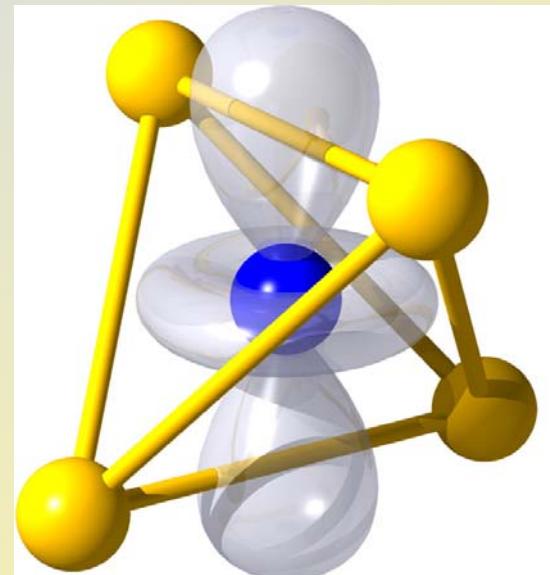
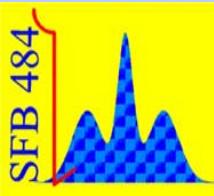


# Frustrated Lattices in Spinel Compounds

Alois Loidl

Center for Electronic Correlations and Magnetism,  
University of Augsburg, 86135 Augsburg, Germany





## Frustrated Lattices in Spinel Compounds

### Contents

- **Introduction**

- Spinel Systems

- Geometrical Frustration (GF)

- **GF at B-sites (the Pyrochlore Lattice)**

- GF in the insulating chromites: Spin-driven Jahn-Teller effect

- **Competing interactions at A-sites (the Diamond Lattice)**

- $\text{FeSc}_2\text{S}_4$ : a spin-orbital liquid

- $\text{MnSc}_2\text{S}_4$ : a spiral spin liquid

- Alumino spinels:  $\text{AAI}_2\text{O}_4$  ( $\text{A} = \text{Mn, Fe, Co}$ )

- **Summary and Conclusions**

Coworkers:

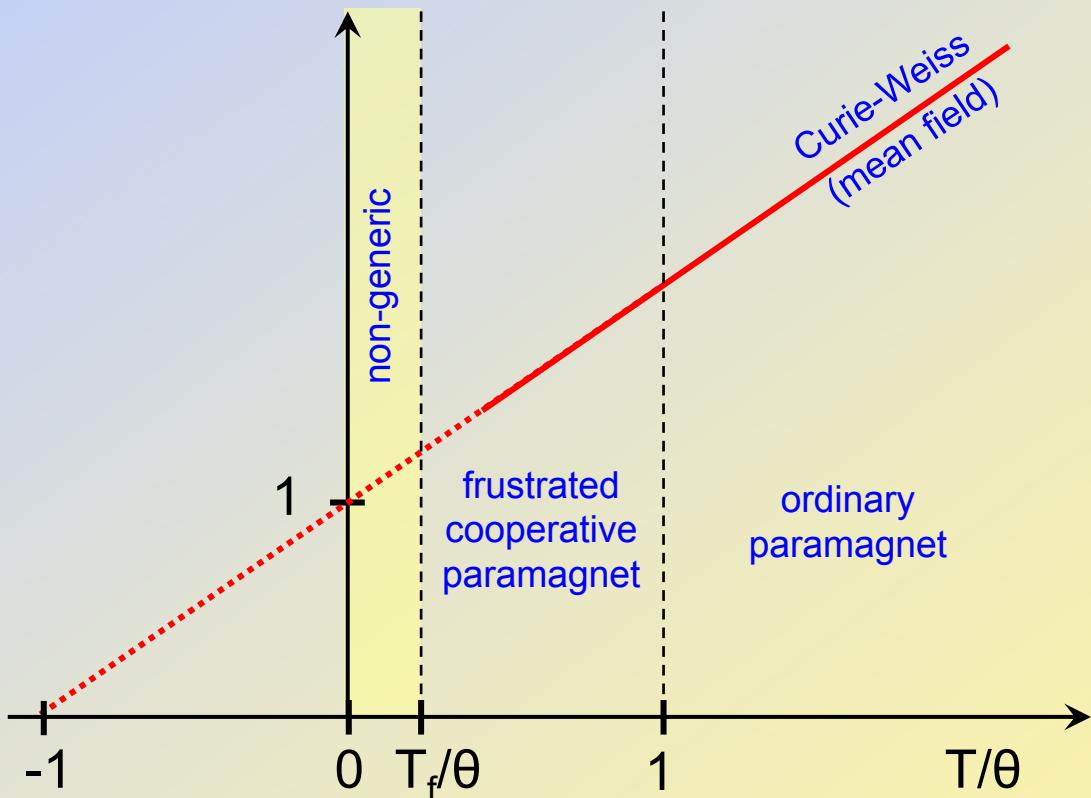
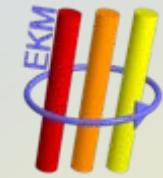
N. Büttgen, V. Fritsch, J. Hemberger,

Ch. Kant, A. Krimmel, H.-A. Krug von Nidda,

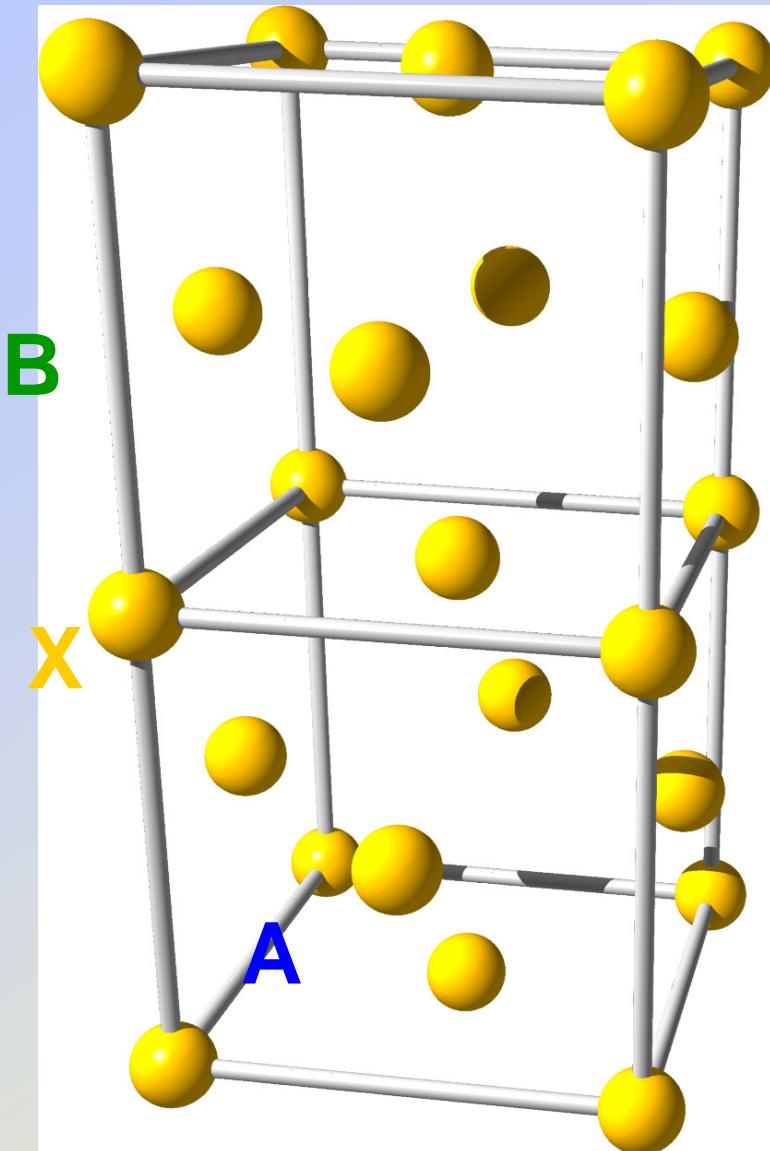
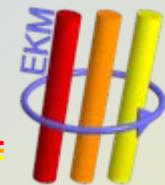
P. Lunkenheimer, T. Rudolf, N. Tristan, V. Tsurkan



# Geometric frustration of spin degrees of freedom

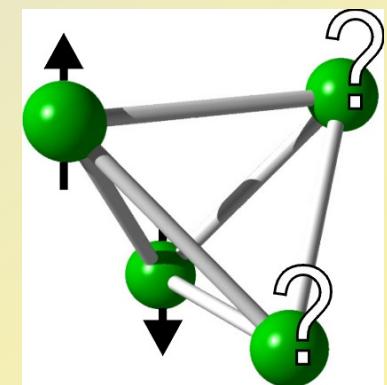
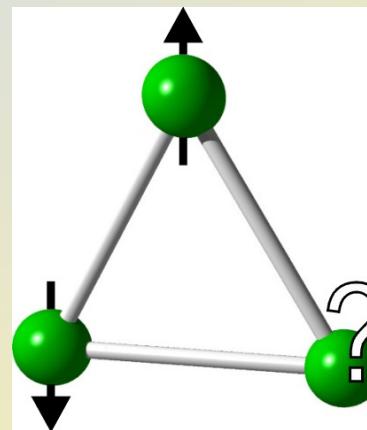


# $\text{AB}_2\text{X}_4$ : The structure of spinels



$\text{AB}_2\text{X}_4$  – normal spinel  
(e.g.  $\text{CdCr}_2\text{S}_4$ ,  $\text{HgCr}_2\text{S}_4$ ,  $\text{FeCr}_2\text{S}_4$ )

B-site: Pyrochlore - lattice  
Geometrically frustrated!



A-site: Diamond lattice  
Frustration via competing interactions!

# $\text{AB}_2\text{X}_4$ : Electronic configuration

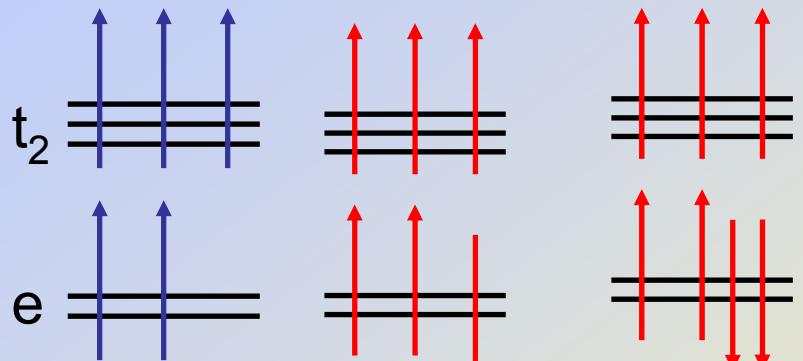


$\text{MnB}_2\text{X}_4$      $\text{FeB}_2\text{X}_4$      $\text{CoB}_2\text{X}_4$

