conical spin order below 25 K.”

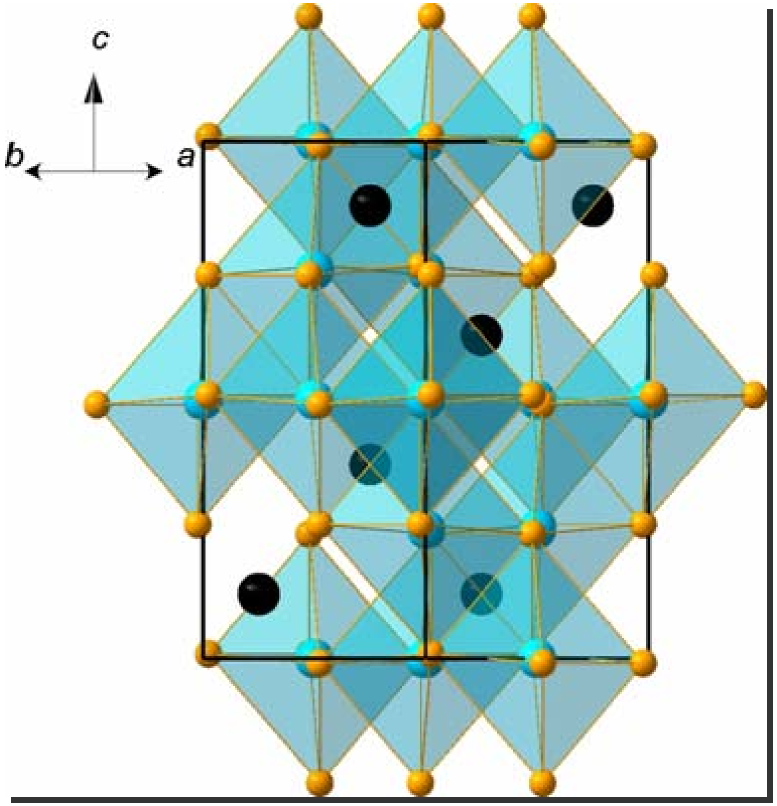


Ferrimagnets: Mn_3O_4

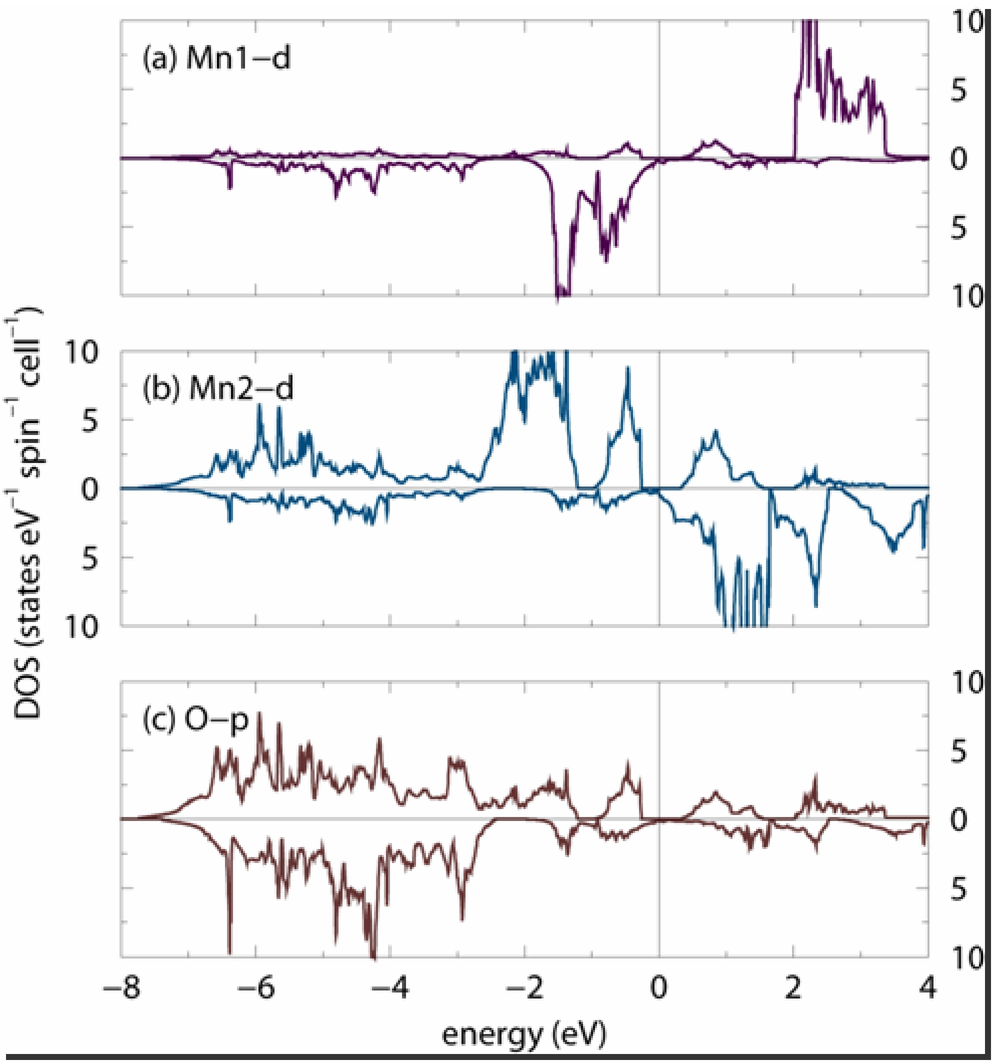
Hausmanite: Jahn-Teller distorted spinel: $Mn^{2+}Mn^{3+}{}_2O_4$



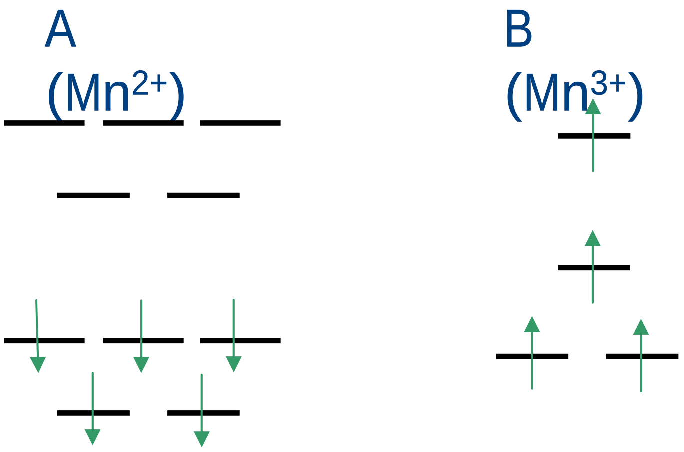
Clean samples obtained by quenching from high temperatures.



