Nanoscale Self-organized Hexamers and Octamers in spinels

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Hexamers in $ZnCr_2O_4$: Nature, Aug. 2002

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S. H. Lee	NIST
C. Broholm	Johns Hopkins U.

Oatamers in $CuIr_2S_4$: Nature, March 2002

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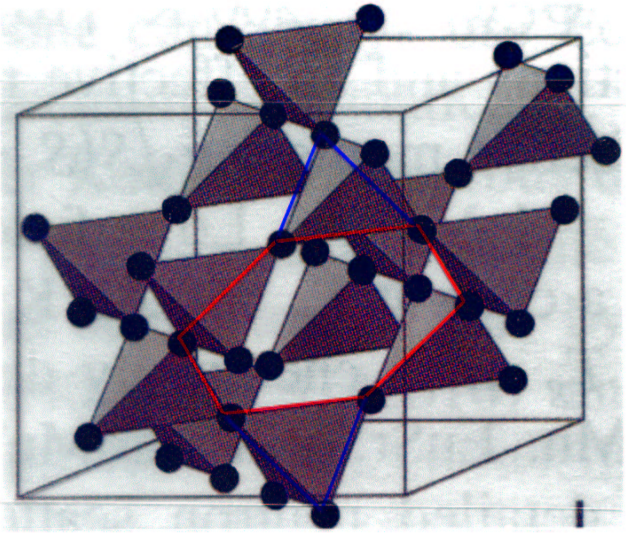
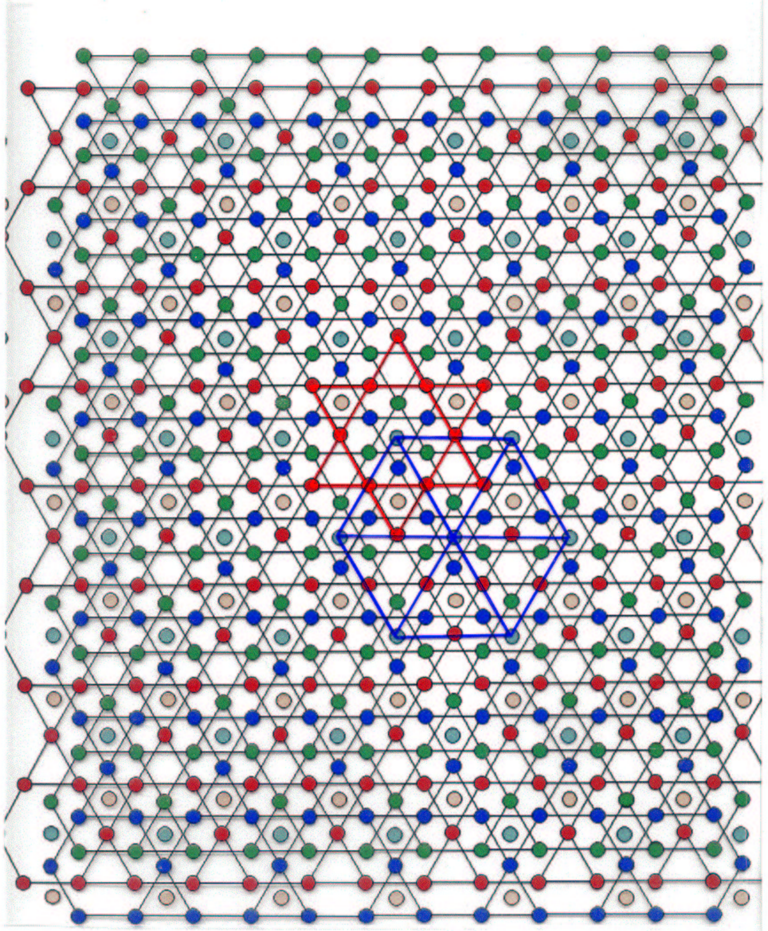
Y. Horibe C. H. Chen	Bell Labs

*** Partially supported by Rutgers/Maryland MRSEC**

Corner Sharing of B-ion Tetrahedra of Spinel $AB_2O(\text{or }S)_4$

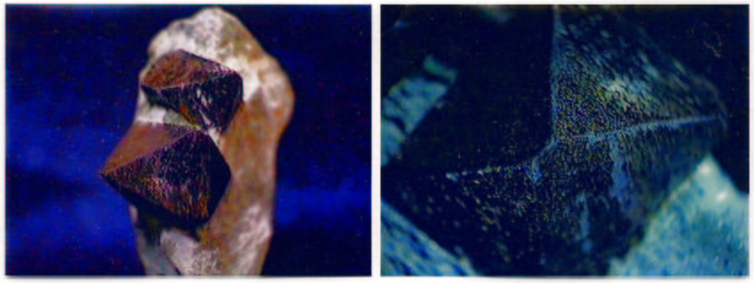


3 Kagome- + 2 Hexagonal layers



History of Spinels

[1] Fe_3O_4: Magnetite: Natural magnet: Discovered in Magnesia
(a part of ancient Greece, now Turkey)



[2] Compass: 4th century A.D. in China

[3] Spinel $MgAl_2O_4$

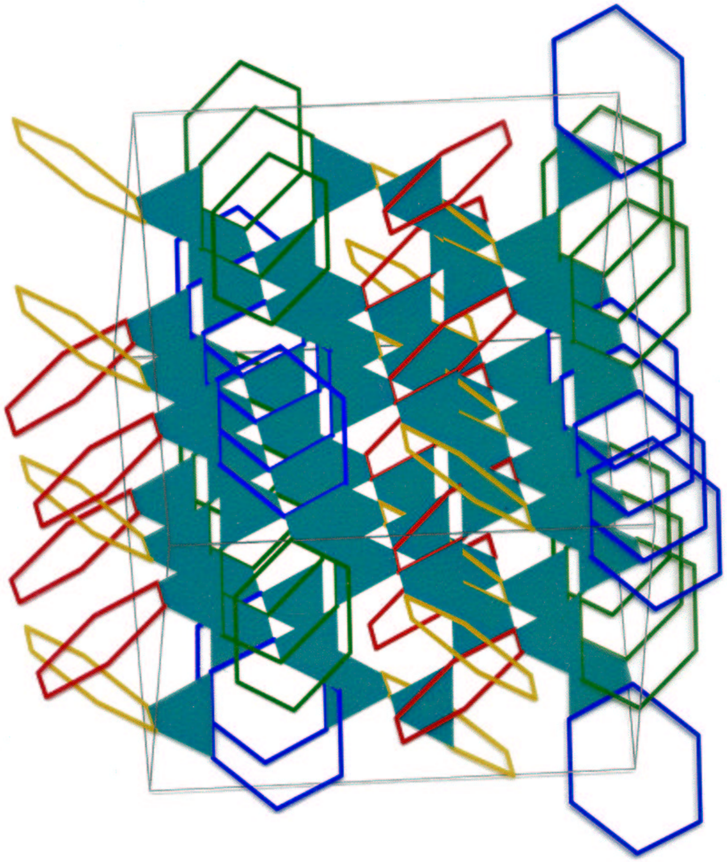
[4] Structural determination by Sir Bragg: Nature **95**, 561 (1915).