$\text{Mn}^{2+}(3d^5)$   
 $S=5/2$

$\text{Fe}^{2+}(3d^6)$   
 $S=2$

$\text{Co}^{2+}(3d^7)$   
 $S=3/2$



Half filled    JT active

weak SO  
coupling

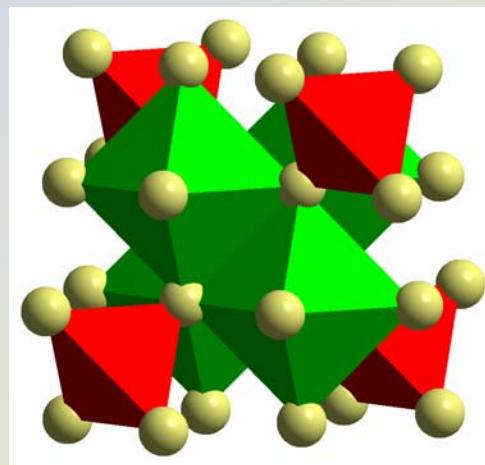
A-sites: tetrahedrally coordinated

Diamond Lattice

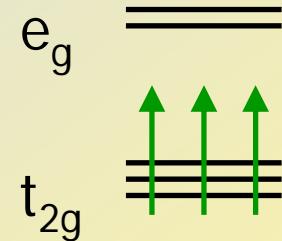
B = Sc, Al

X = O, S

B-sites  
octahedrally  
coordinated



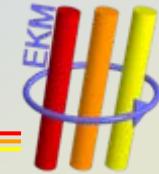
Pyrochlore Lattice



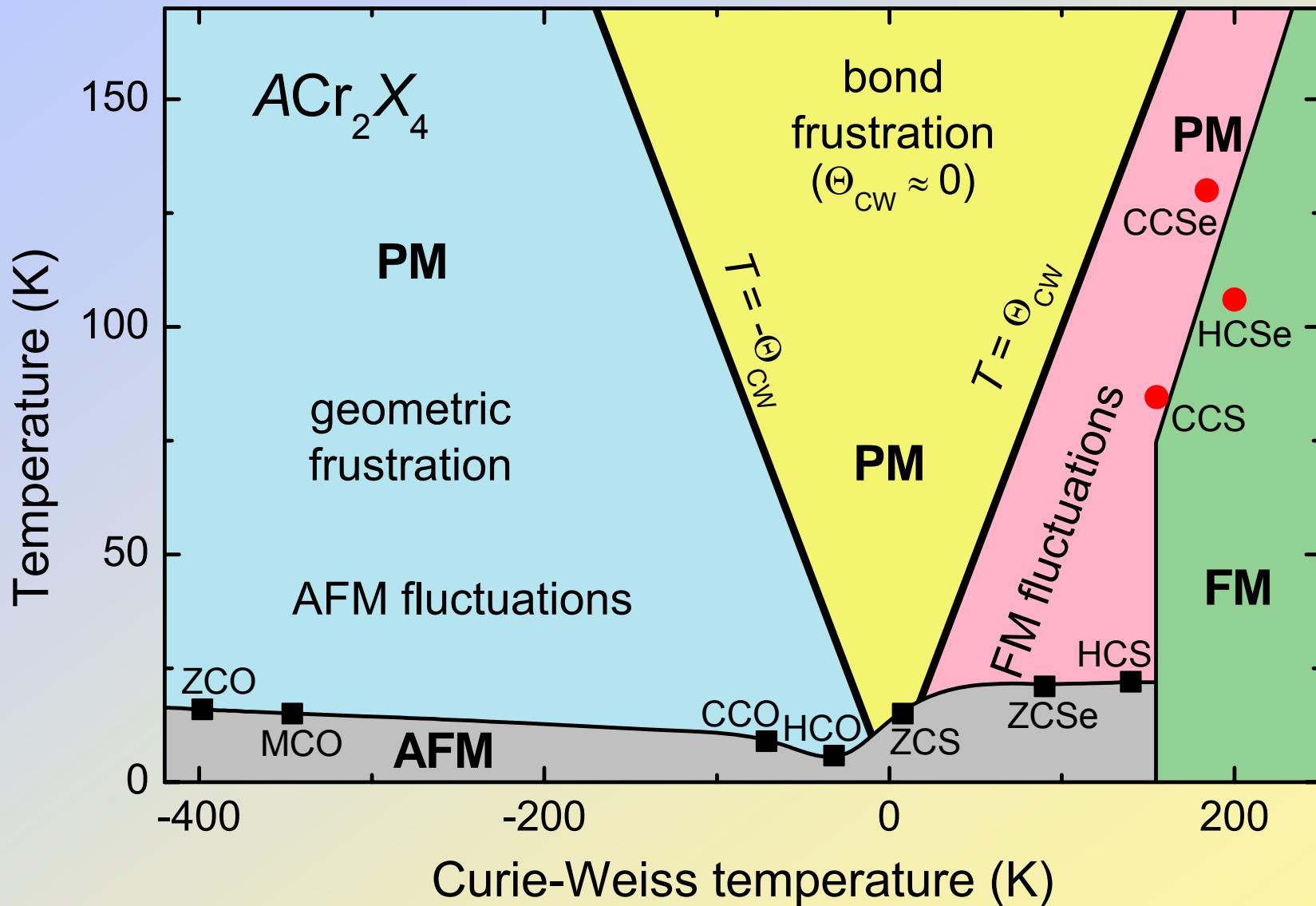
$\text{Cr}^{3+}(3d^3), J=3/2$   
No spin-orbit coupling!

$\text{ACr}_2\text{X}_4$   
A = Zn, Cd, Hg  
X = O, S, Se

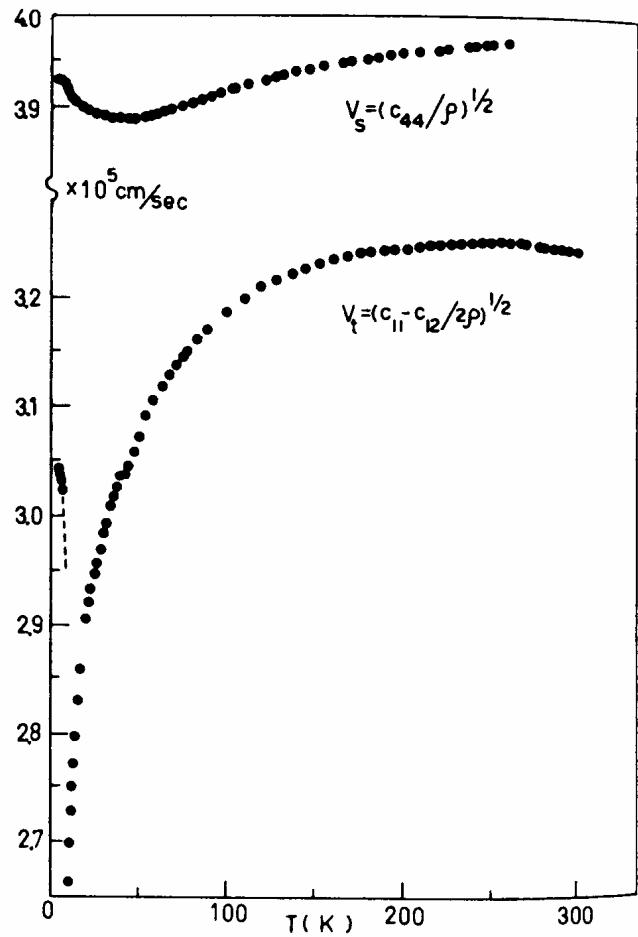
# Chromite spinels: Phase diagram



Rudolf et al., New J. Physics **9**, 76, 2007



# Cr-Spinels: Spin-driven Jahn-Teller effect



Spin-driven Jahn-Teller effect in chromite spinels  
( $\text{ZnCr}_2\text{O}_4$  and  $\text{CdCr}_2\text{O}_4$ )

Tchernyshyov *et al.*, Phys. Rev. Lett. **88**, 067203, 2002  
Yamashita and Ueda, Phys. Rev. Lett. **85**, 4960, 2000

Dynamic symmetry breaking in antiferromagnets:  
Splitting of phonon modes by magnetic exchange interactions, decoupled from lattice distortions  
(splitting of phonon modes even in cubic lattices)

Theory:

Massida *et al.*, Phys. Rev. Lett. **82**, 430, 1999  
Fennie and Rabe, Phys. Rev. Lett. **96**, 205505, 2006

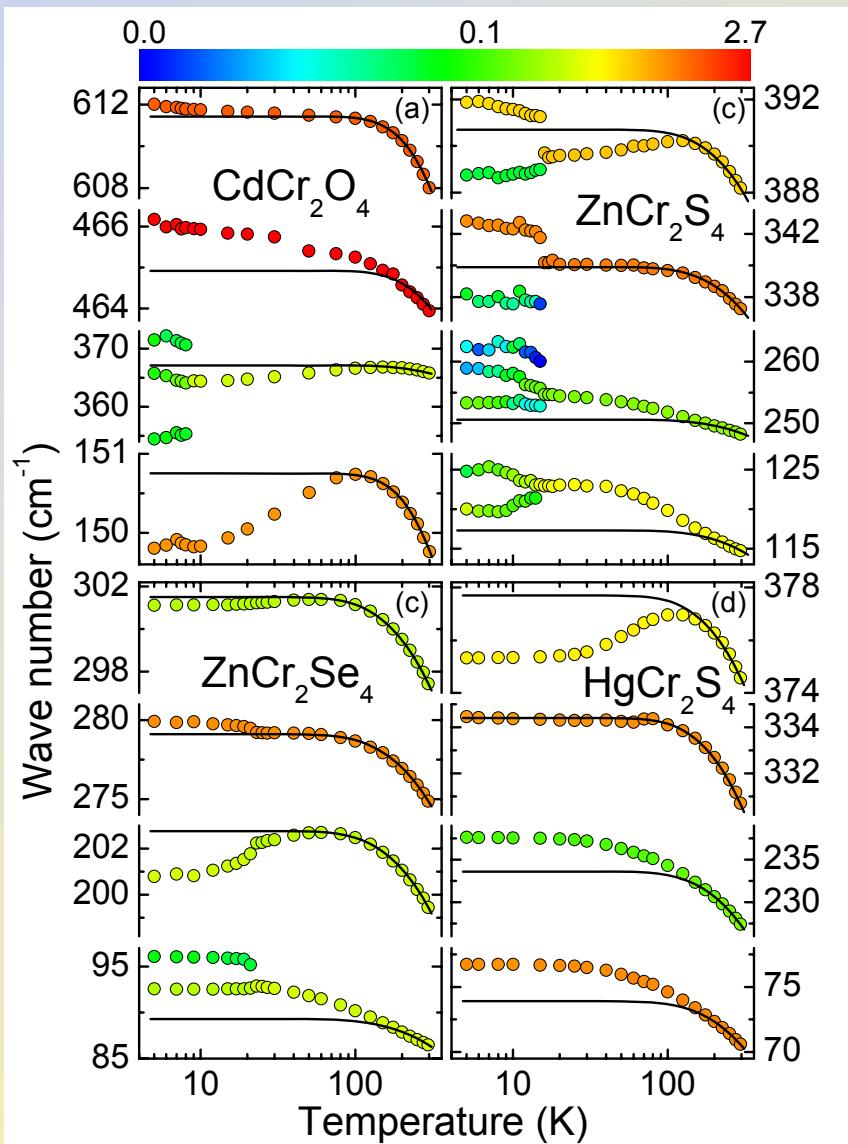
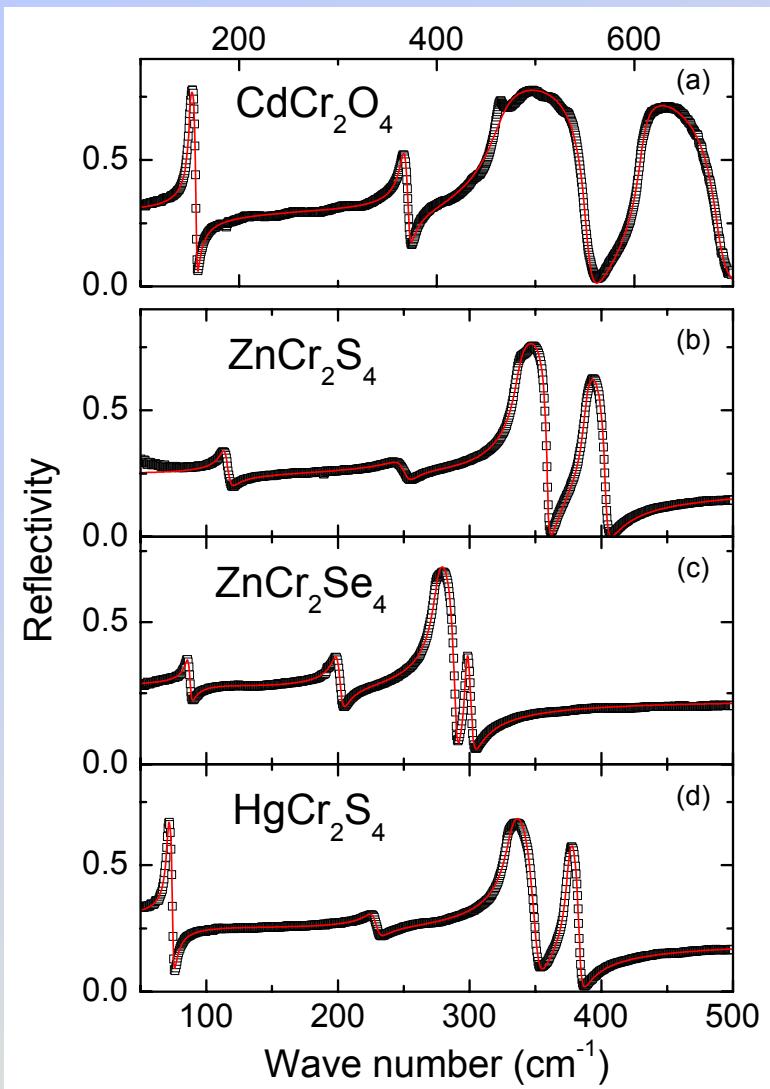
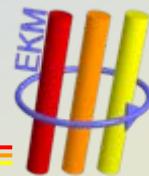
FIR experiments in  $\text{ZnCr}_2\text{O}_4$ :