Ferrimagnets: Mn_3O_4



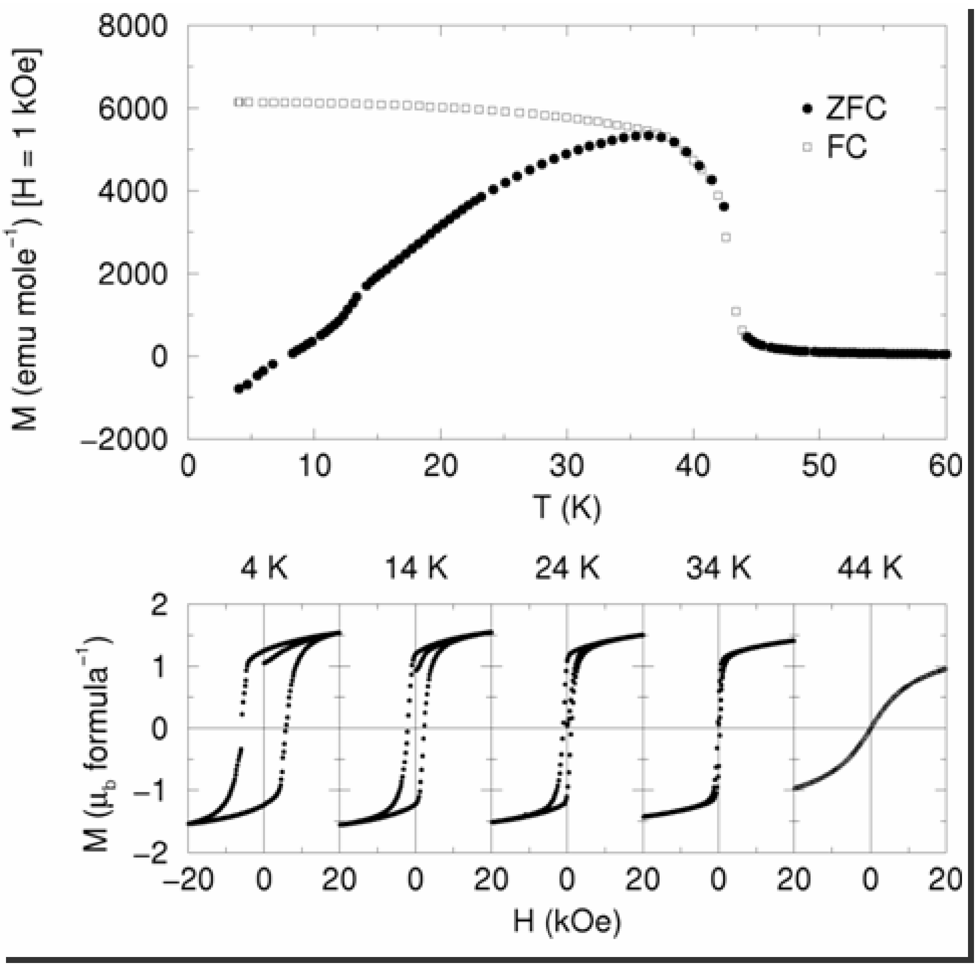
GGA-DFT calculation on the Néel state: Ferrimagnetic semiconductor (the samples are brown).

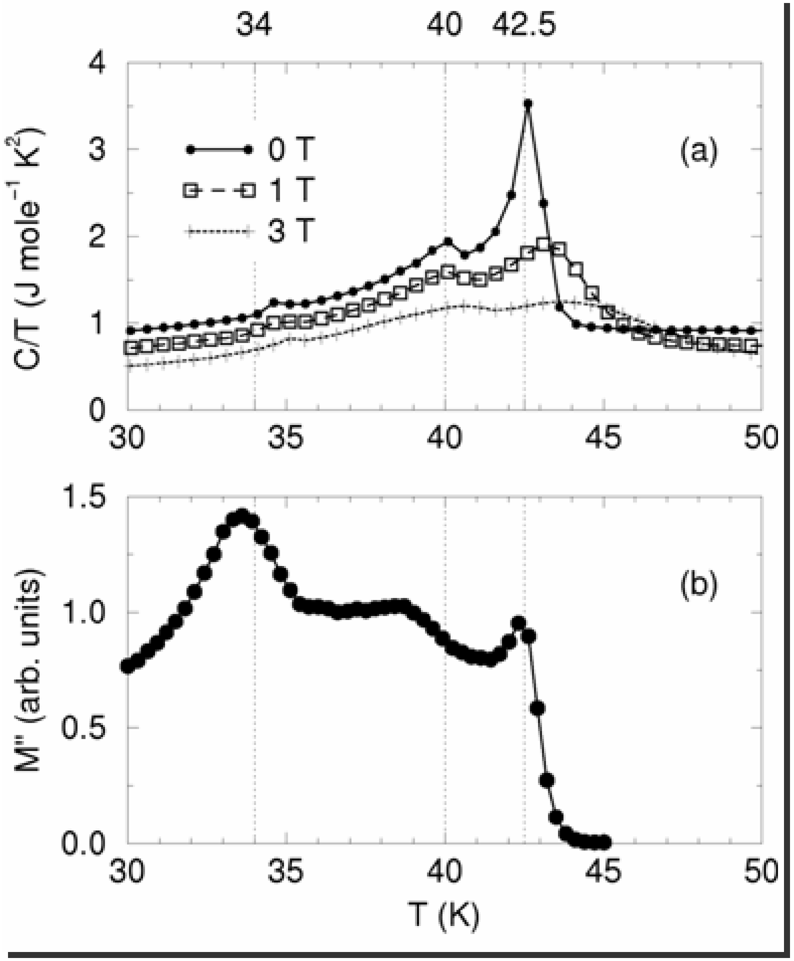


A (Mn^{2+})

B (Mn^{3+})