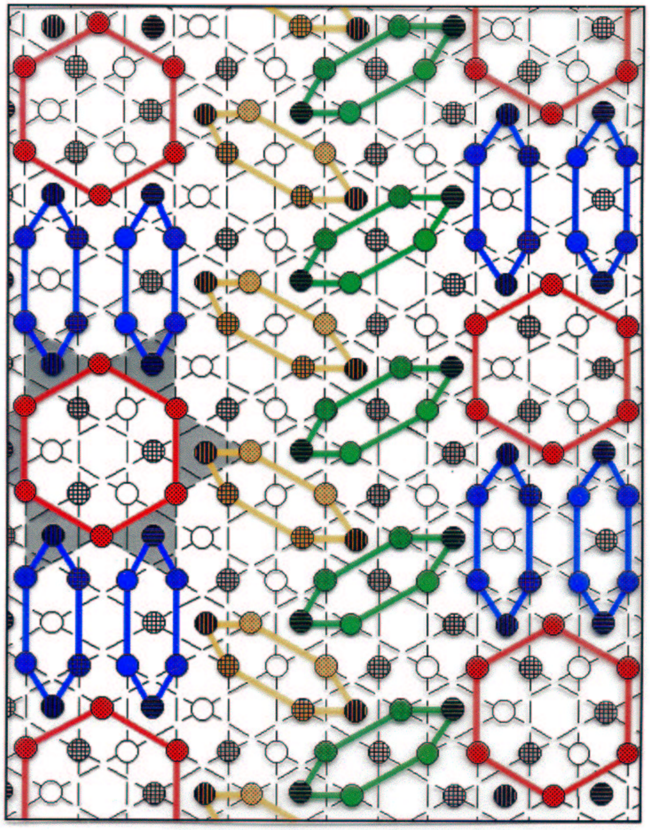
[5] Verwey transition in Fe_3O_4:
R. W. Millar: J. Am. Chem Soc. **51**, 215 (1929)
E. J. Verwey and P. W. Haaymann, Physica **8**, 979 (1941).

[6] Firrites: RF core

[7] 1st oxide superconductor: $LiTi_2O_4$ (T_c=13.7 K):
D. C. Johnston, J. Low Temp. Phys. **25**, 145 (1976)
1st oxide heavy fermion: LiV_2O_4:
D. C. Johnston, C. A. Swenson, and S. Kondo, Pys. Rev. B **59**, 2627 (1999).

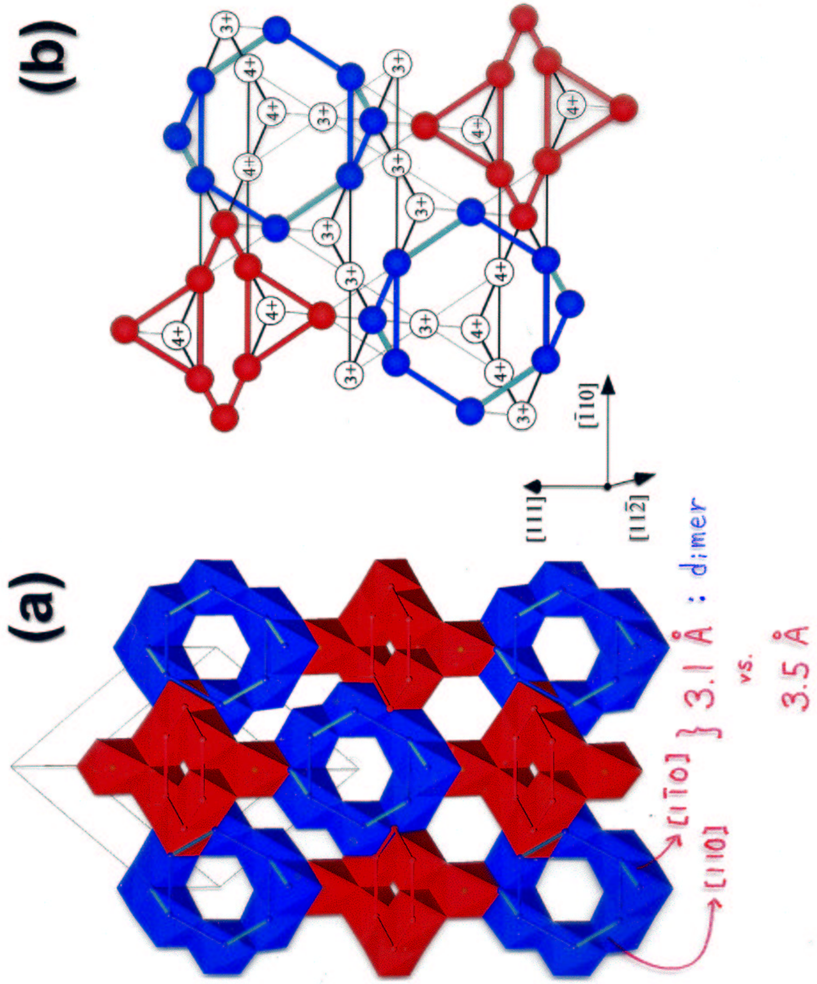
[8] Geometric Frustration Problem

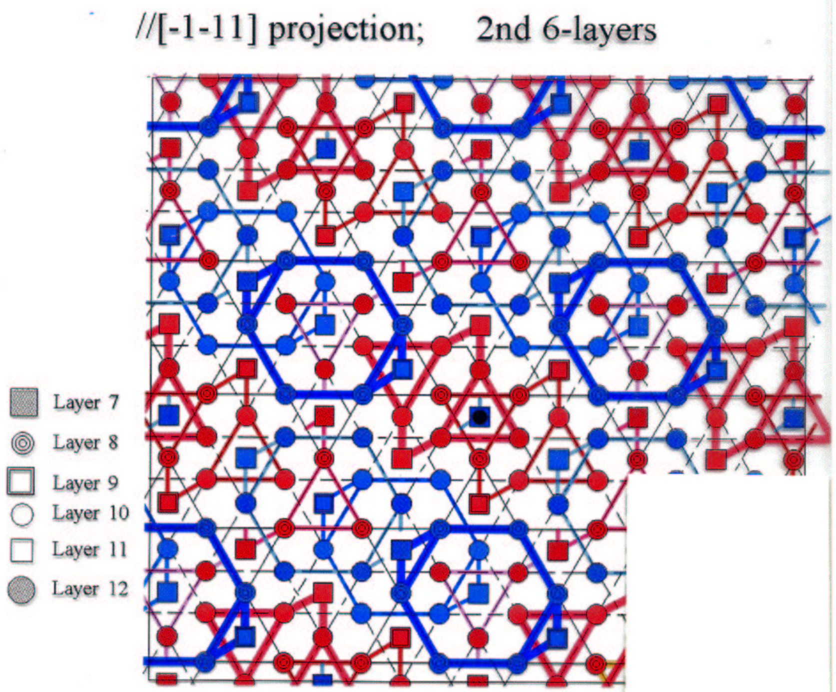




Hexamers in Spinel

(2 triangular layers & 3 kagome layers)