Sushko *et al.*, Phys. Rev. Lett. **94**, 137202, 2005

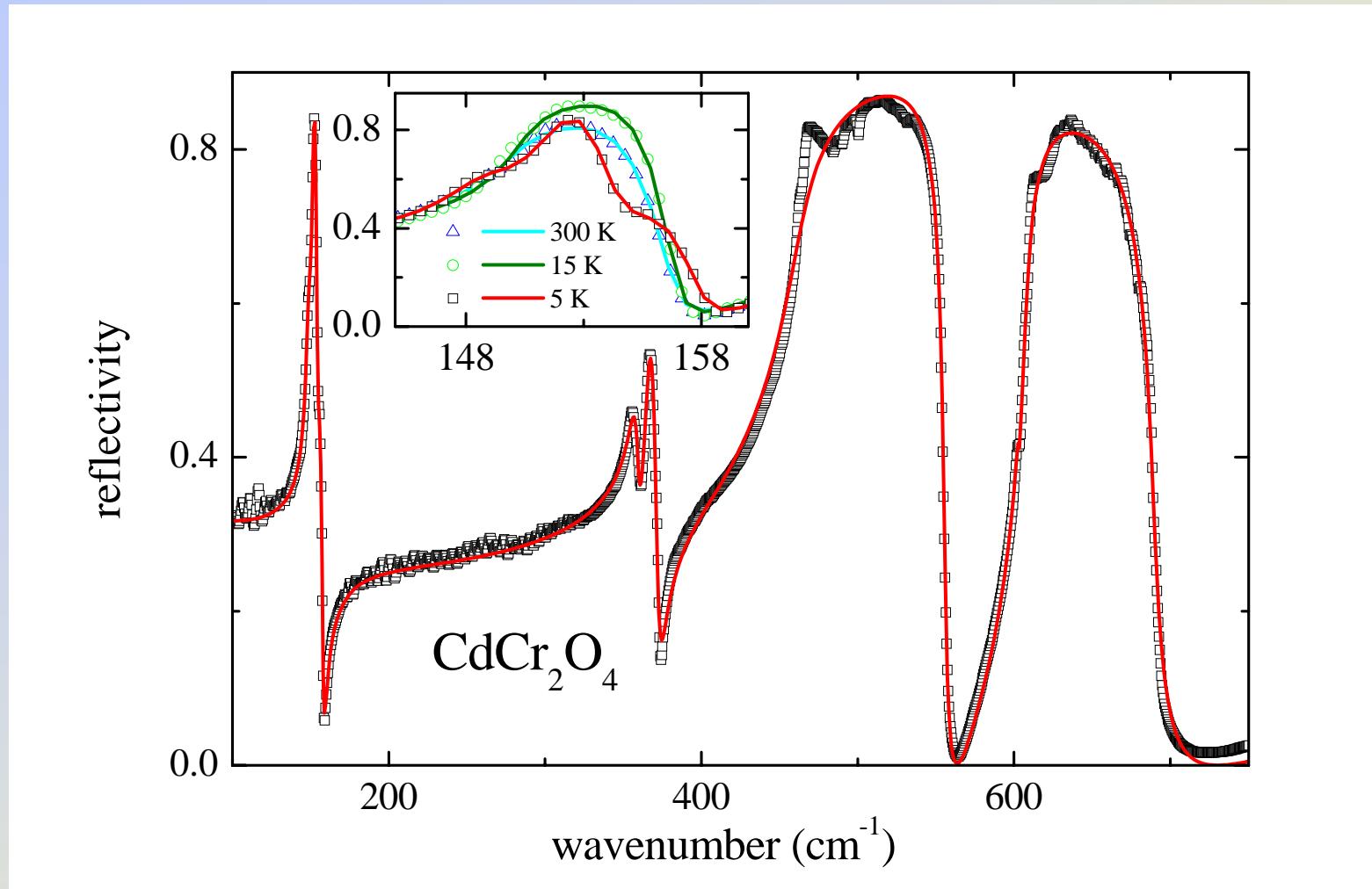
Softening of elastic constants in  
 $\text{ZnCr}_2\text{O}_4$  at magnetic phase transition

Kino and Lüthi, Solid State Commun. **9**, 805, 1971

# Chromite spinels: Spin-phonon coupling

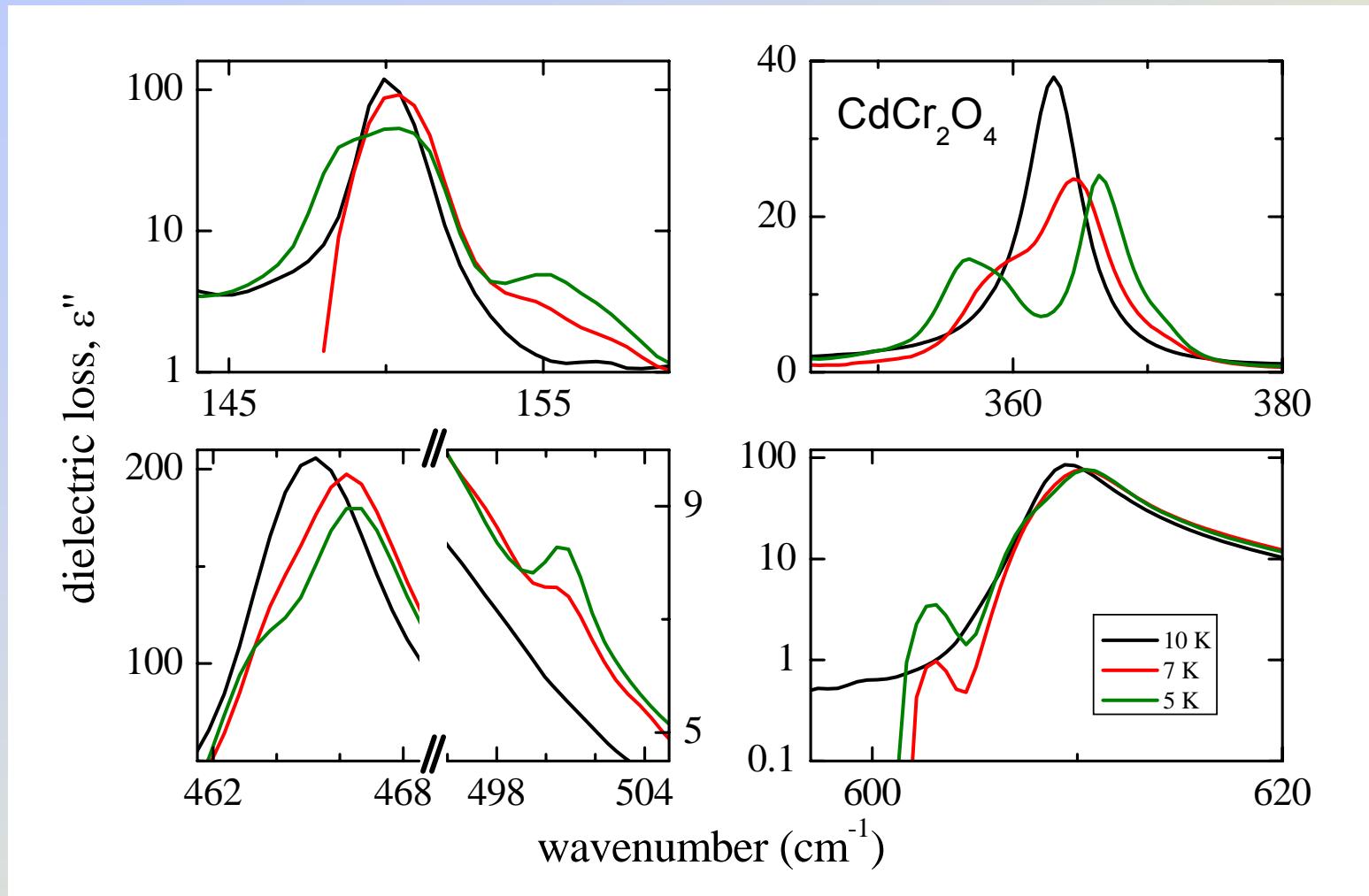
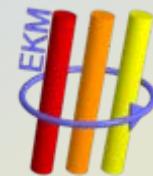