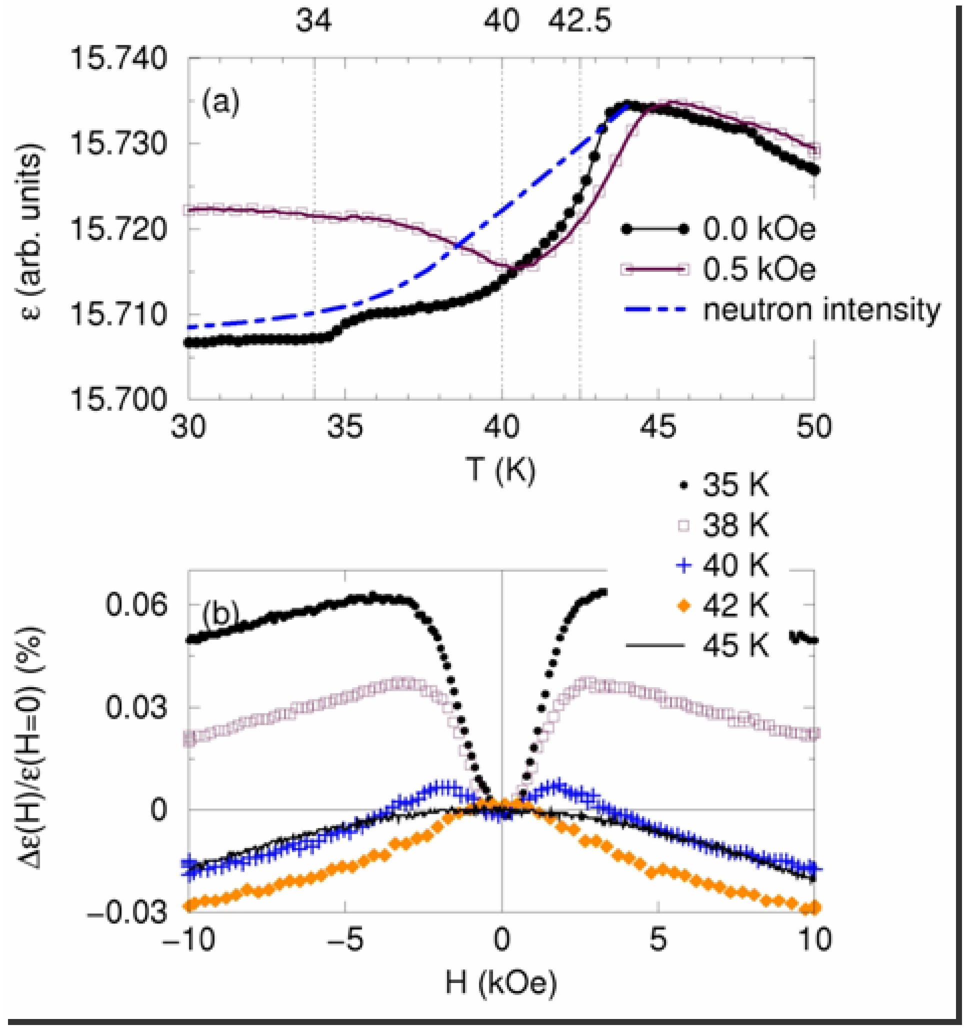
Ferrimagnets: Mn_3O_4





Multiple magnetic transitions observed in AC susceptibility and heat capacity

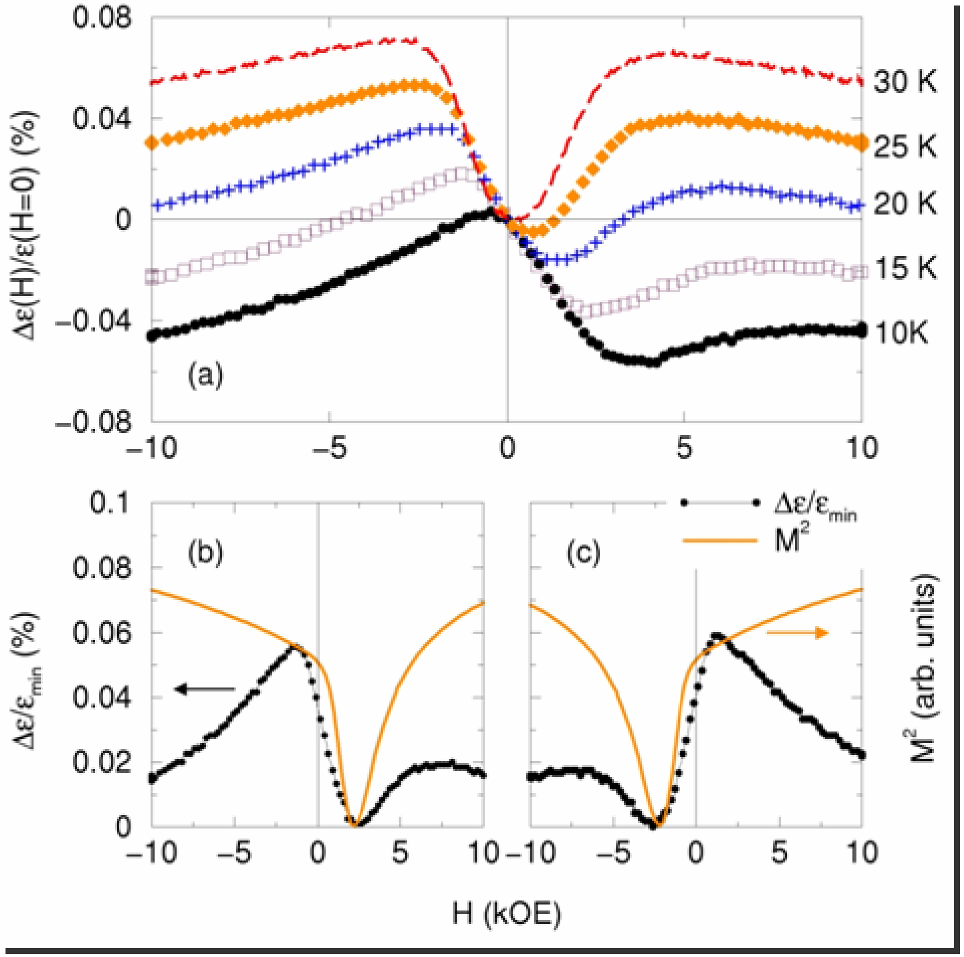
Ferrimagnets: Mn_3O_4



Changes in the capacitance at the magnetic transitions. The sample capacitance becomes magnetic field tunable.

120 neutron intensity from Jensen and Nielson, *J. Phys. C: Solid State Phys.* **7** (1974) 409.

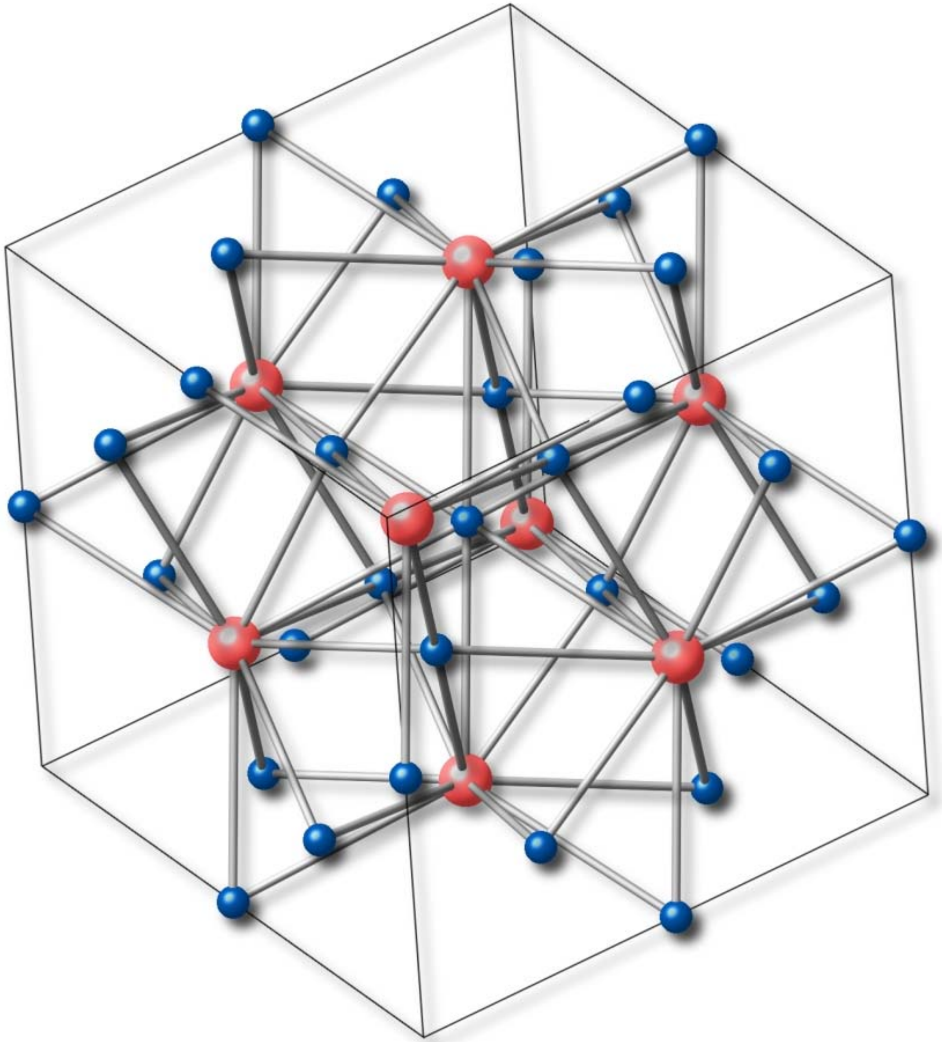
Ferrimagnets: Mn_3O_4



The field-dependence becomes hysteretic at low temperatures. The minimum magnetocapacitance corresponds to $M^2 \rightarrow 0$.

Tackett, Lawes, Melot, Grossman, Toberer, Seshadri, *Phys. Rev. B* **76** (2007) 024409(1-6).