(a)
(b)
3+
4+
[1̄10]
[111]
[112̄]
[11̄0]
[110]
} 3.1 Å : dimer
vs.
3.5 Å


//[-1-11] projection; 2nd 6-layers
Layer 7
Layer 8
Layer 9
Layer 10
Layer 11
Layer 12

B-lattice of spinel AB_2O_4:

identical with B-lattice of pyrochlore $A_2B_2O_7$

[1] Corner sharing 3D network of tetrahedra.

[2] Alternating 2D Kagome and hexagonal (or triangular) layers along [111] direction.

[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

$ZnCr^{3+}{}_2O_4$: insulator
($T_N \approx 12$ K and $\theta_{CW} \approx 390$ K)

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

$Cu^{1+}Ir^{3.5+}{}_2S_4$: metal-insulator
transition at ~220 K.

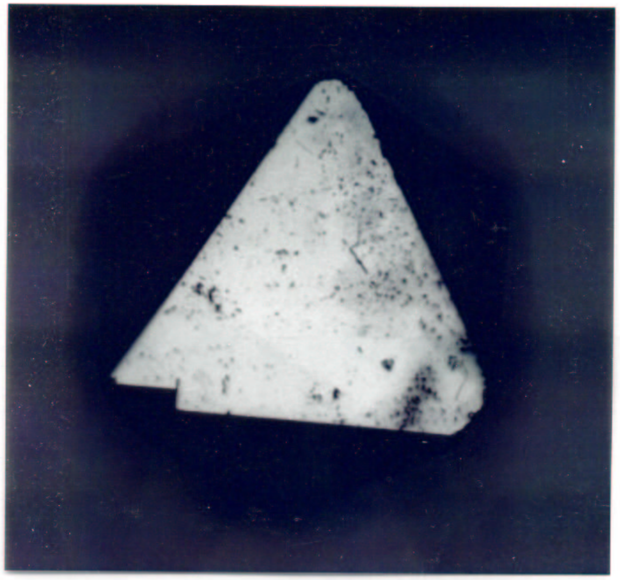
Ir^{3+}: $5d^6$: S=0
Ir^{4+}: $5d^5$: S=1/2