# Chromite spinels: Reflectivity $\text{CdCr}_2\text{O}_4$

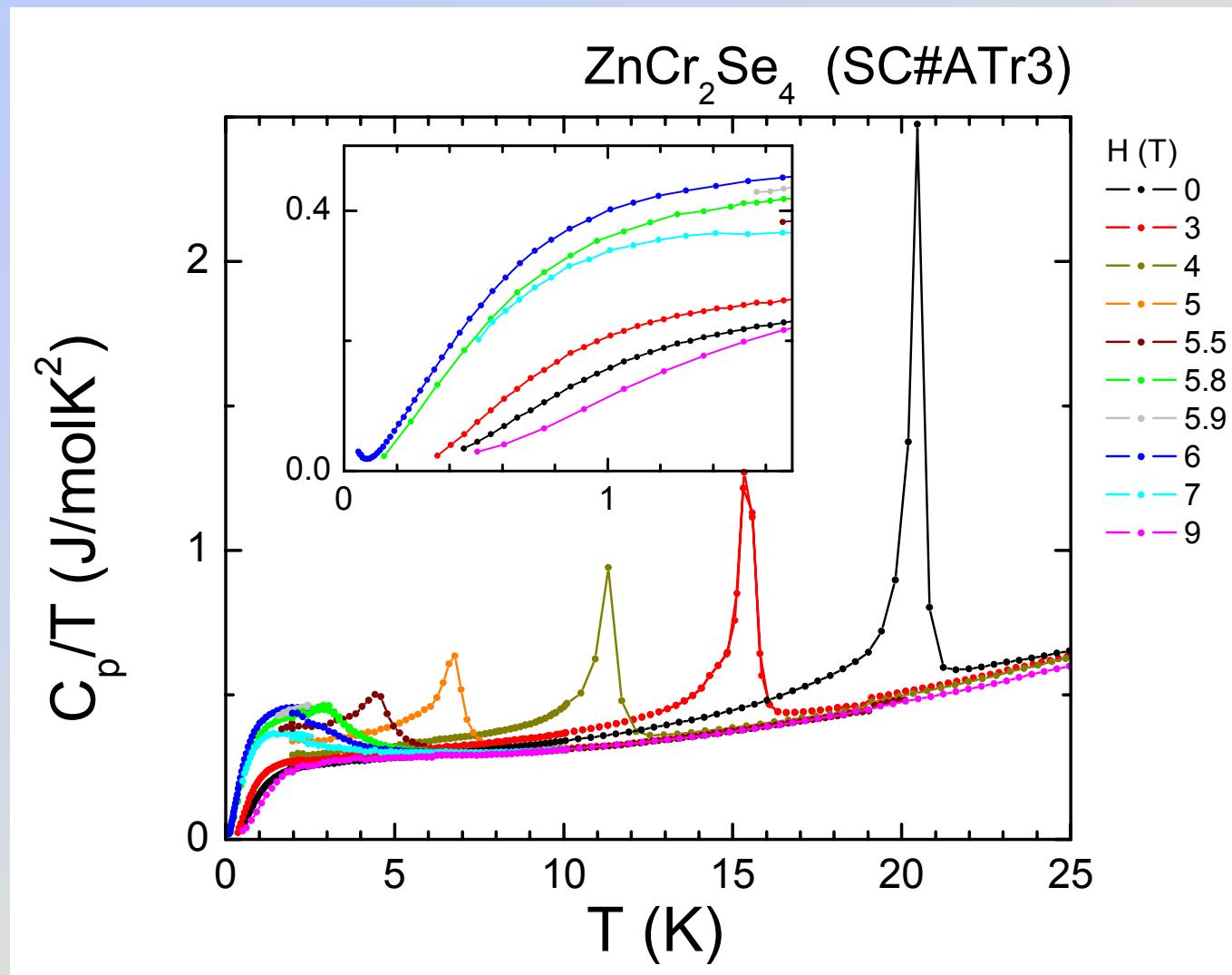


Rudolf *et al.*, unpublished

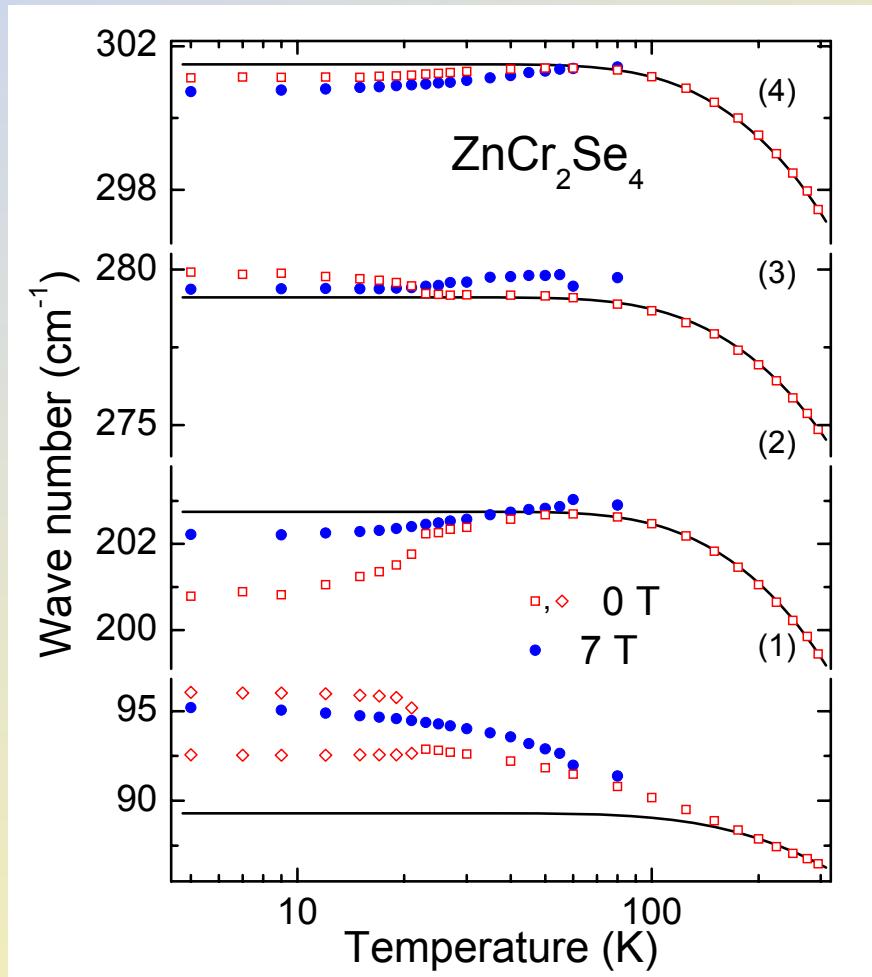
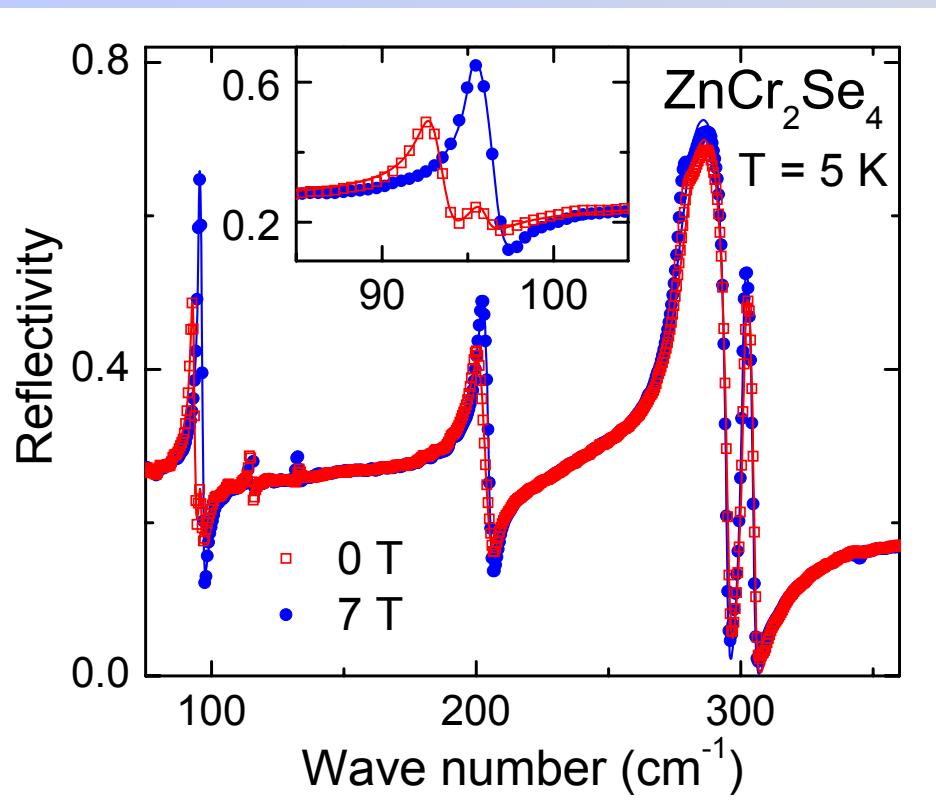
# Chromite spinels: Phonon splitting in $\text{CdCr}_2\text{O}_4$



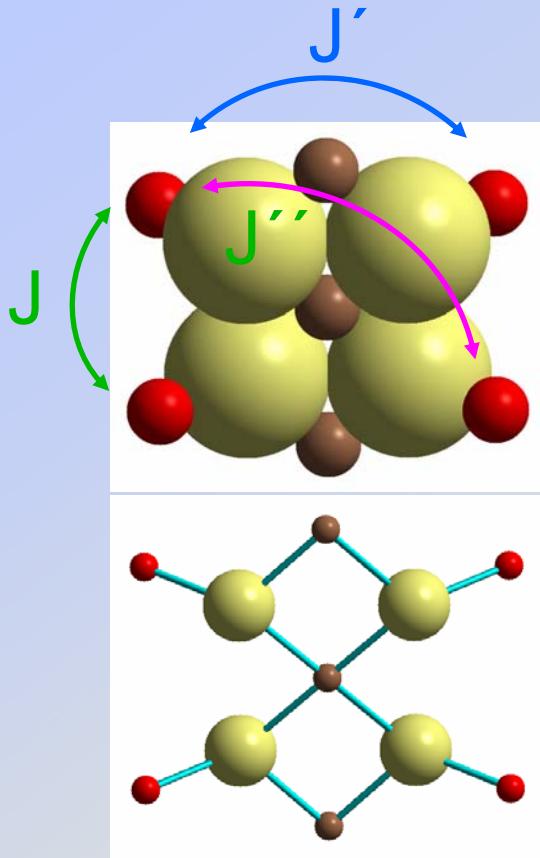
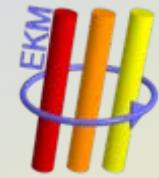
# ZnCr<sub>2</sub>Se<sub>4</sub>: Suppression of antiferromagnetic order



# $\text{ZnCr}_2\text{Se}_4$ : Magnetic-field dependence of spin-phonon coupling



# A-site magnetism: Competing interactions



$J$  and  $J''$  couple two fcc-sublattices ( $J_1$ )

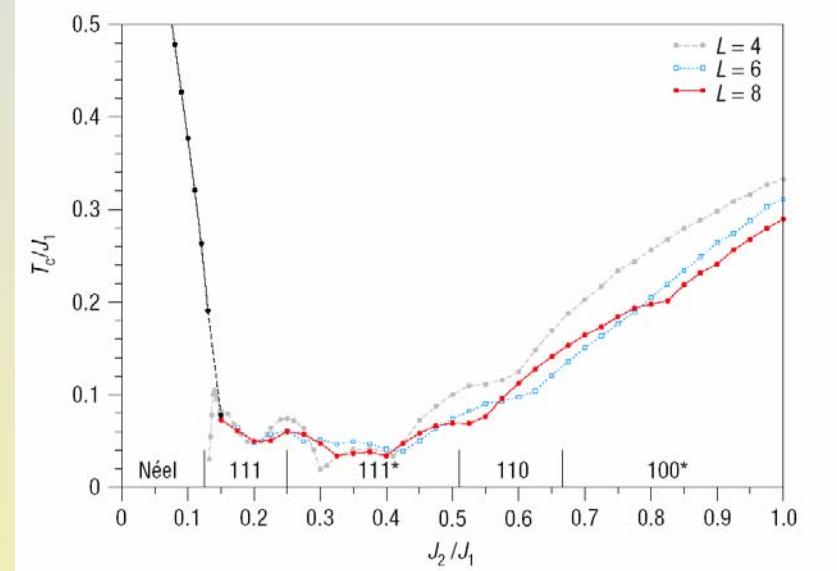
$J'$  exchange within one fcc-sublattice ( $J_2$ )

**Competing Interactions in Diamond Lattice**  
A-sites in spinels form diamond lattice which is bipartite: Two interpenetrating fcc lattices

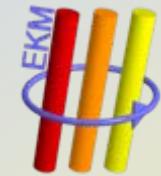
Depending on ratio  $J_2/J_1$ , strong frustration with complex magnetic ground states can occur:

Spiral Spin Liquid Phase

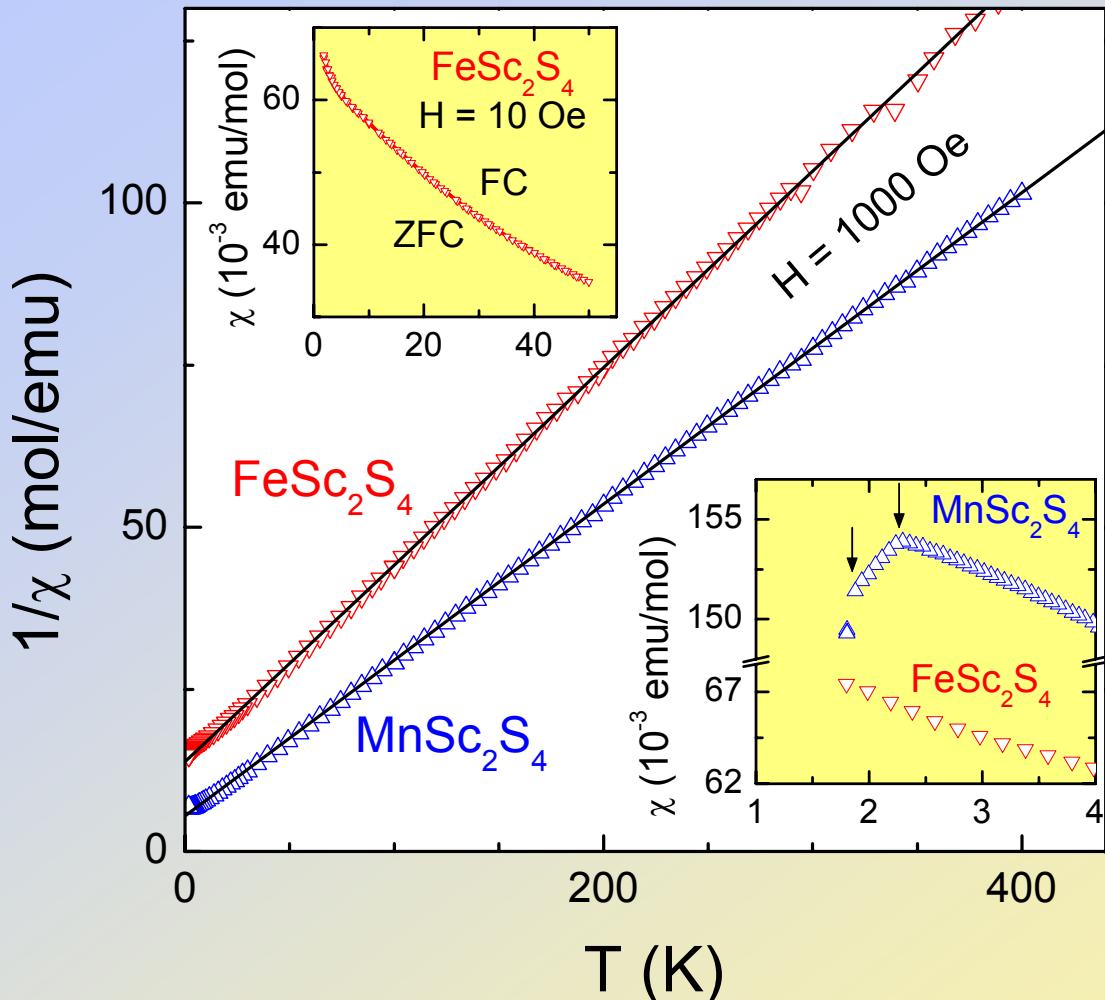
Bergman et al., Nature Physics 3, 487, 2007



# $\text{ASc}_2\text{S}_4$ (A = Fe, Mn): Spin Frustration



## Competing interactions on A-site: Diamond lattice



$\text{FeSc}_2\text{S}_4$ :  $\theta_{\text{CW}} = 50$  K  
 $T > 30$  mK:  
no long-range magnetic order  
no spin-glass

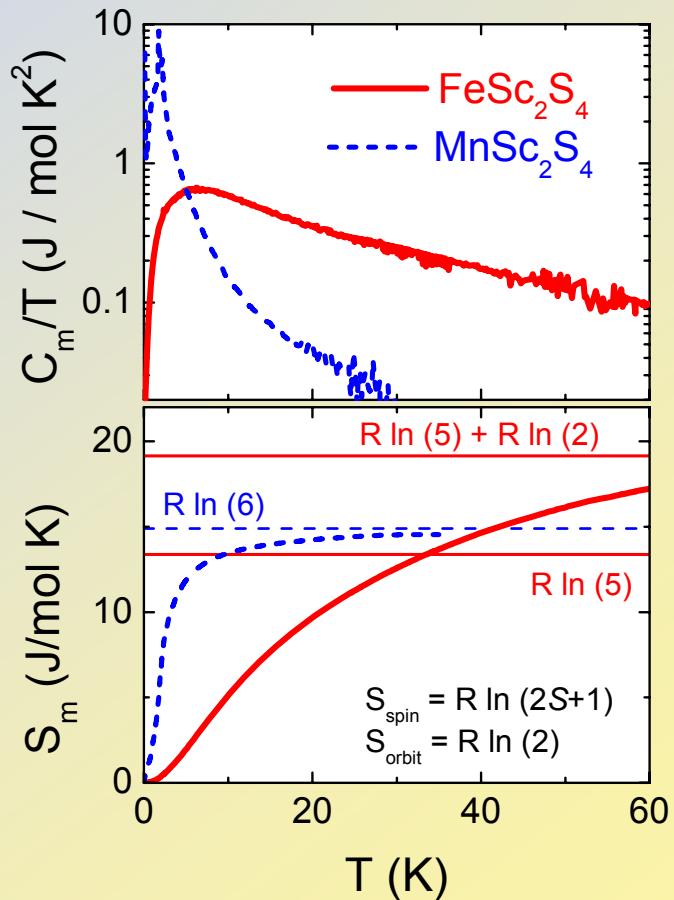
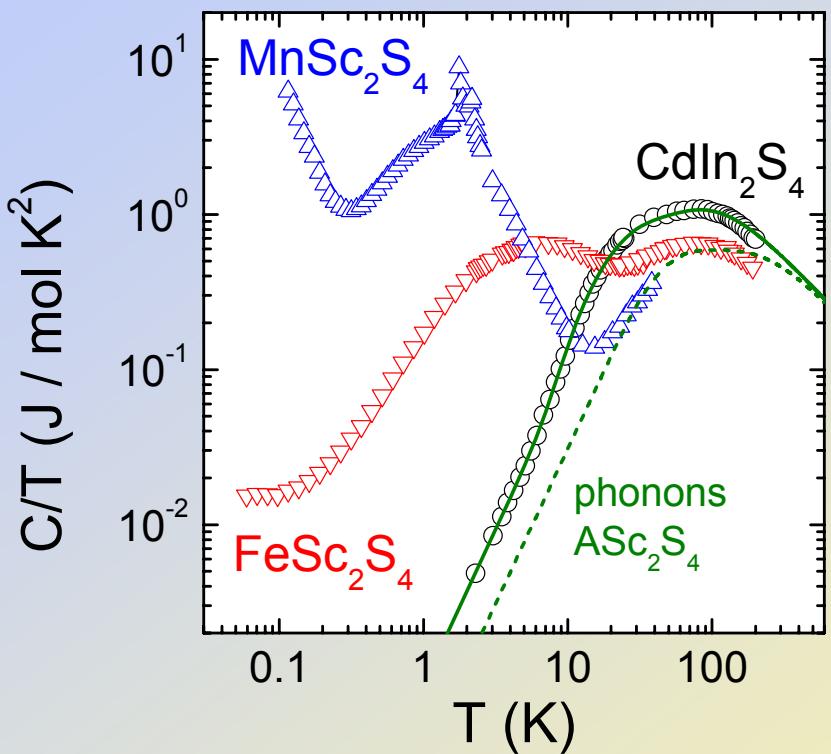
$\text{MnSc}_2\text{S}_4$ :  $\theta_{\text{CW}} = 25$  K  
AFM transition @ 2 K

# Specific heat in $\text{FeSc}_2\text{S}_4$ : Spin and orbital contributions



$\text{MnSc}_2\text{S}_4$ : Spin liquid for  $T < 20 \text{ K}$ ,  $T_N = 2 \text{ K}$

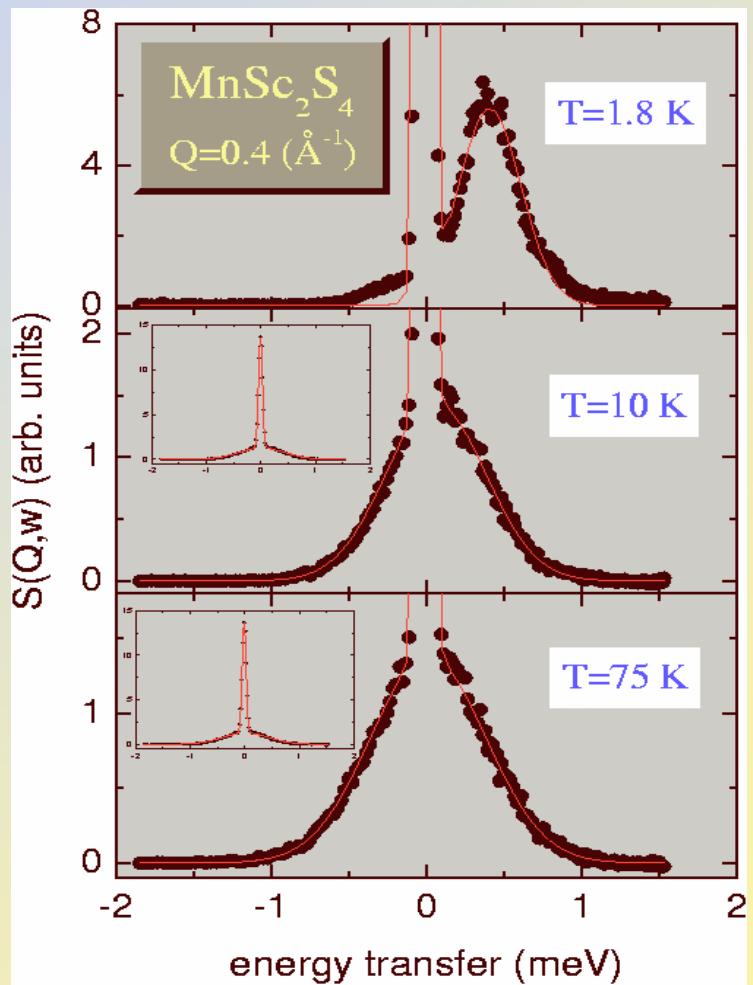
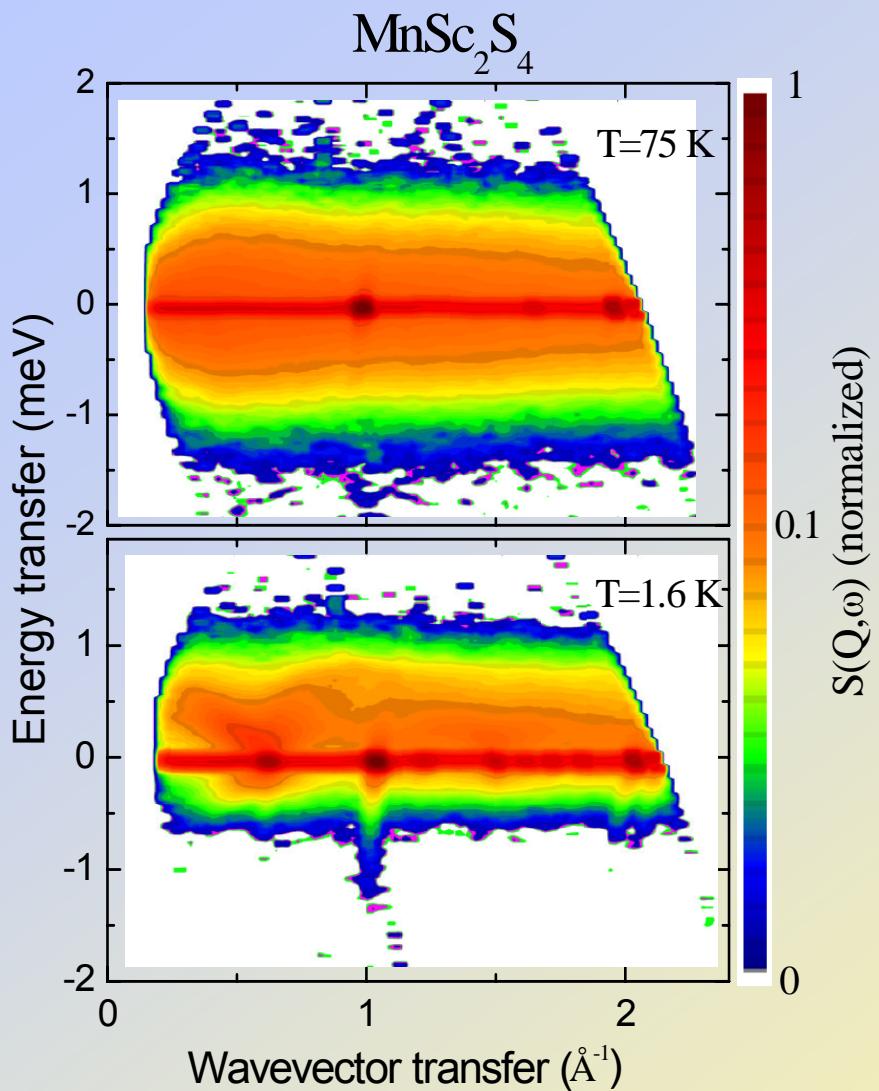
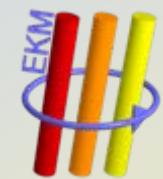
$\text{FeSc}_2\text{S}_4$ : Ground state - Spin liquid and orbital glass