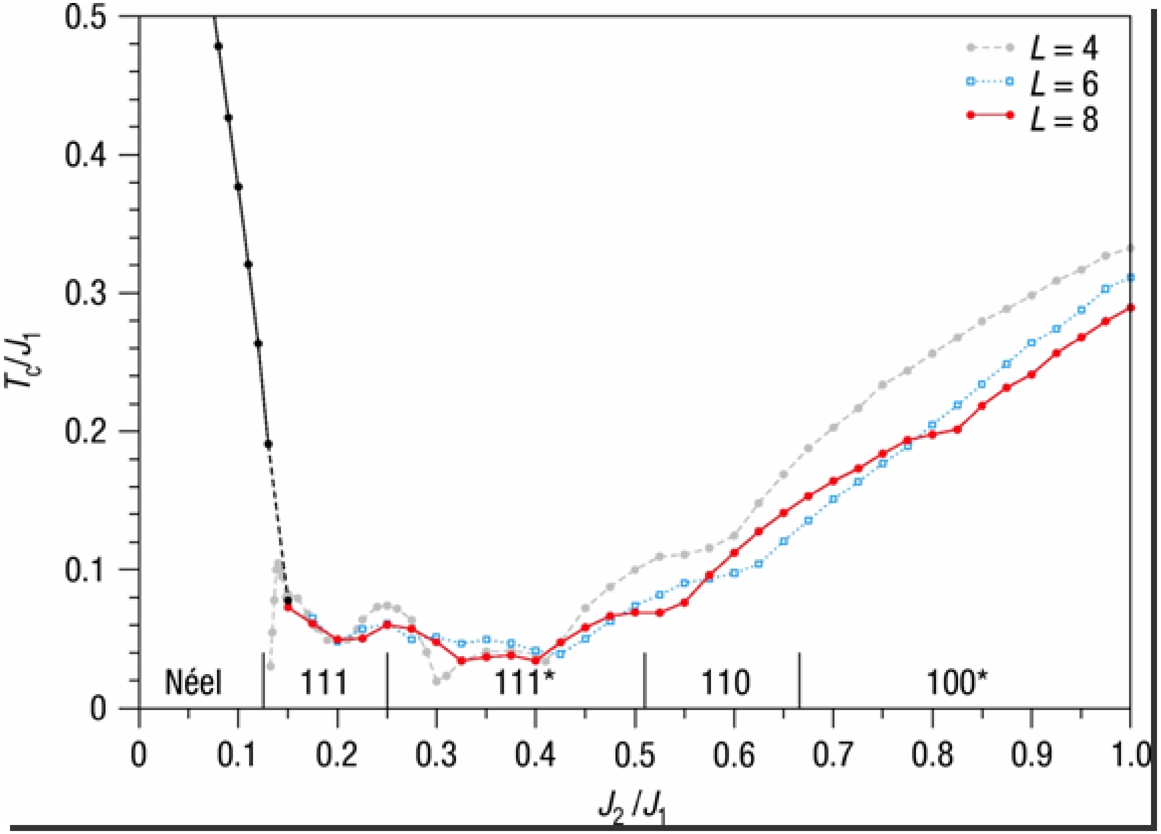
A-site magnetism in Co spinels:



The A sites form a diamond lattice: two interpenetrating *fcc* lattices. All couplings are antiferromagnetic. *fcc* lattices can be frustrated.

Tristran, Hemberger, Krimmel, Krug von Nidda, Tsurkan, Loidl, *Phys. Rev. B* **72** (2005) 174404.

A-site magnetism in Co spinels:



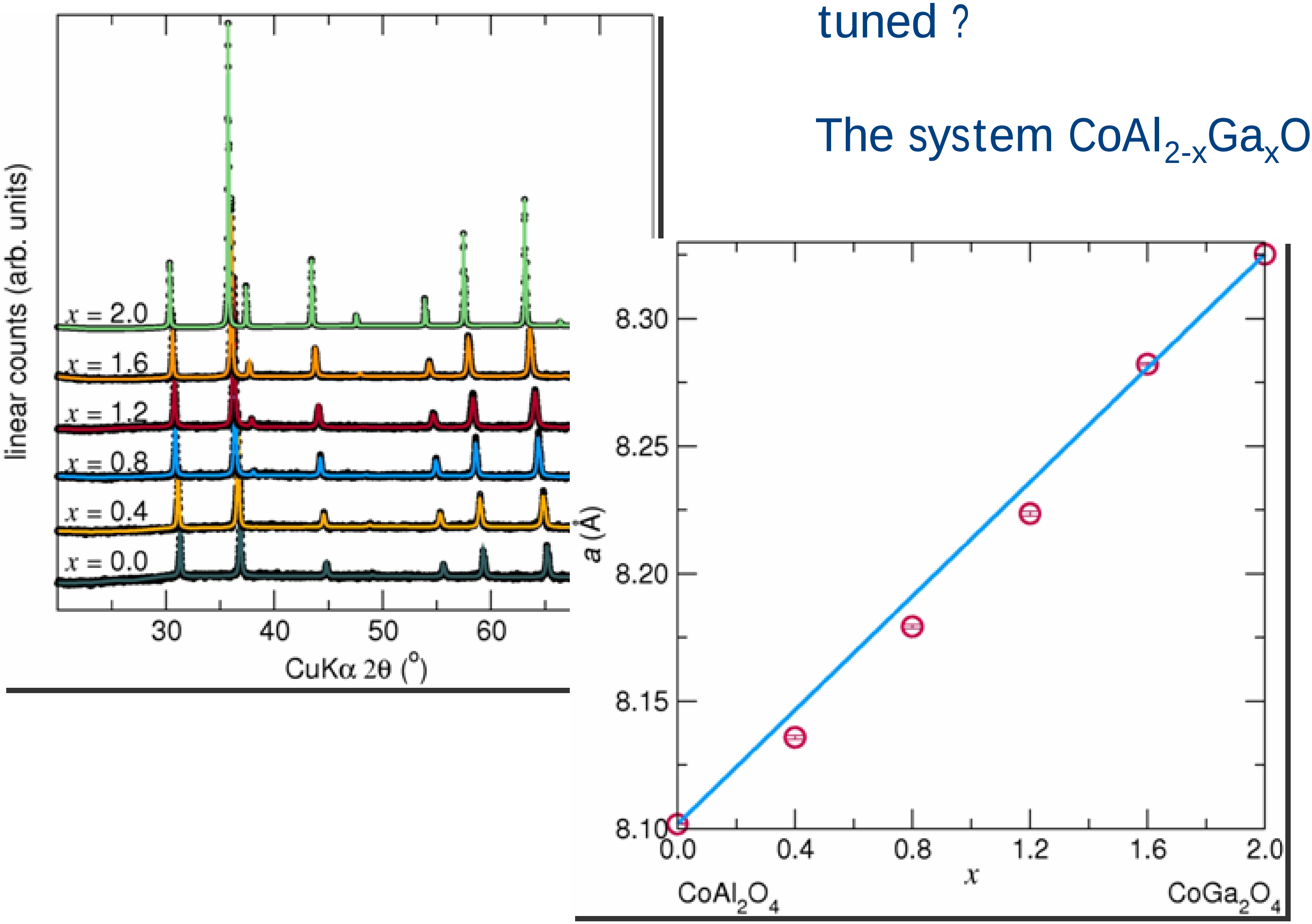
Magnetic ordering and frustration decided by the ratio of the next-near-neighbor (J_2) and near neighbor (J_1) couplings.

Bergman, Alicea, Gull, Trebst, and Balents, *Nature Phys*. **3** (2007) 487-491.