Spinel $CuIr_2S_4$ crystal

F3dm: normal spinel

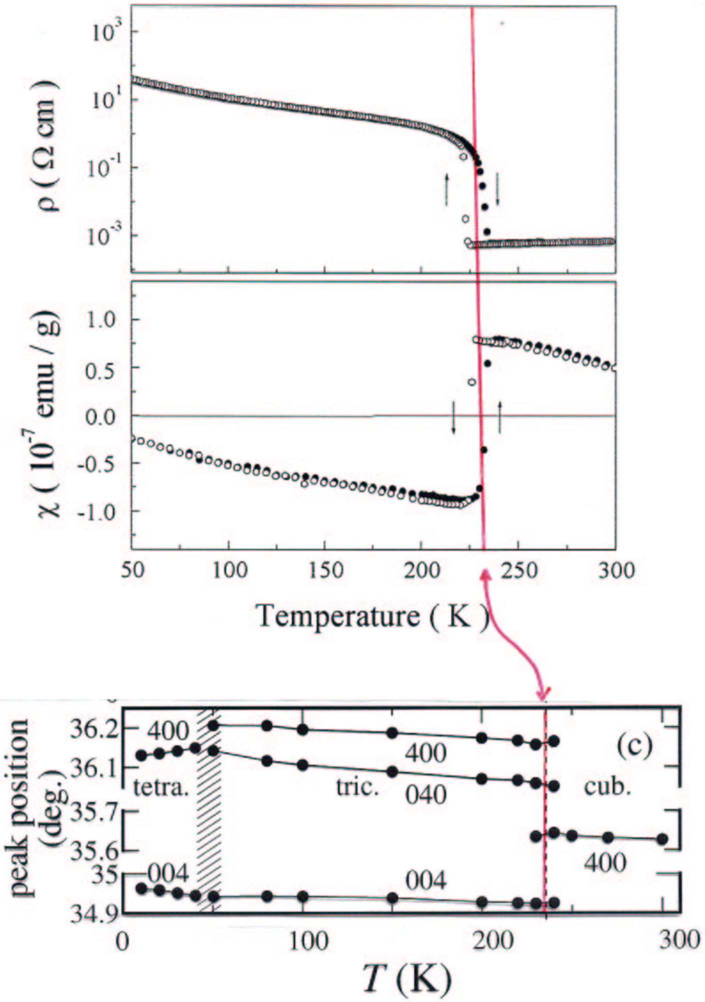
A ≈9Å

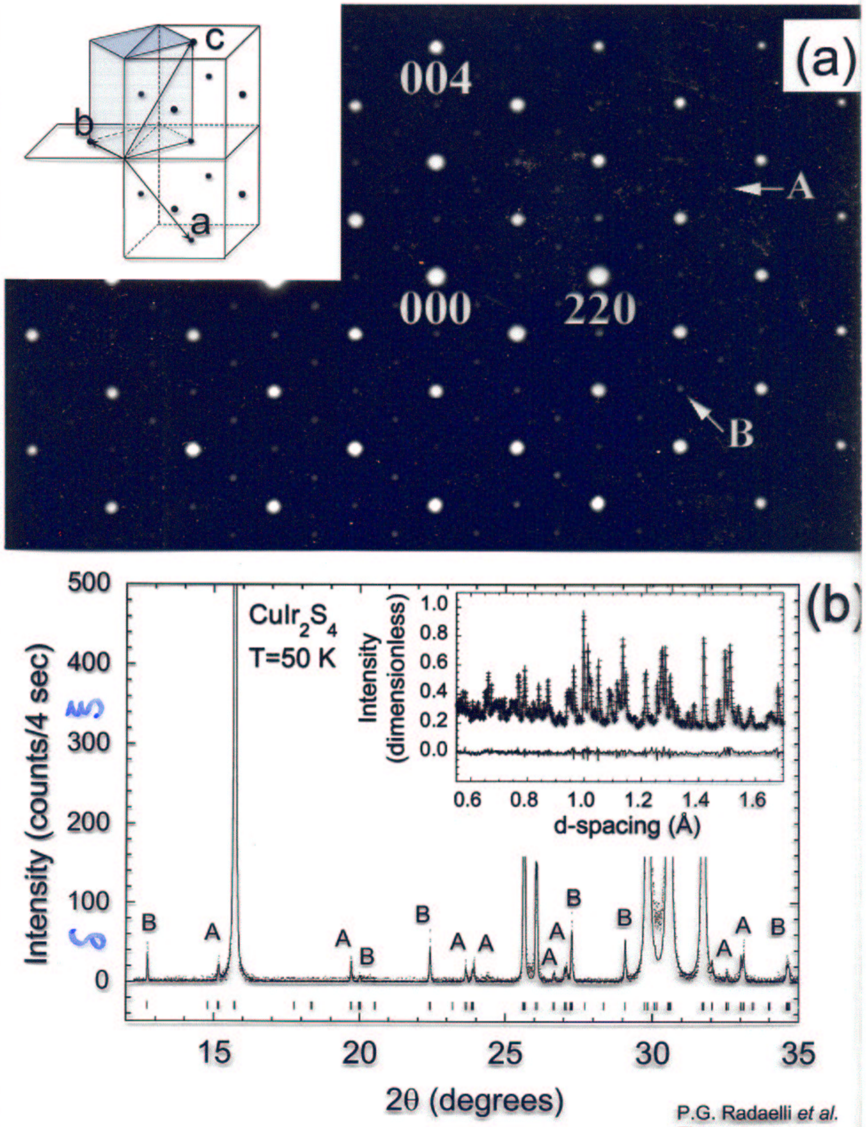
Y. S. Hor, W. Ratcliff, N. J. Hur, and S-W. Cheong



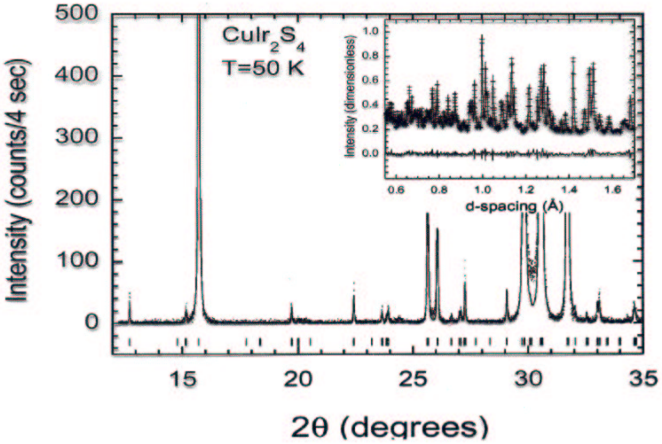
S.H. Lee NIST

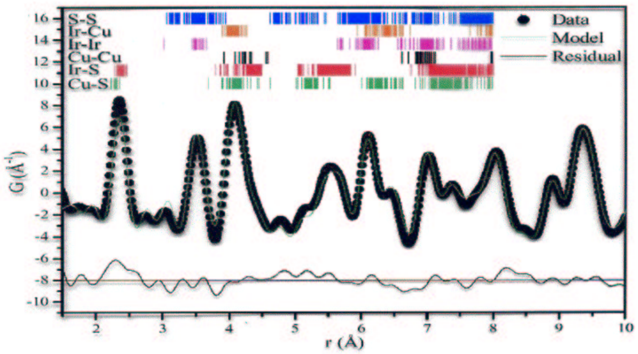
$Cu\,Ir_2S_4$





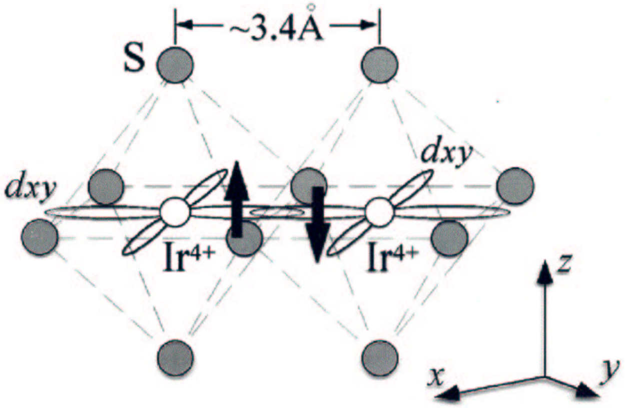
P.G. Radaelli *et al.*
Figure 1

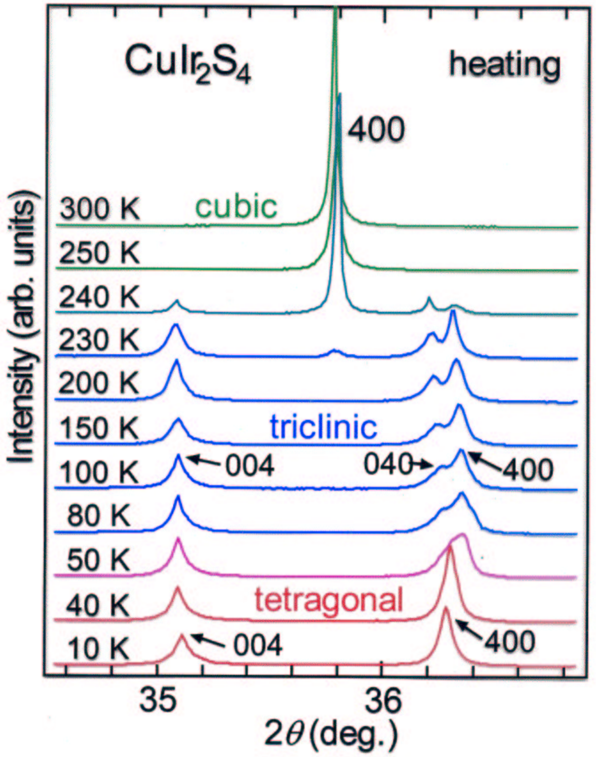




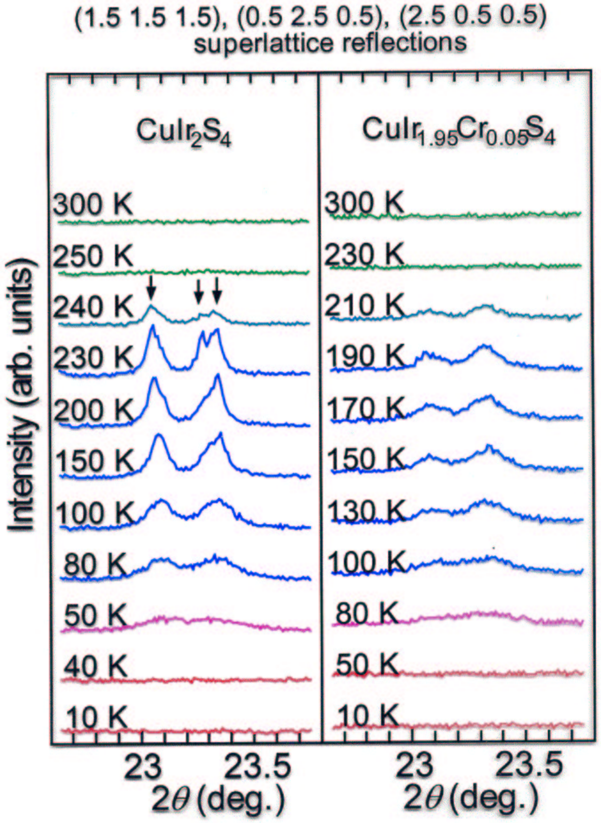
Spin dimerization within a Ir^{4+}(S=1/2: 5d^{5})-octamer