$\text{FeSc}_2\text{S}_4$ : Spin and orbital contributions to specific heat and entropy

Fritsch *et al.*, PRL 92, 116401, 2004

# Neutron scattering: $\text{MnSc}_2\text{S}_4$



# Neutron scattering: $\text{MnSc}_2\text{S}_4$



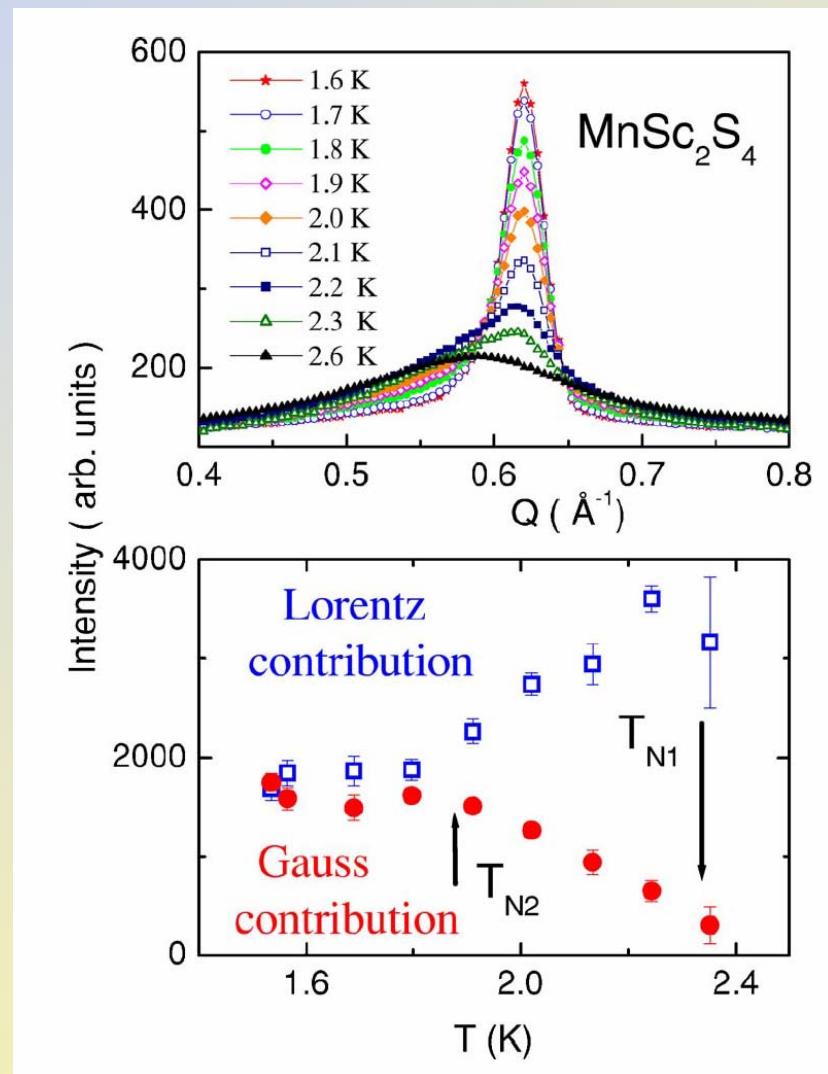
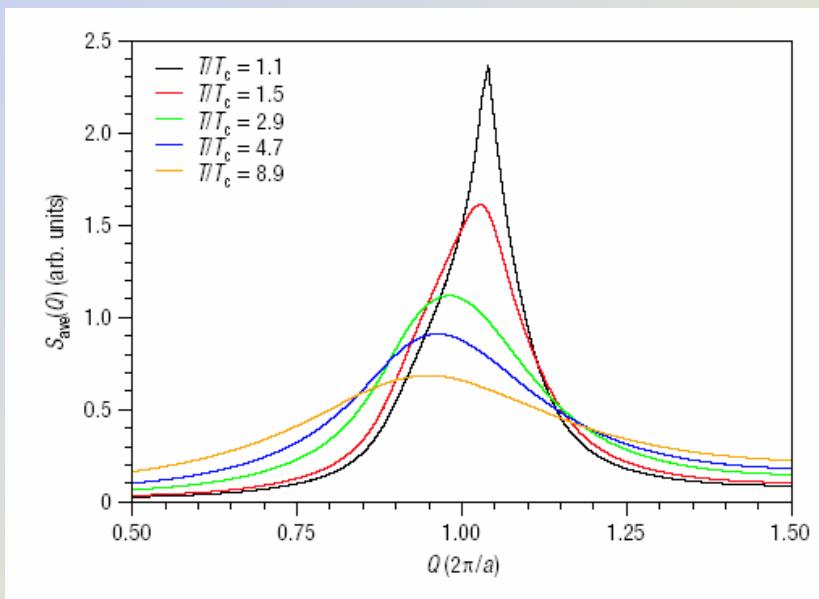
Diamond lattice is a bipartite lattice:

Only nearest neighbour coupling: No frustration!  
But strong frustration taking second nearest  
neighbours into account.

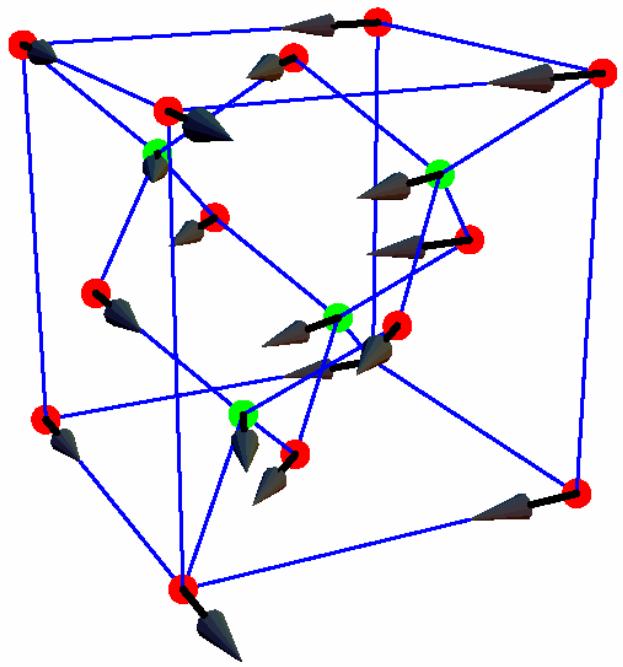
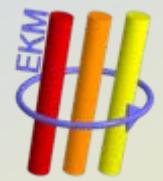
**Frustration results in a spin-spiral liquid:**

"ground state degeneracy develops amongst  
spin spirals whose propagation wave vectors  
reside on a continuous two-dimensional  
surface in momentum space"

Bergman *et al.*, Nature Physics 3, 487, 2007

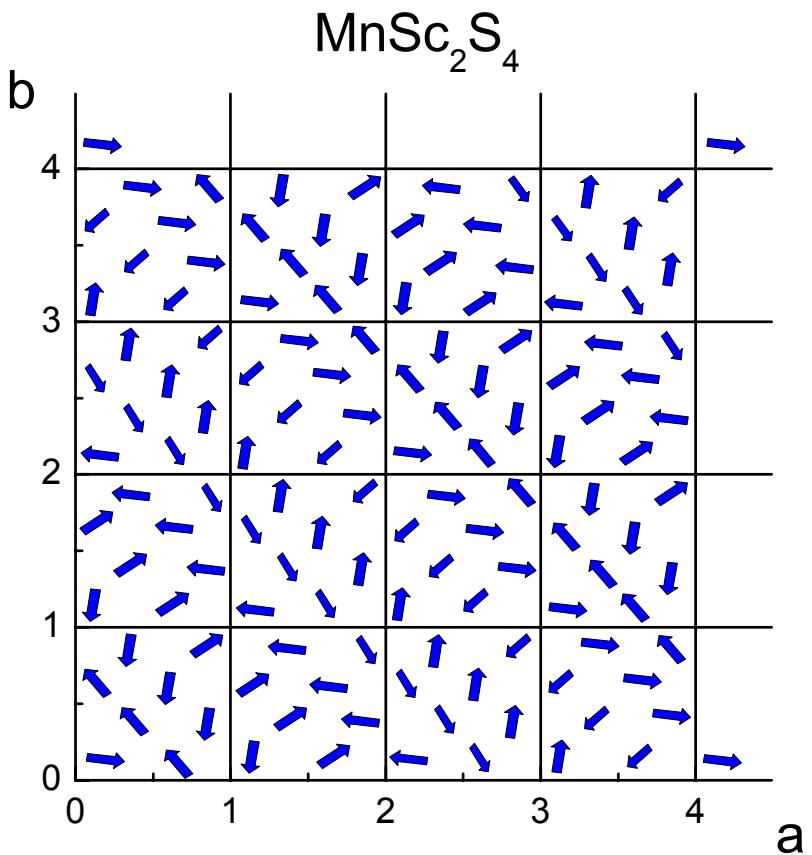


# MnSc<sub>2</sub>S<sub>4</sub>: Frustrated diamond lattice



At low temperatures:

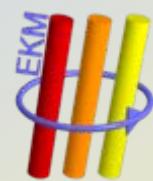
Order by disorder mechanism stabilizes  
long-range magnetic order