A-site magnetism in Co spinels:

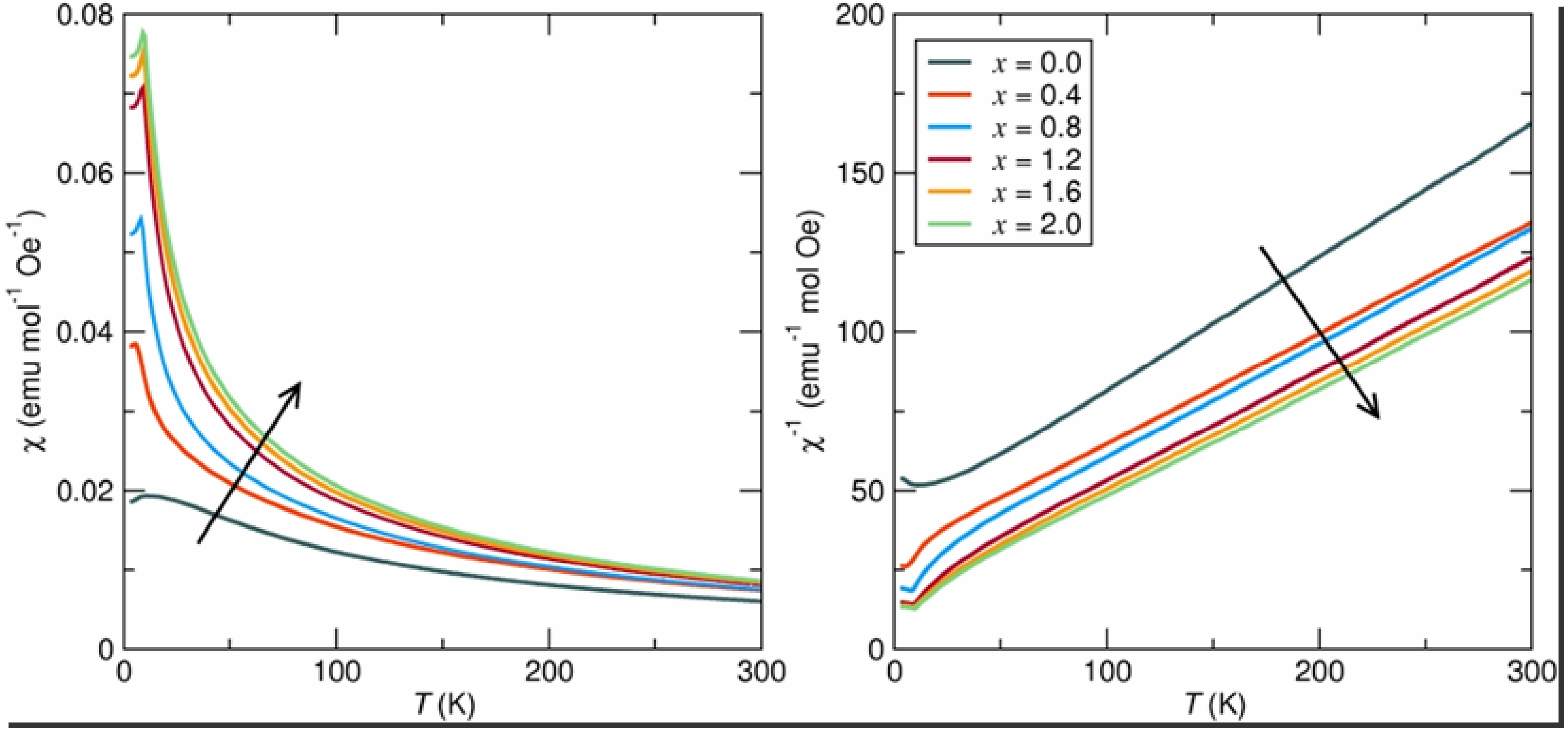
Can J_2/J_2 be systematically tuned ?

The system $CoAl_{2-x}Ga_xO_4$

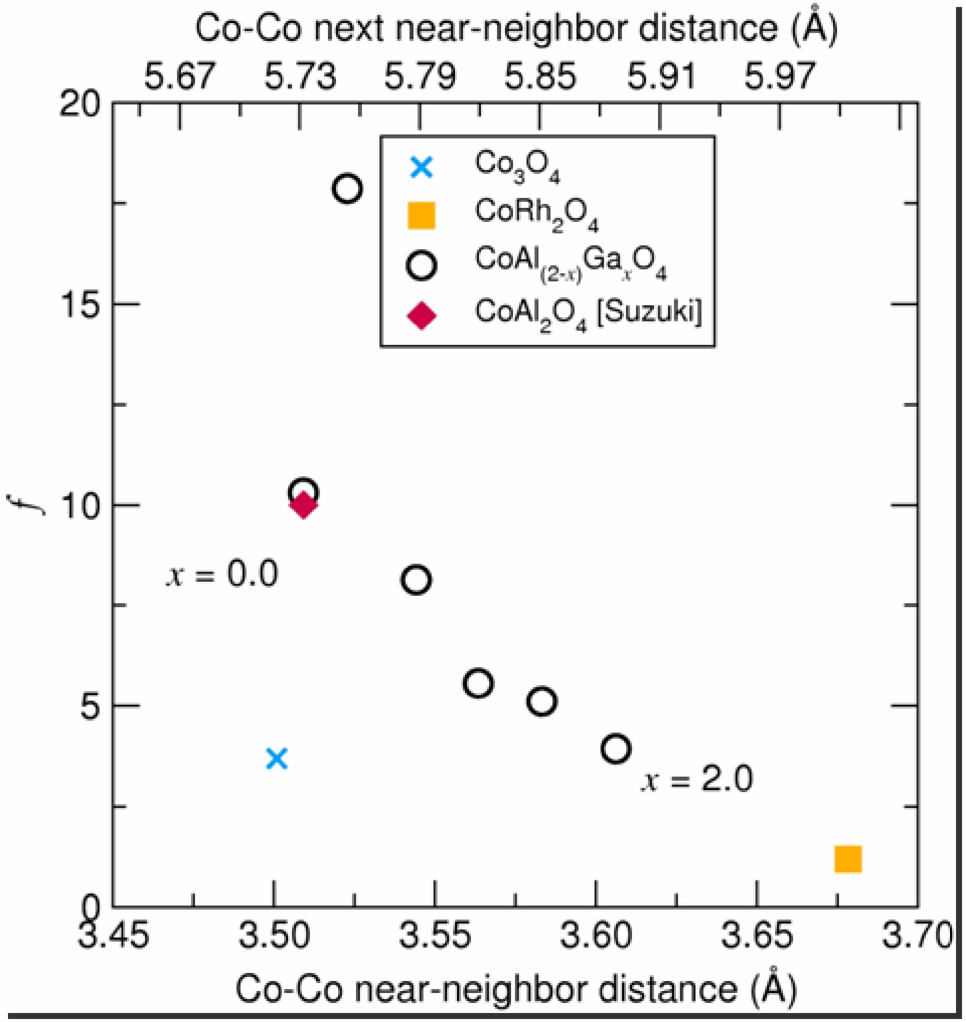


A-site magnetism in Co spinels:

All samples are antiferromagnetic with Néel temperatures below 10 K. μ_{eff} between 4.4 and 4.8 μ_B/Co^{2+} for all *x*.