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





Bragg peak profiles of CuIr$_2$S$_4$ in the vicinity of the 400 cubic spinel peak.

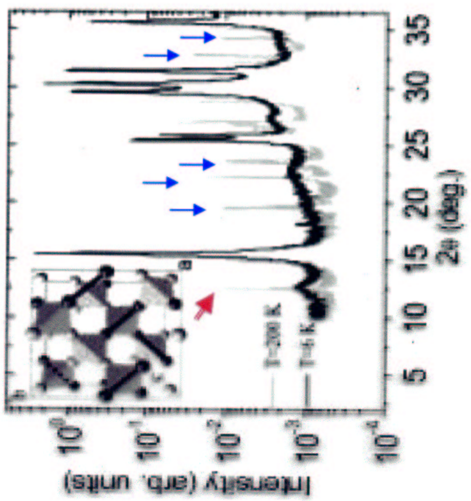


Superlattice reflections of $CuIr_2S_4$ and $CuIr_{1.95}Cr_{0.05}S_4$.

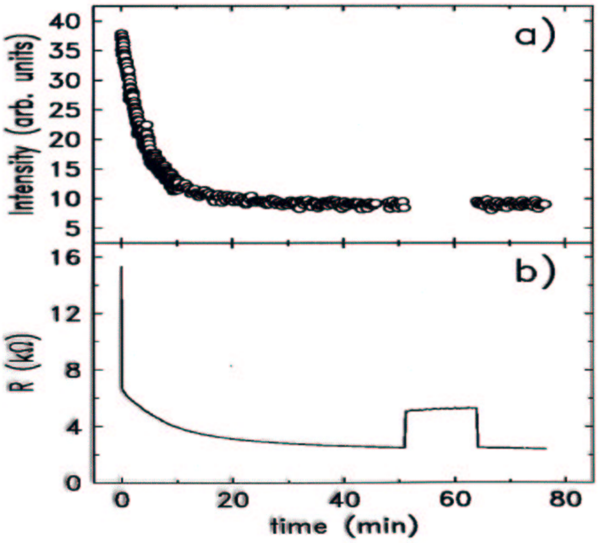
X-ray-induced transition in $CuIr_2S_4$

Forbidden peak

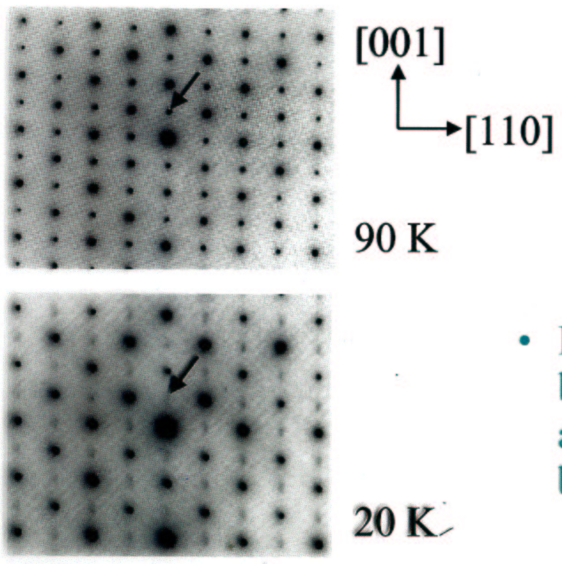
Superlattice peaks



X-ray-induced reduction of (001) superlattice peak intensity and resistivity in $CuIr_2S_4$ at 10 K



Electron-beam-induced transition in $CuIr_2S_4$



- Forbidden peaks become diffusive at low T. in e-beam.

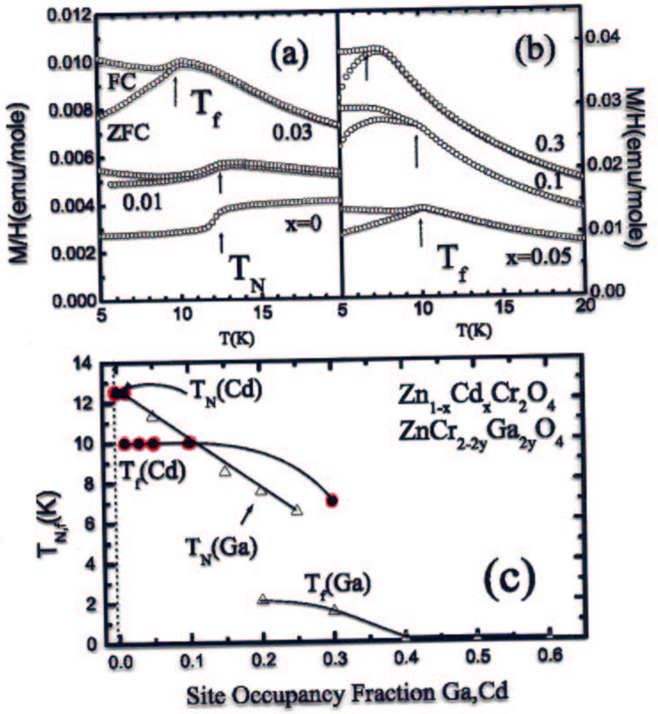
Enhanced symmetry of average structure of $CuIr_2S_4$ with cooling:

possibly due to x-ray-induced nematic-like phase?