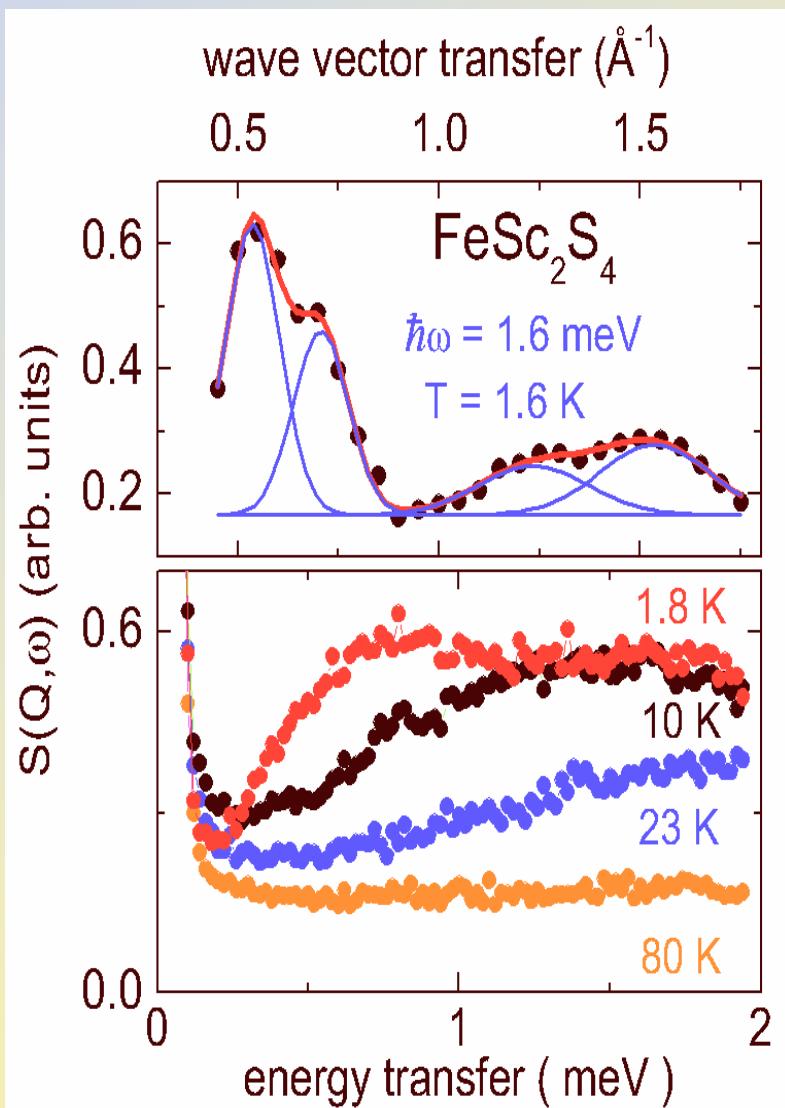
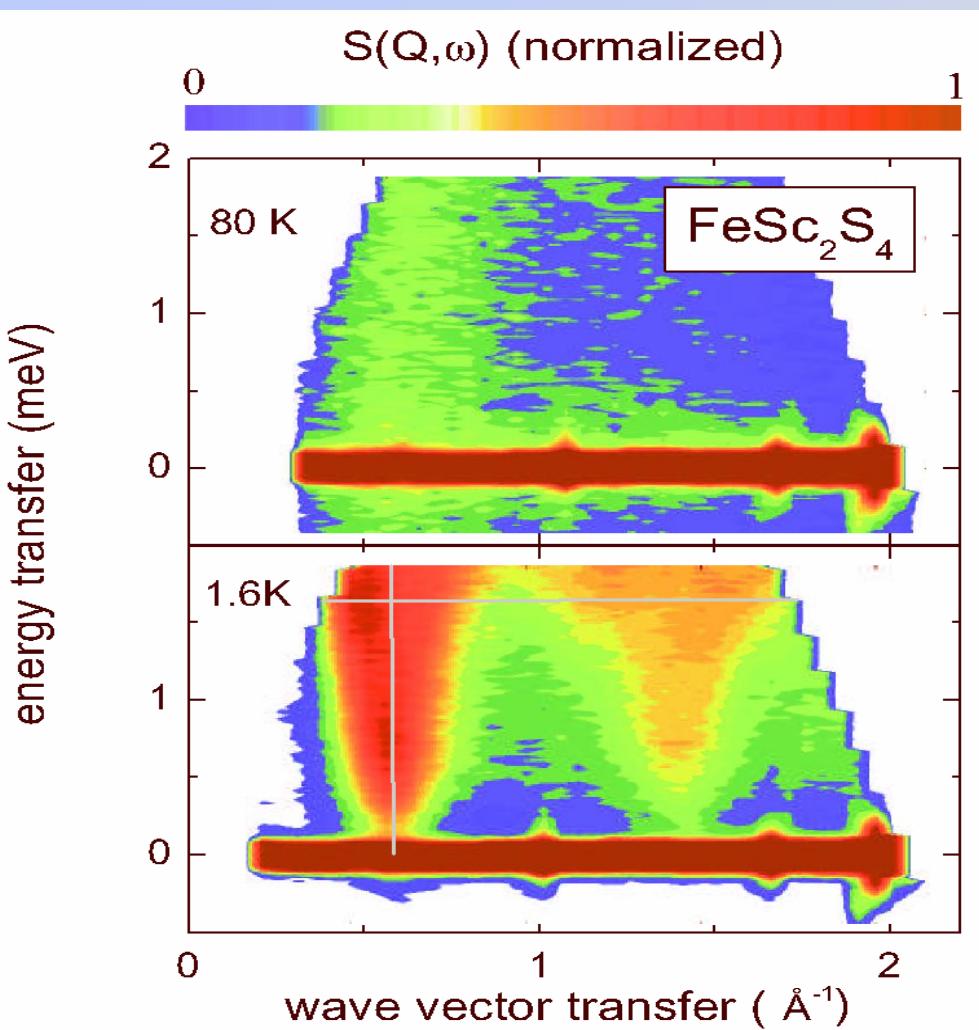
Krimmel *et al.* Phys. Rev. B **73**, 014413, 2006

Bergman *et al.*, Nature Physics **3**, 487, 2007

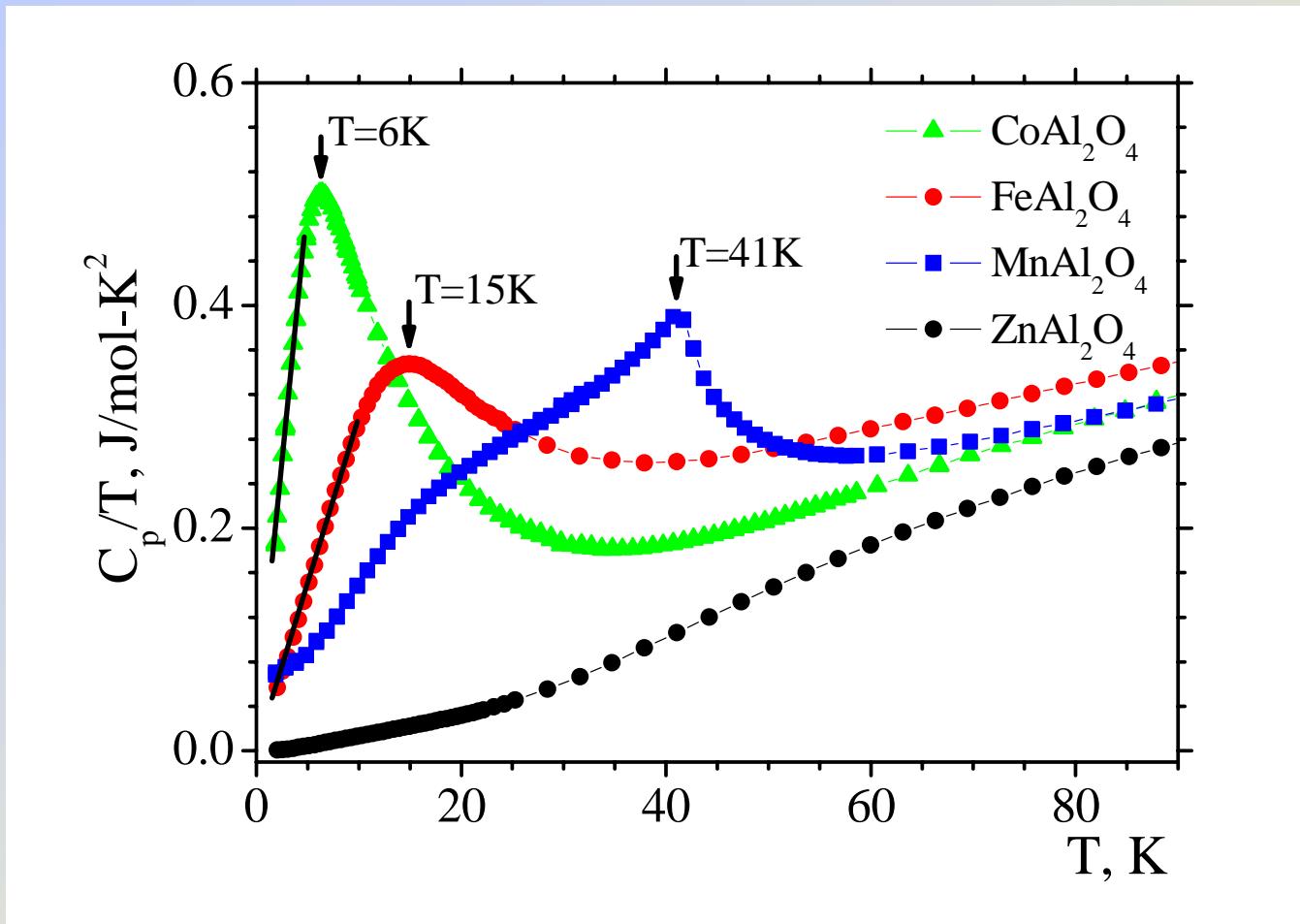
# Neutron scattering in $\text{FeSc}_2\text{S}_4$ : Spin liquid state



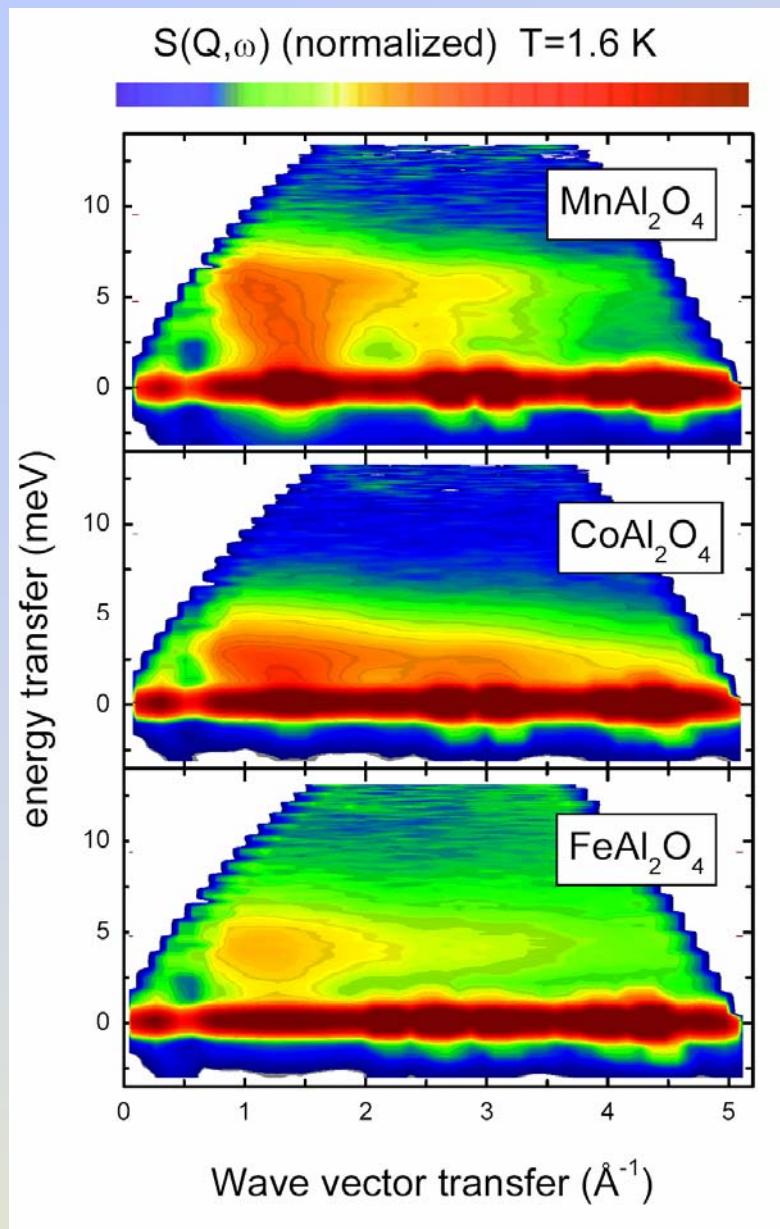
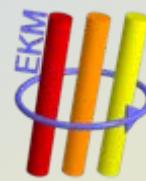
## Opening of a spin gap in $\text{FeSc}_2\text{S}_4$