A-site magnetism in Co spinels:

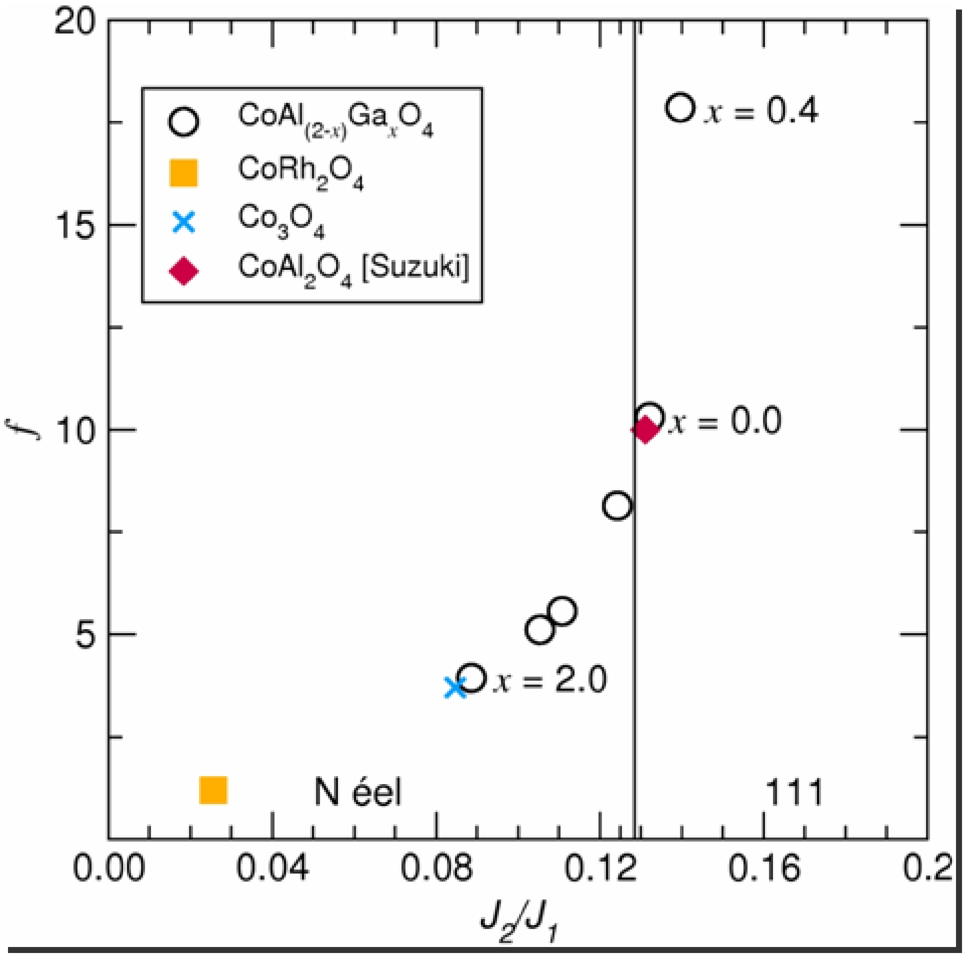


The frustration index

$$f = \frac{\Theta_{CW}}{T_N}$$

Is high for the smaller lattice constants, near $CoAl_2O_4$

A-site magnetism in Co spinels:



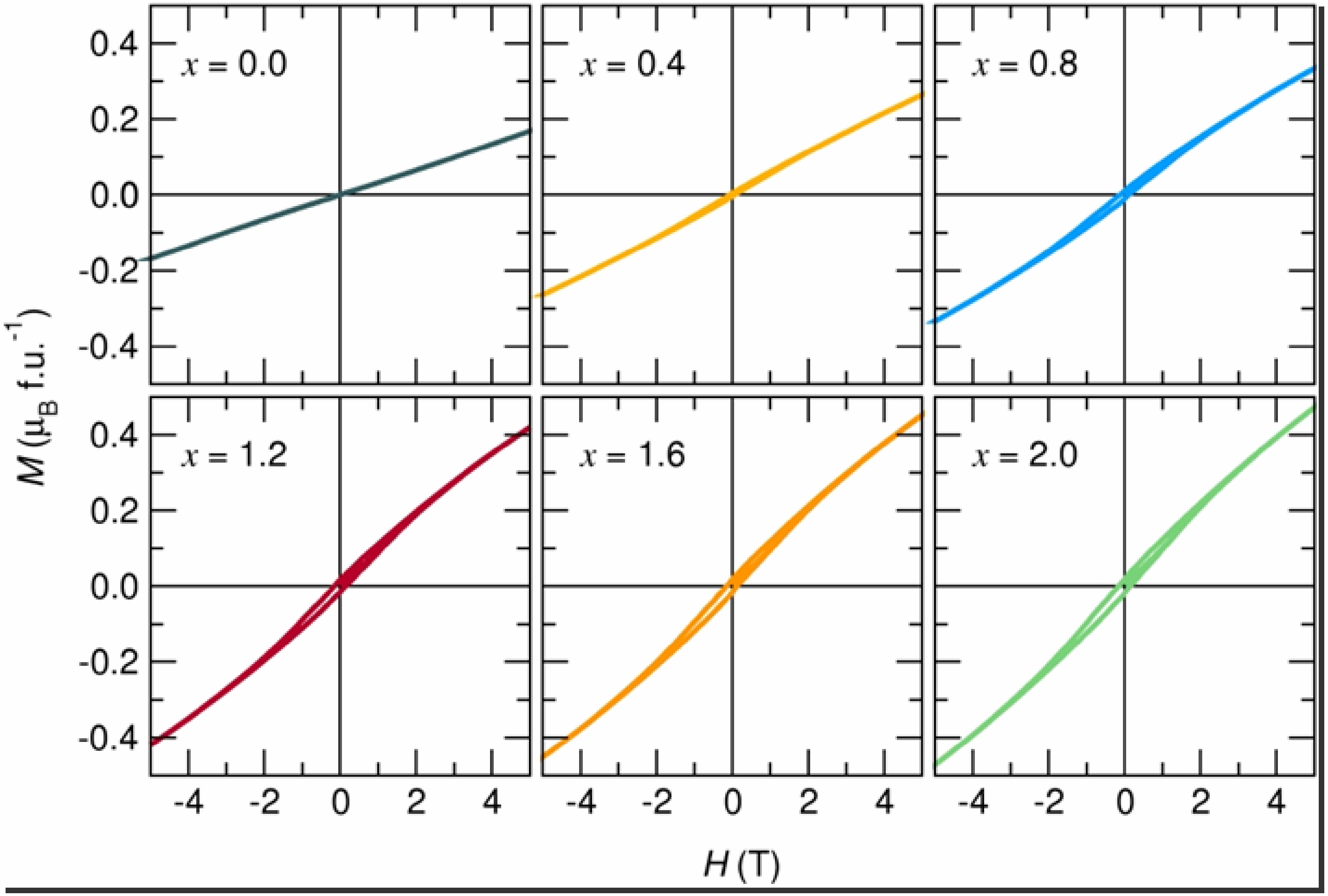
J_1 and J_2 extracted from χ-T plots by Monte-Carlo simulations of Heisenberg spins on lattices [Doron Bergman]

At least two of the samples are in the strongly frustrated 111 magnetic ordering regime.

To be tested by neutron scattering. Is there magnetocapacitive coupling ?

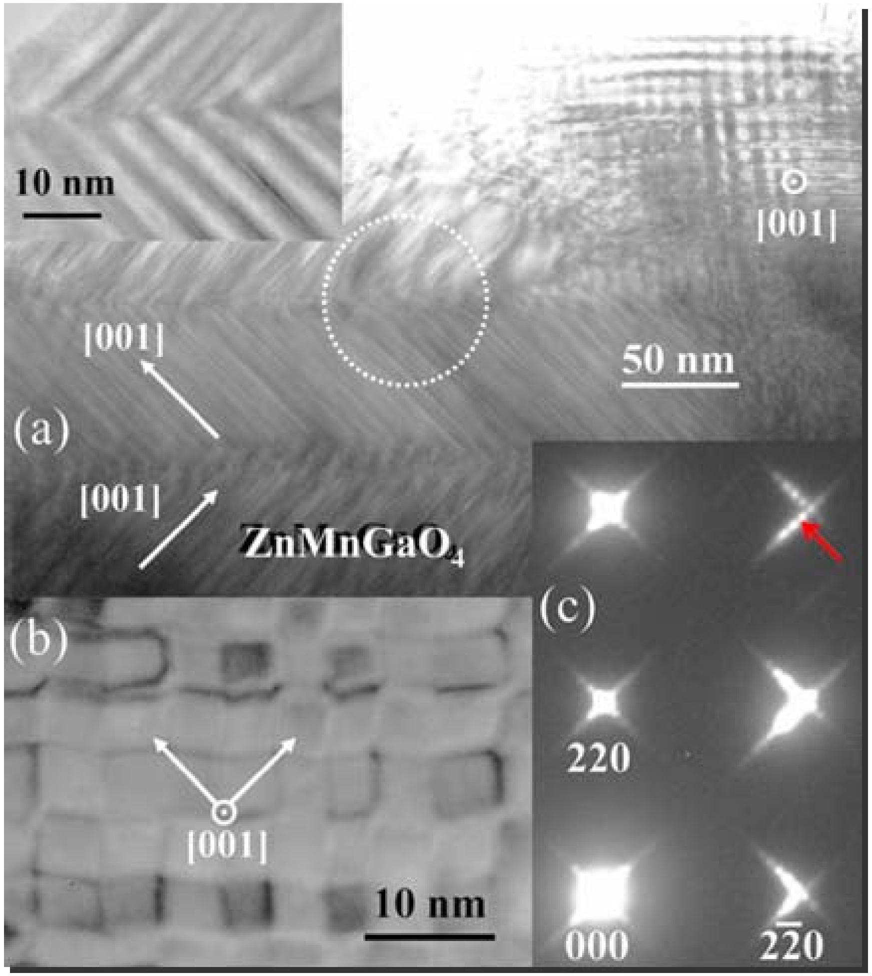
A-site magnetism in Co spinels:

A small glitch: greater inversion as *x* gets larger.



T = 5 K.

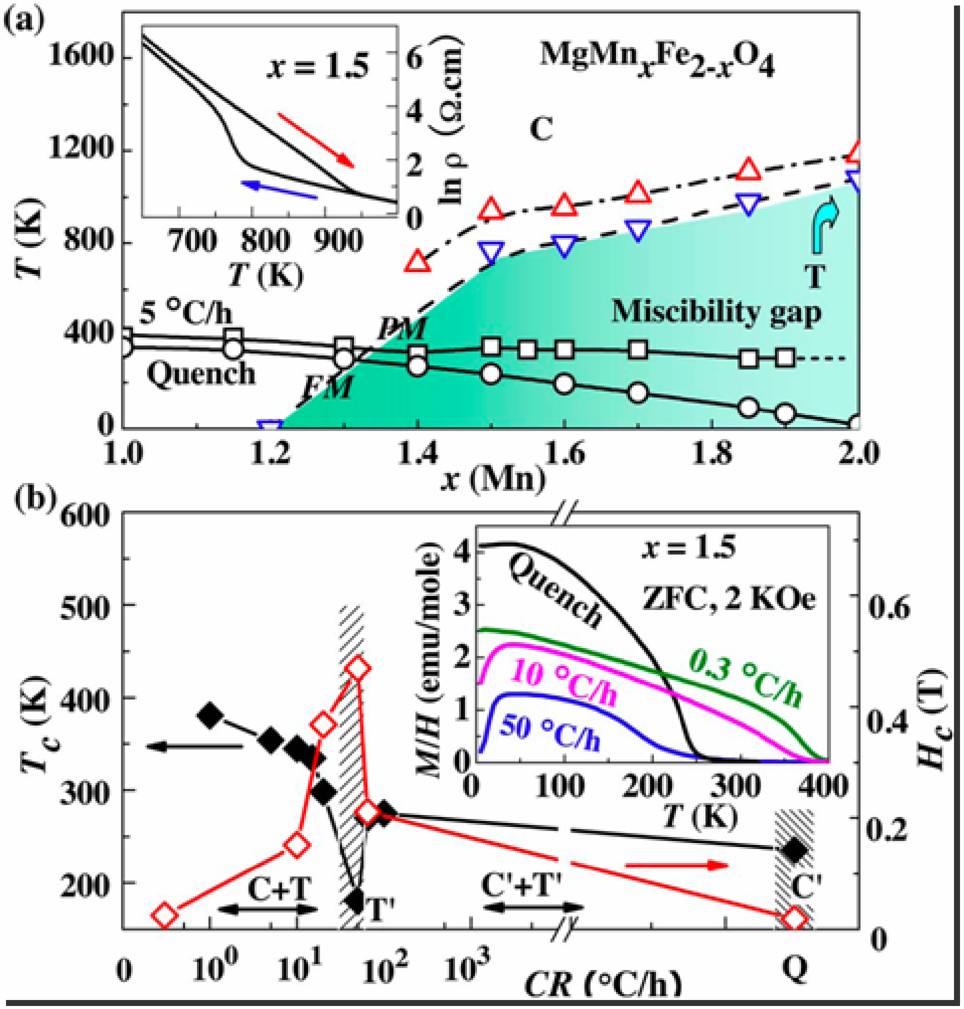
Jahn-Teller phenomena and phase separation in spinels



Solid state self-assembly of nanocheckerboards, Yeo, Horibe, Mori, Tseng, Chen, Khachaturyan, Zhang, Cheong, *Appl. Phys. Lett.* **83** (2006) 233120(1-3).

Slowly cooled $ZnMnGaO_4$

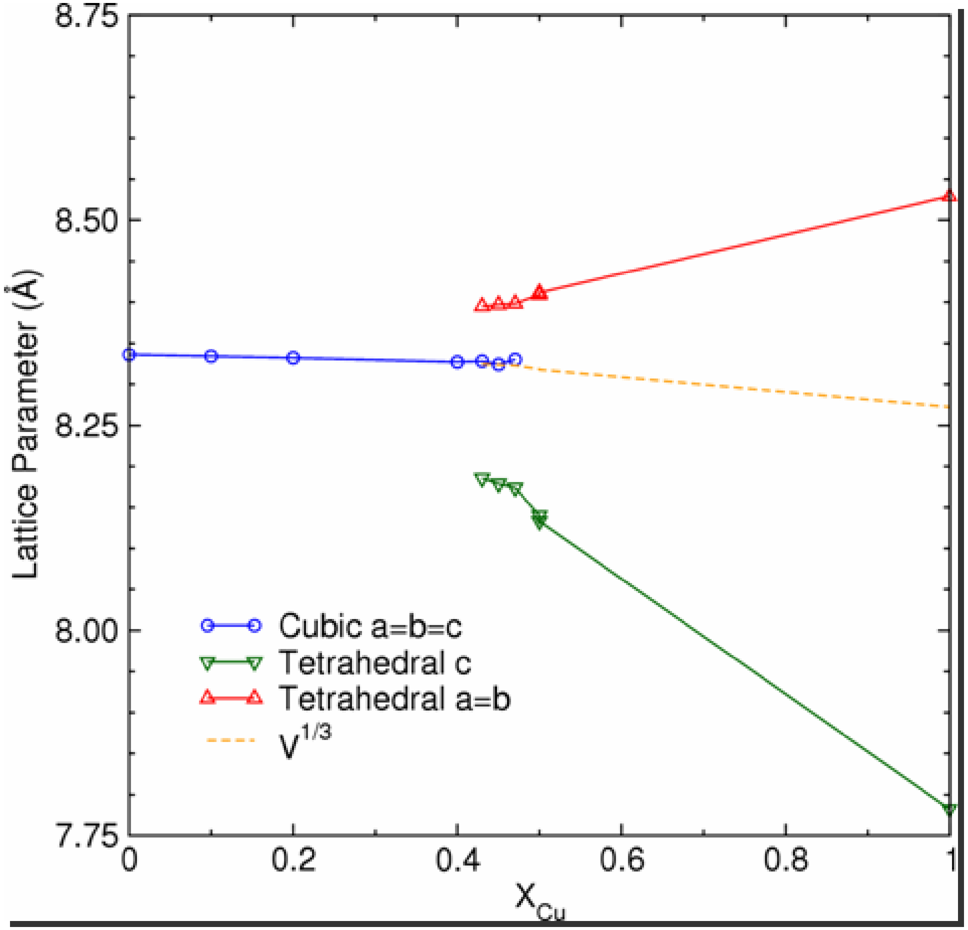
Jahn-Teller phenomena and phase separation in spinels



Coercivity and nanostructure in magnetic spinel Mg(Mn,Fe)$_2$O$_4$, Zhang, Yeo, Horibe, J. Choi, Guha, Croft, Cheong, Mori, *Appl. Phys. Lett.* 90 (2007) 133123(1-3).