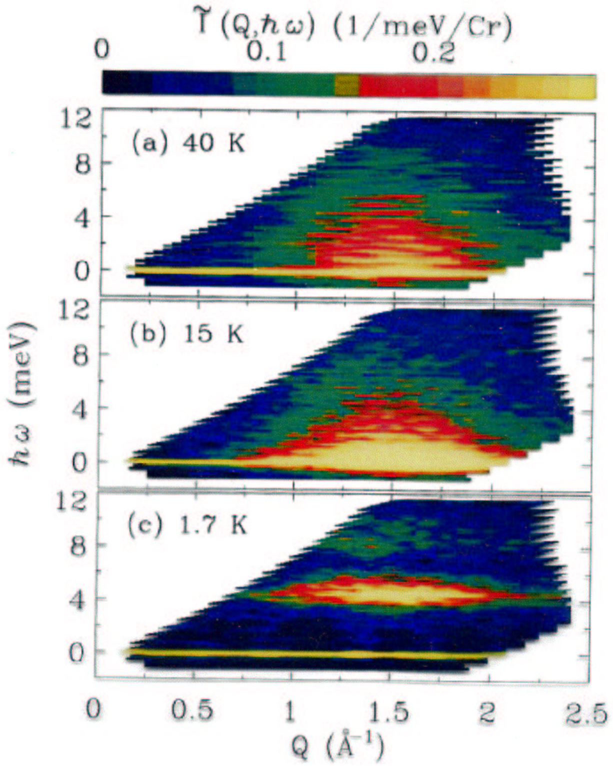
i.e., octamers are disordered, but the orientation of octamers as well as the dimerization directions are maintained.

i.e., short-range translational ordering and long-range orientation ordering of octamers.

Spin freezing in Cd-doped $ZnCr_2O_4$



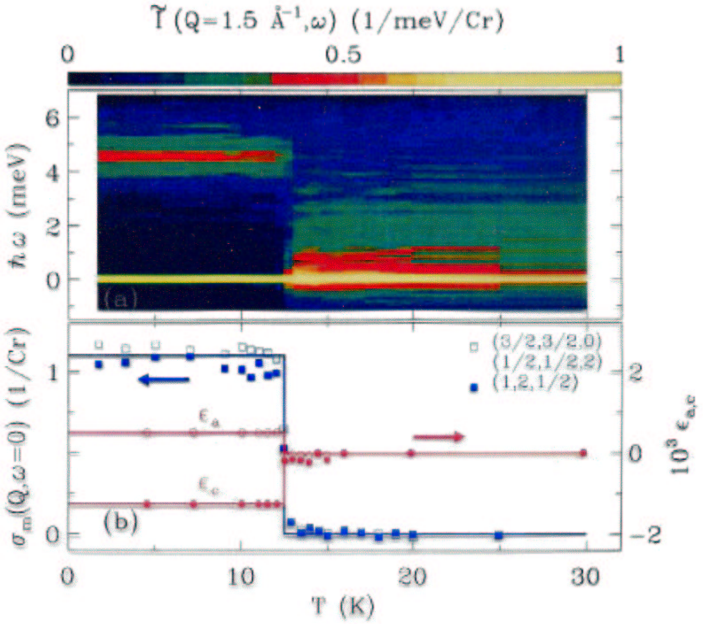
Magnetic neutron scattering near Q=1.5 Å^{-1} in *$ZnCr_2O_4$*

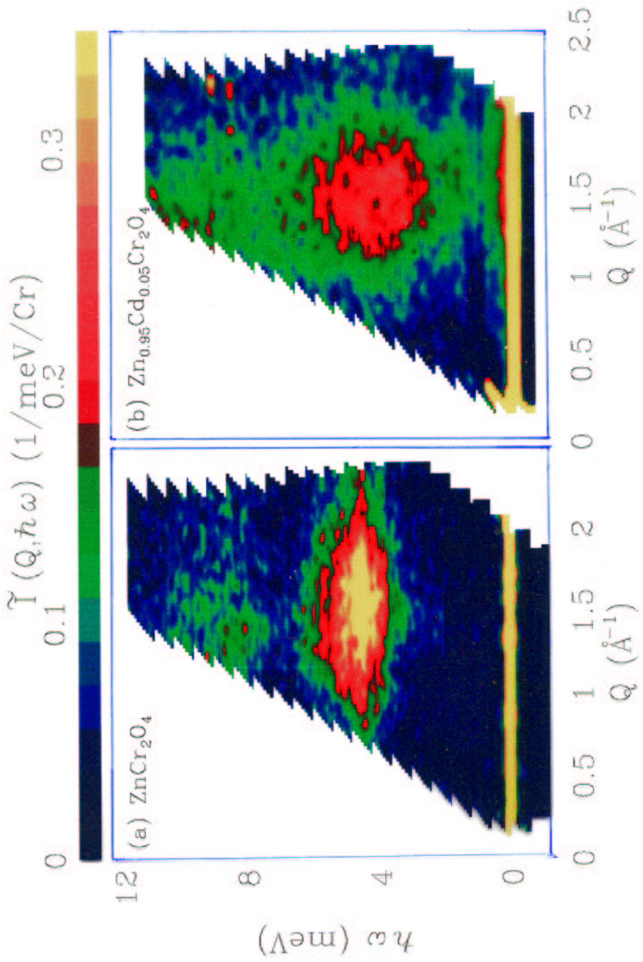


$ZnCr_2O_4$

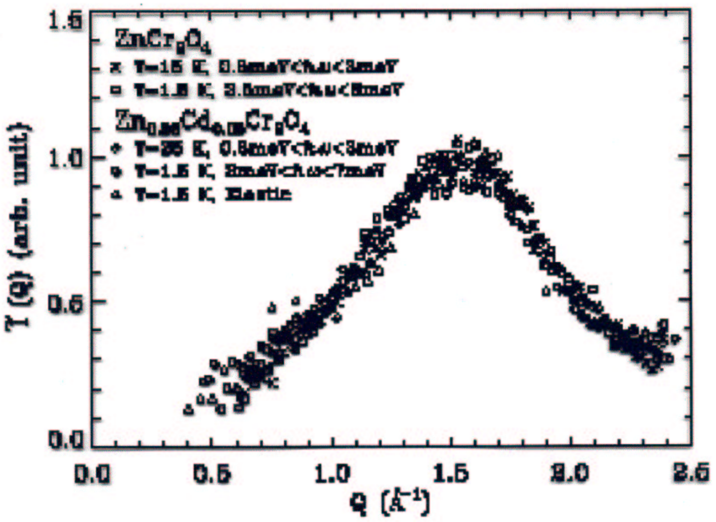
(a) Energy of inelastic magnetic scattering near Q=1.5Å^{-1} vs. Temp.

(b) Magnetic (elastic) Bragg scattering and lattice constants vs. Temp.