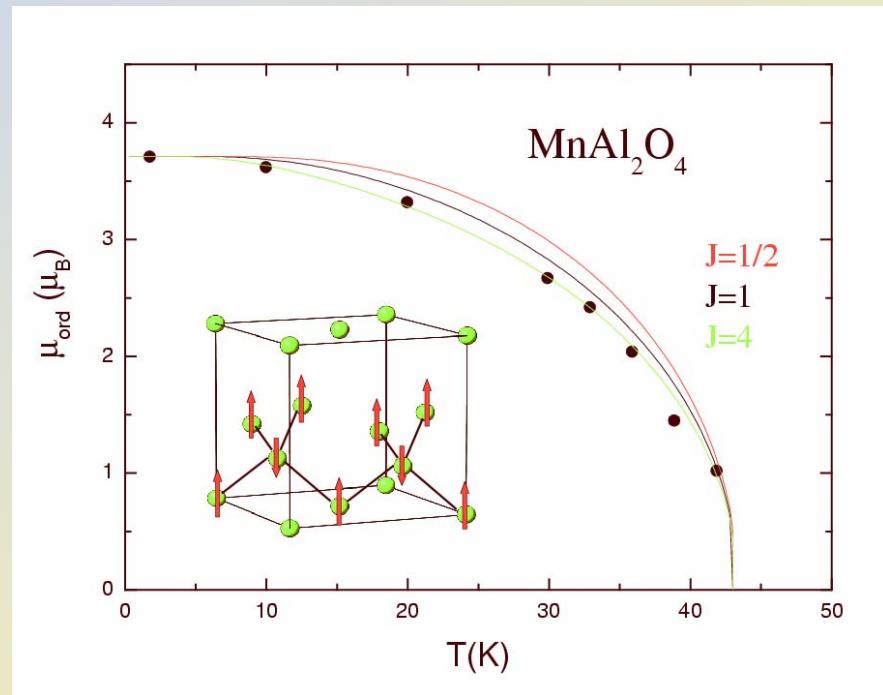
# Specific heat of Alumino Spinels: $\text{AAI}_2\text{O}_4$ ( $\text{A} = \text{Mn, Fe, Co}$ )



# Neutron scattering: $\text{AAI}_2\text{O}_4$ ( $\text{A} = \text{Mn, Fe, Co}$ )



$\text{MnAl}_2\text{O}_4$ : Long range spin order,  
spin-wave dispersion

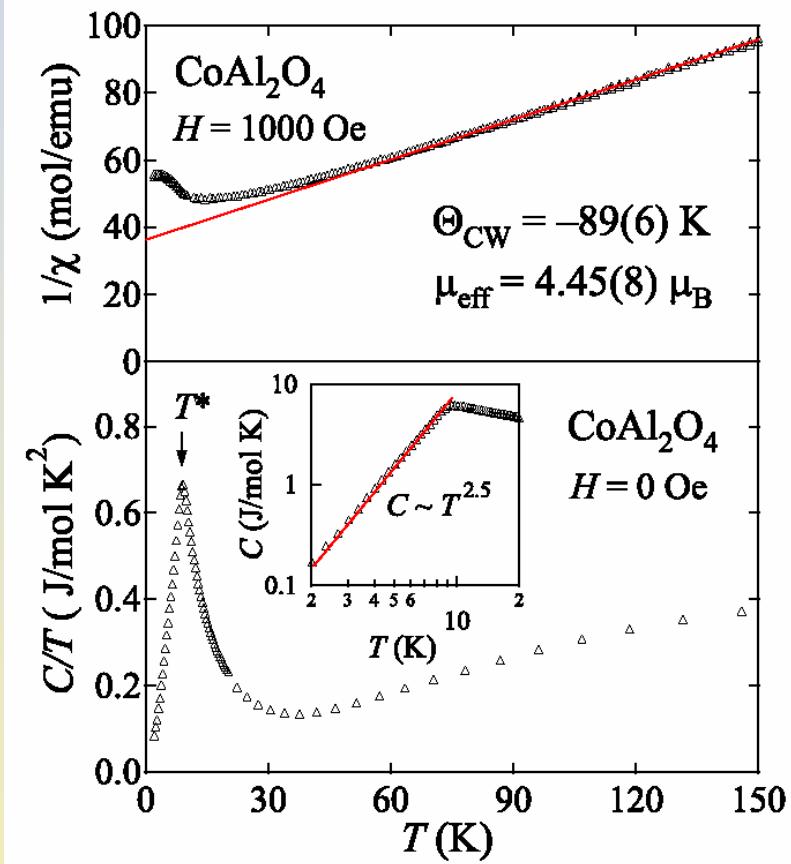
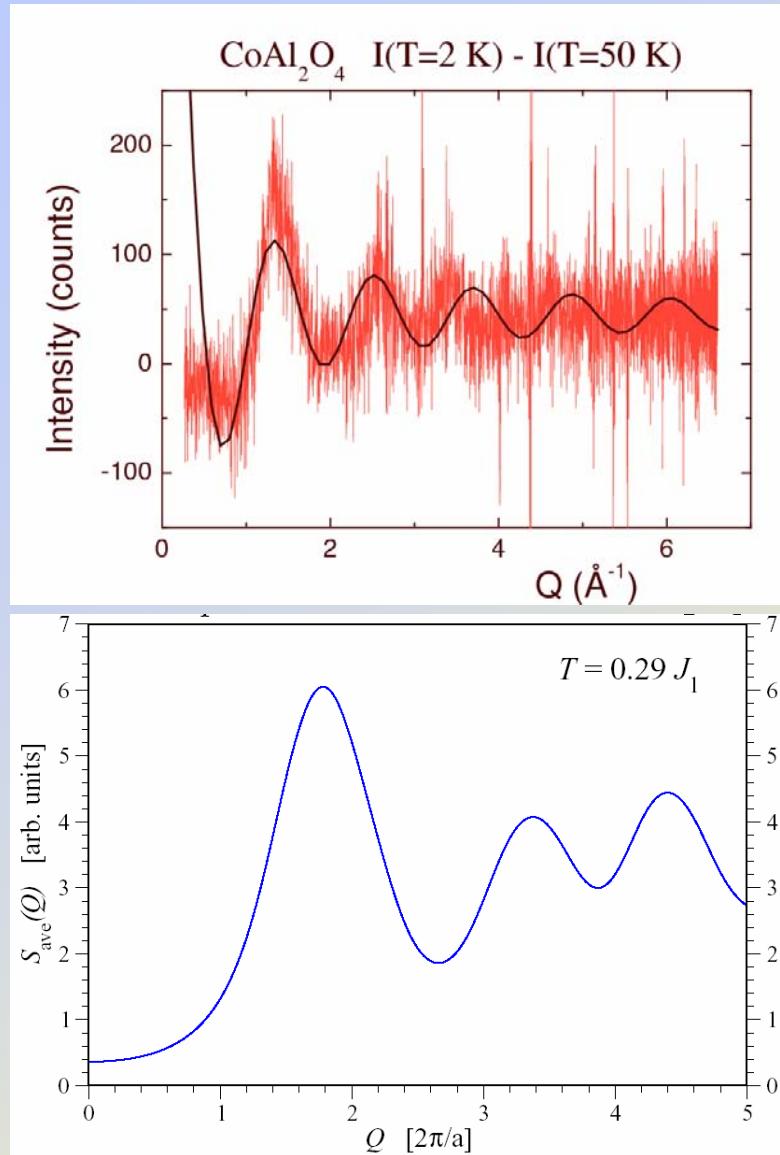


$\text{AAI}_2\text{O}_4$  ( $\text{A} = \text{Co, Fe}$ ):  
No long range spin order

# A-site spinels: $\text{CoAl}_2\text{O}_4$



**Structure factor  $\text{CoAl}_2\text{O}_4$ : Exp.: Krimmel et al. 2007; Theory: Bergman et al. 2006;**

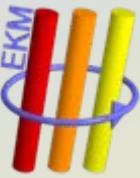


**Heat capacity:  $C \sim T^{2.5}$**

T. Suzuki *et al.*,  
J. Phys. Condens. Matter **19**, 145265, 2007

# Conclusion and Summary

---



**AB<sub>2</sub>X<sub>4</sub> spinels:**

A treasure chest for solid state physics and material science

**B-site pyrochlore lattice:**

**Geometrical Frustration**

The chromite spinels:

Spin-driven Jahn-Teller effect

**A-site diamond lattice:**

**Frustration by competing interaction**

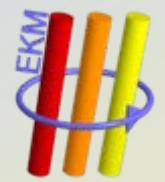
FeSc<sub>2</sub>S<sub>4</sub>, FeAl<sub>2</sub>O<sub>4</sub>

Frustration of spin and orbital degrees of freedom:

Cooperative paramagnet; opening of a spin gap at low temperatures

MnSc<sub>2</sub>S<sub>4</sub>; MnAl<sub>2</sub>O<sub>4</sub>, CoAl<sub>2</sub>O<sub>4</sub>

Competing interactions of spin moments on a diamond lattice:  
spiral spin liquid



# The wonderful world of Spinels



„Black Prince's Ruby“

„Neuschwanstein 3“

Drummond, Nature 423, 023 (2003)

**Catch a falling star**

Jack Drummond

concluded that most meteors were of interstellar origin. In New Mexico, in the late 1940s and early 1950s, Fred Whipple and colleagues made photographic studies using a rotating shutter in front of fast cameras to measure the meteors' velocities. In what is some of the most precise work ever by today's standards, these experiments showed that most meteors in fact originated from comets, but that a substantial fraction were in asteroid-like orbits—that is, the furthest points of their orbit from the Sun (their "aphelia") fell in the asteroid belt, between Mars and Jupiter.

Shortly thereafter, astronomers began to develop methods for tracing the paths of meteors through the atmosphere. The first was to photograph the meteor's path through the atmosphere, and its orbit in the Solar System was calculated. Because the

meteors stream had been thought,

where it came from, a big piece of the puzzle might be uncovered. As a result, several networks of cameras, spanning areas of a million square kilometres, were set up in Europe, Canada and the United States. The first meteor whose orbit could be calculated, was of magnitude  $-19$ , much brighter than the full Moon.

The following night, his fireball network had photographed and tracked the meteor's path through the atmosphere, and its orbit in the Solar System was calculated. Because the