Nanoscale Self-organized Hexamers and Octamers in spinels

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Hexamers in ZnCr₂O₄: Nature, Aug. 2002
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Octamers in CuIr₂S₄: Nature, March 2002
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3 Kagome- + 2 Hexagonal layers

History of Spinels

[1] Fe$_2$O$_4$: Magnetite: Natural magnet: Discovered in Magnesia (a part of ancient Greece, now Turkey)


[3] Spinel MgAl$_2$O$_4$


[5] Verwey transition in Fe$_2$O$_4$:
   - E. J. Verwey and P. W. Haaymann, Physica 8, 979 (1941).


[7] 1st oxide superconductor: LiTi$_2$O$_4$ ($T_c=13.7$ K):
1st oxide heavy fermion: LiV$_2$O$_4$:

[8] Geometric Frustration Problem
**B-lattice of spinel** $AB_2O_4$:

identical with B-lattice of pyrochlore $A_2B_2O_7$


[3] Completely tiled by

*Hexamers (with 6 B ions) or Octamers (with 8 B ions)*

* they are decoupled,  
i.e., no (corner, edge, or face) sharing

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$\text{ZnCr}^{3+}_2\text{O}_4$: insulator  
($T_N \approx 12$ K and $\theta_{CW} \approx 390$ K)  

$\text{Cr}^{3+}$: $3d^3$: $S=3/2$

$\text{Cu}^{1+}\text{Ir}^{3.5+}_2\text{S}_4$: metal-insulator transition at $\sim 220$ K.  

$\text{Ir}^{3+}$: $5d^6$: $S=0$  
$\text{Ir}^{4+}$: $5d^5$: $S=1/2$
Spinel \( \text{CuIr}_2\text{S}_4 \) crystal

\( F_{3dm} \): normal spinel
\( A \approx 9 \text{Å} \)

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Spin dimerization within a Ir\(^{4+}\)(S=1/2; 5d\(^5\))-octamer

\(~3.4\ \text{Å}\) separation between Ir\(^{4+}\) pairs becomes
\(~3\text{Å}\) (for dimerized pairs) and
\(~3.5\ \text{Å}\) (for non-dimerized pairs)

Bragg peak profiles of CuIr\(_2\)S\(_4\) in the vicinity of the 400 cubic spinel peak.
Superlattice reflections of Cul$_2$S$_4$ and Cul$_{1.95}$Cr$_{0.05}$S$_4$.

X-ray-induced transition in Cul$_2$S$_4$.
X-ray-induced reduction of $(001)$ superlattice peak intensity and resistivity in $\text{CuI}_2\text{S}_4$ at 10 K

Electron-beam-induced transition in $\text{CuI}_2\text{S}_4$

- Forbidden peaks become diffusive at low $T$, in e-beam.
Enhanced symmetry of average structure of CuIr$_2$S$_4$ with cooling: *possibly due to x-ray-induced nematic-like phase?*

\[ i.e., \text{octamers are disordered, but the orientation of octamers as well as the dimerization directions are maintained.} \]

\[ i.e., \text{short-range translational ordering and long-range orientation ordering of octamers.} \]
Magnetic neutron scattering
near $Q=1.5$ Å$^{-1}$ in ZnCr$_2$O$_4$

ZnCr$_2$O$_4$

(a) Energy of inelastic magnetic scattering near $Q=1.5$ Å$^{-1}$ vs. Temp.

(b) Magnetic (elastic) Bragg scattering and lattice constants vs. Temp.
Magnetic neutron scattering near $Q = 1.5 \text{ Å}^{-1}$

The magnetic feature:
changes from inelastic to elastic as well as quasi-elastic (depending on temp. and disorder), but occurs always near $Q=1.5 \text{ Å}^{-1}$

$\Rightarrow$ Similar shape or configuration in real space
Hexamer: antiferromagnetic hexagonal spin loop

Hexamers with four different orientations

**Hexamer form factor:**

\[ F_6(Q) \propto \left\{ \sin \frac{\pi}{2} h \cdot \left( \cos \frac{\pi}{2} k - \cos \frac{\pi}{2} l \right) \right\}^2 + \left\{ \sin \frac{\pi}{2} k \cdot \left( \cos \frac{\pi}{2} l - \cos \frac{\pi}{2} h \right) \right\}^2 + \left\{ \sin \frac{\pi}{2} l \cdot \left( \cos \frac{\pi}{2} h - \cos \frac{\pi}{2} k \right) \right\}^2 \]

Magnetic neutron scattering intensity:

\[ I(Q) = |F_6(Q)|^2 |f(Q)|^2, \]

where \( f(Q) \) is the \( \text{Cr}^{3+} \) magnetic form factor.
Collinear 6 spins in a hexamer can freely change the overall spin direction!
CONCLUSION

[1] Hexamers or octamers can tile the entire spinel or pyrochlore B-lattice.

[2] Hexamers in ZnCr$_2$O$_4$:
Fundamental unit for low-energy spin excitations
   * Nature, accepted.

[3] Octamers in CuIr$_2$S$_4$:
Charge ordering induces isomorphic Ir$^{3+}$- and Ir$^{4+}$- octamers.
Spin dimerization within Ir$^{4+}$(S=1/2)-octamers.