Magnetic neutron scattering near Q= 1.5 Å^{-1}

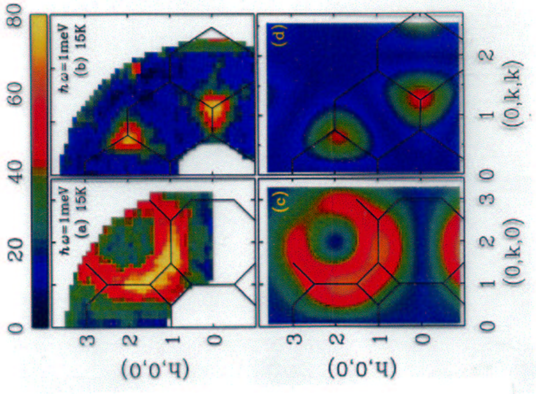


The magnetic feature:

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

⇒ Similar shape or configuration in real space

Hexamers in $ZnCr_2O_4$: geometrically frustrated magnet



Hexagonal spin loops dominate spin dynamics

Hexamer: antiferromagnetic hexagonal spin loop

Hexamers with four different orientations

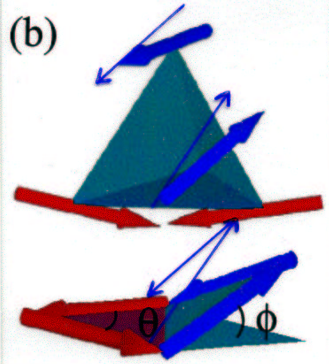
Hexamer form factor:

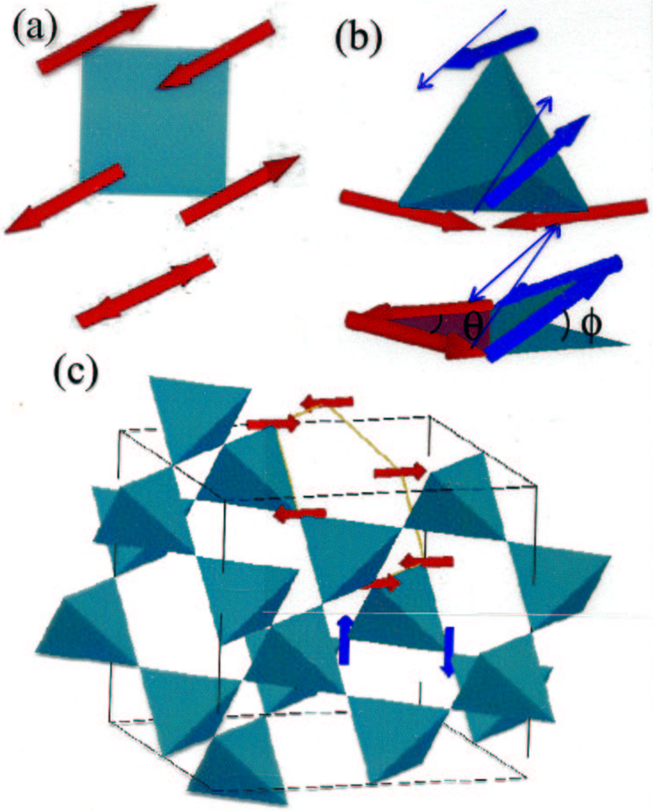
$$F_6(\mathbf{Q}) \propto \{\sin\frac{\pi}{2}h\cdot(\cos\frac{\pi}{2}k-\cos\frac{\pi}{2}l)\}^2 + \{\sin\frac{\pi}{2}k\cdot(\cos\frac{\pi}{2}l-\cos\frac{\pi}{2}h)\}^2 + \{\sin\frac{\pi}{2}l\cdot(\cos\frac{\pi}{2}h-\cos\frac{\pi}{2}k)\}^2$$

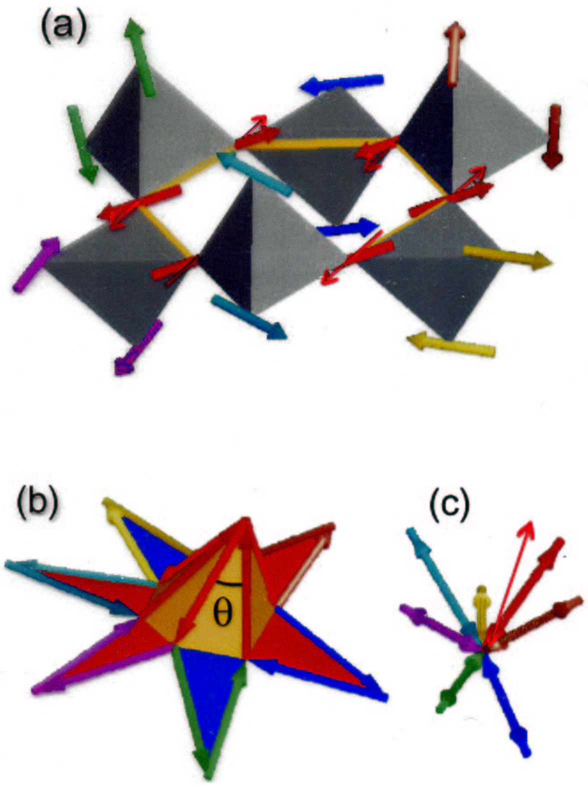
Magnetic neutron scattering intensity:

$I(\mathbf{Q}) = |\mathbf{F}_6(\mathbf{Q})|^2|f(Q)|^2$,

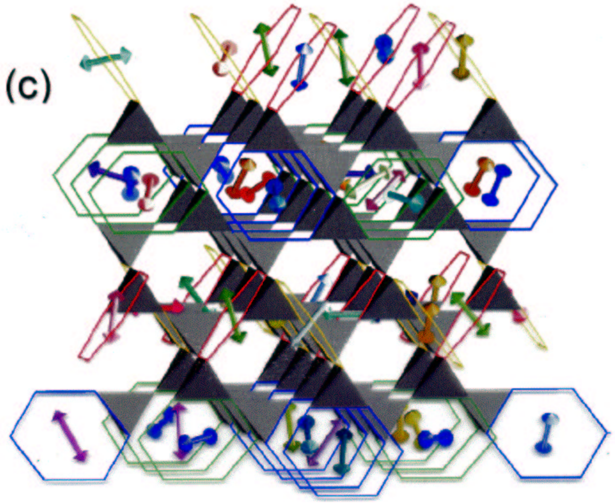
where f(Q) is the Cr^{3+} magnetic form factor.