Jahn-Teller phenomena and phase separation in spinels

$Mg_{1-x}Cu_xCr_2O_4$



Room temperature lattice parameters of $(Mg_{1-x}Cu_x)Cr_2O_4$:

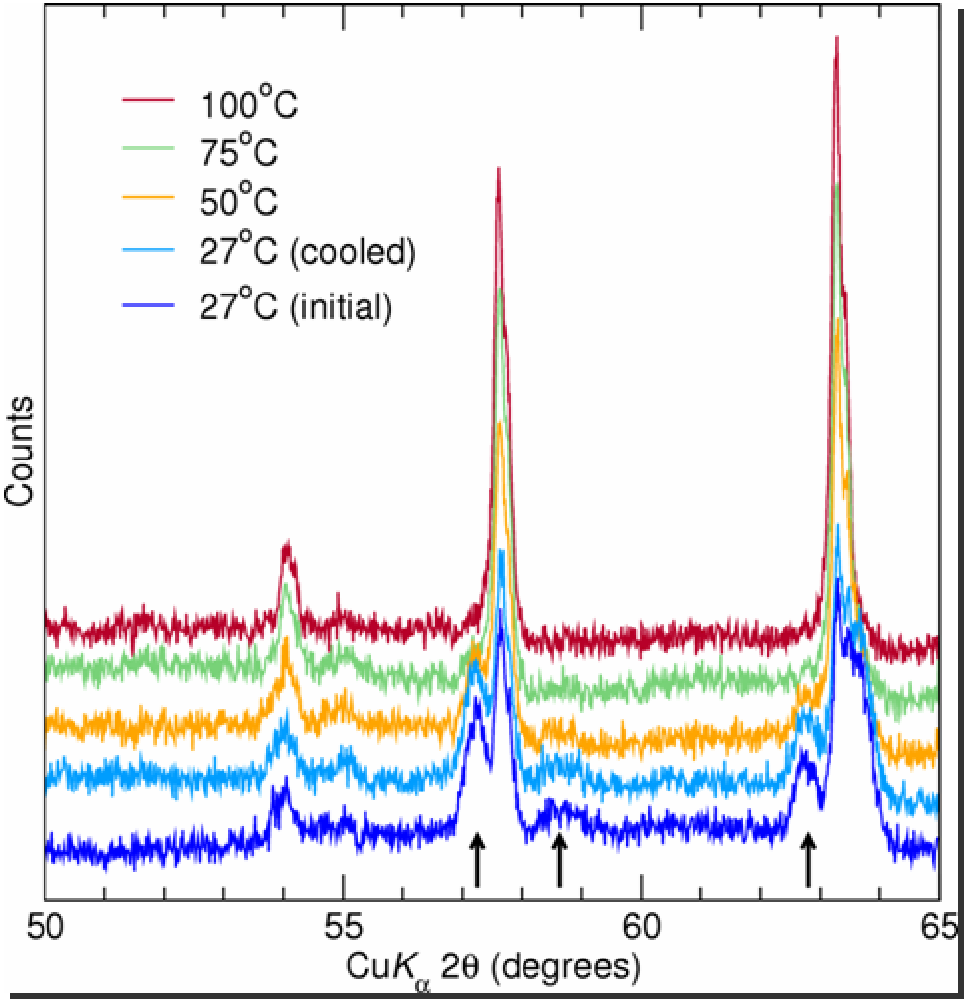
From X_{cu} = 0.43 to 0.47 is a 2-phase mix at RT.

X_{Cu} = 0.45 is cubic by ~100°C.

$MgCr_2O_4$ is AFM (T_N ~ 50 K)
$CuCr_2O_4$ is FiM (T_C ~ 150K)

Jahn-Teller phenomena and phase separation in spinels

$Mg_{0.55}Cu_{0.45}Cr_2O_4$



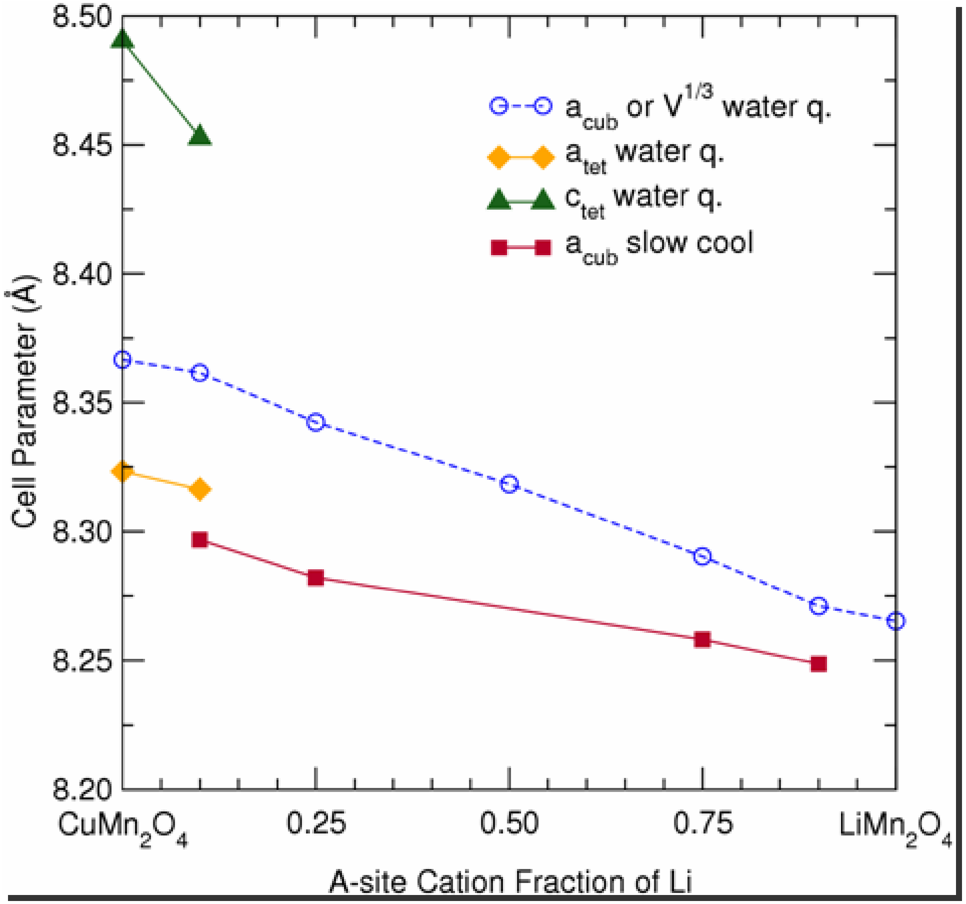
The JT transition temperature for $CuCr_2O_4$ is about 580°C.

Going more Mg-rich and cooling should result in regimes where there is insufficient kinetic energy for phase separation.

Small undercooling: Analogy with deep eutectics/ metallic glasses.

Jahn-Teller phenomena and phase separation in spinels

$Cu_{1-x}Li_xMn_2O_4$



One end-member is cubic at RT, and charge orders when cooled. The other end-member is strongly JT distorted.

Conclusion

Resurgent interest in spinels as a structure type with complex magnetic phenomena, and as a source of complex phase separated materials.