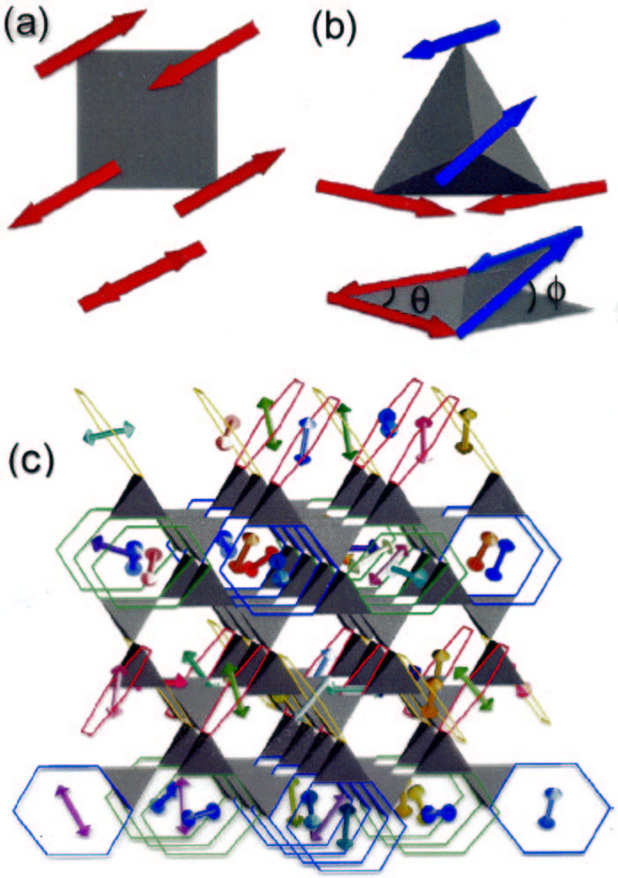

(b)
θ
ϕ


(a)
(b)
θ
ϕ
(c)

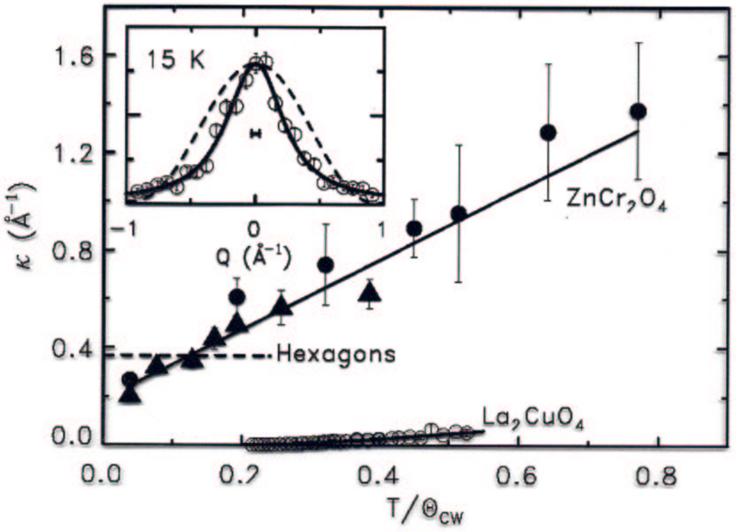


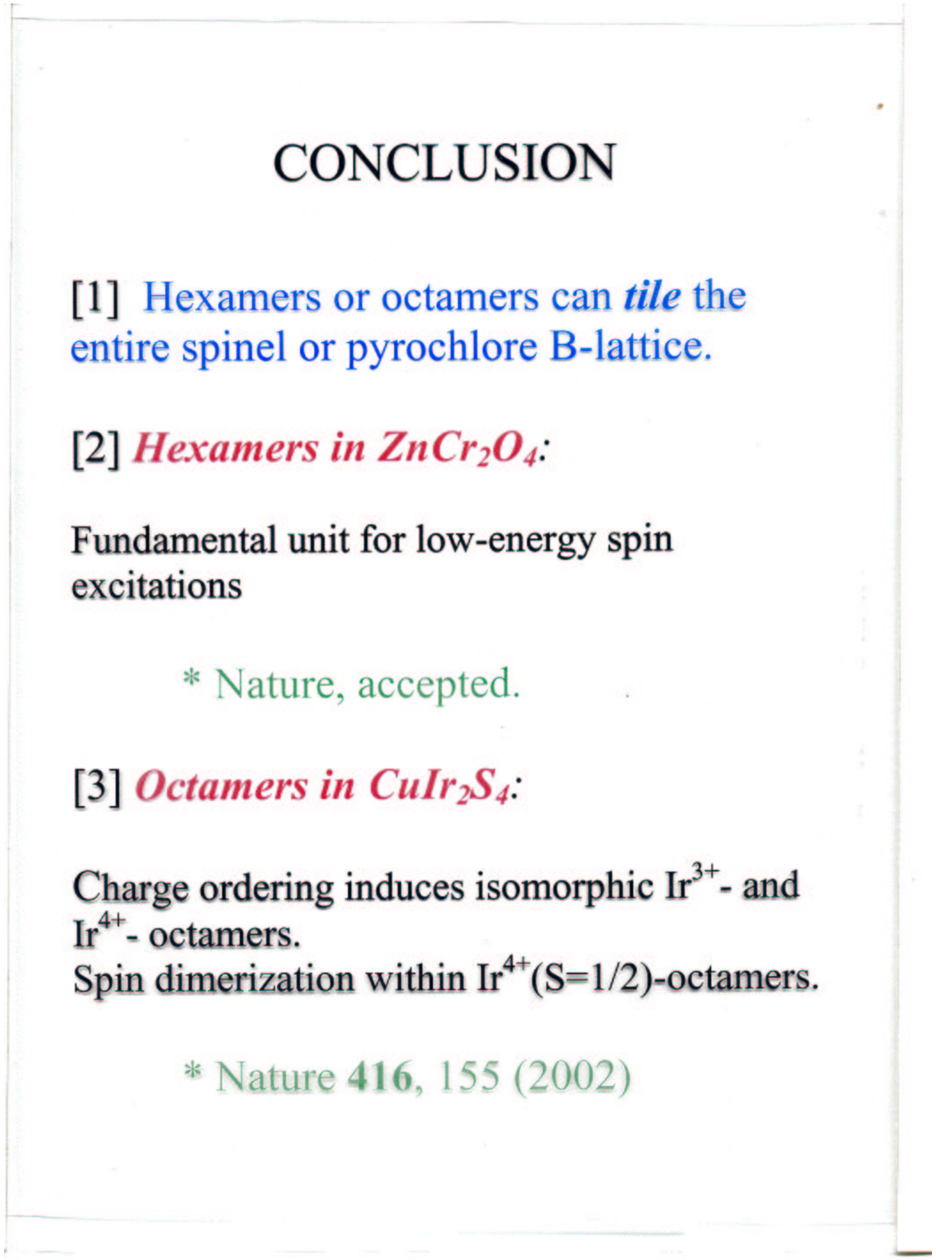
Collinear 6 spins in a hexamer can freely change the overall spin direction !





Magnetic correlation length (κ) vs. Temp. in ZnCr$_2$O$_4$





CONCLUSION

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

[2] ***Hexamers in $ZnCr_2O_4$***:

Fundamental unit for low-energy spin excitations

* Nature, accepted.

[3] ***Octamers in $CuIr_2S_4$***:

Charge ordering induces isomorphic Ir^{3+}- and Ir^{4+}- octamers.
Spin dimerization within Ir^{4+}(S=1/2)-octamers.

* Nature **416**, 155 (2002)