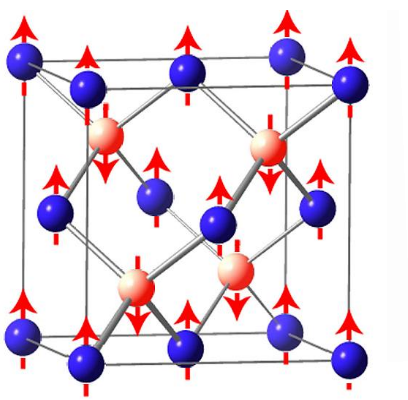
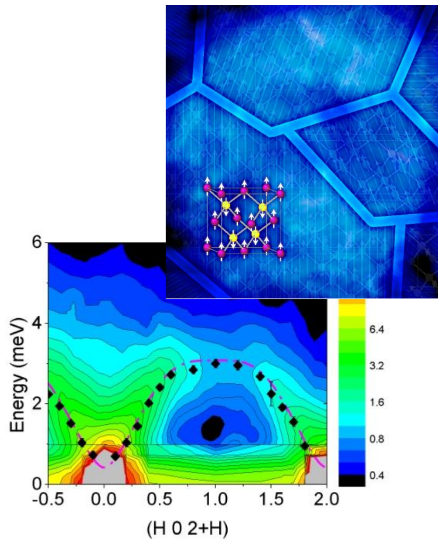
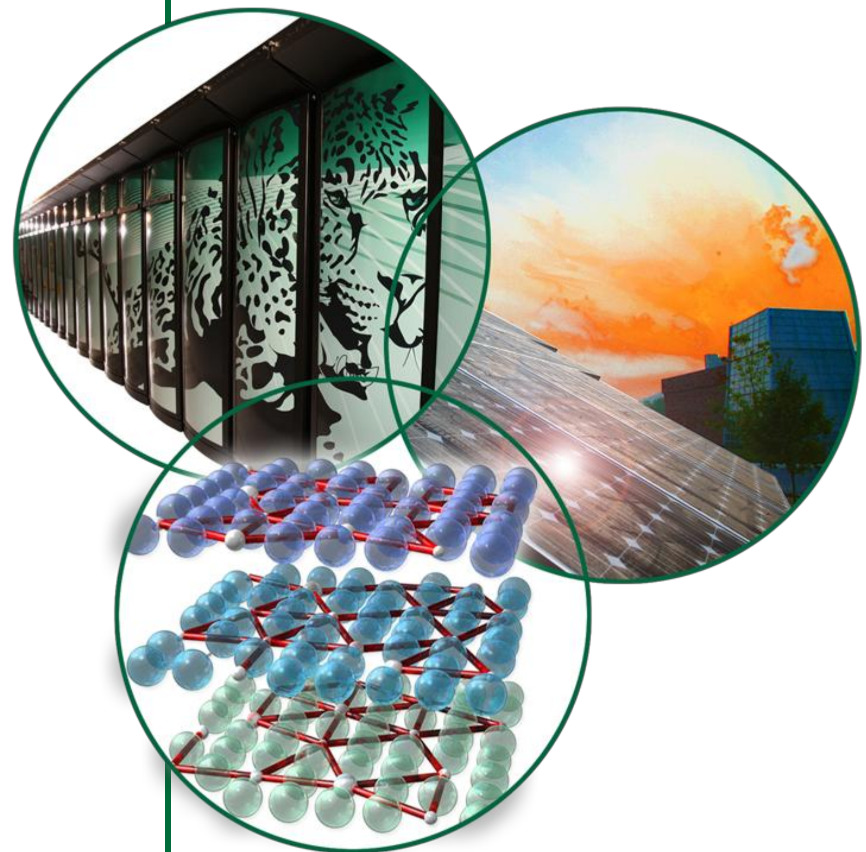
Consequences of Frustration for Order in A-site Spinel Antiferromagnets

G.J. MacDougall

Oak Ridge National Laboratory







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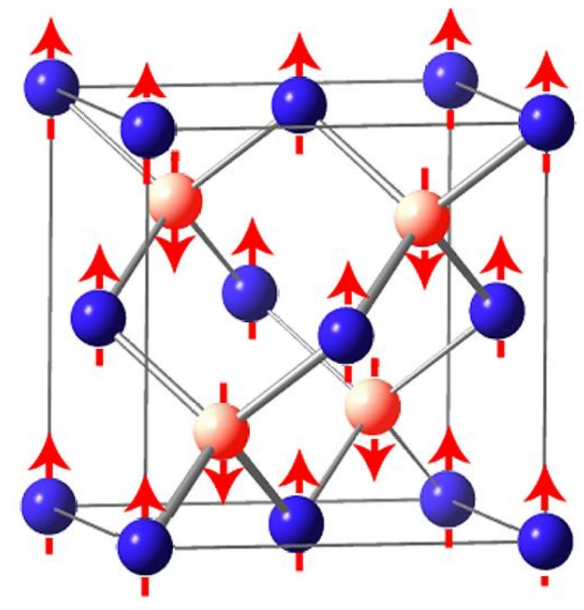
Outline

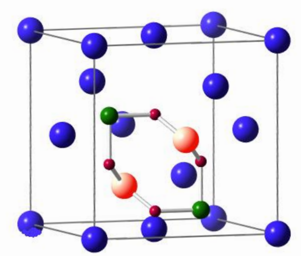
- Introduction to the A-site spinels
  - Frustration and predictions
  - J_2-T phase diagram
- $MnAl_2O_4$
  - Existing work on powders/ motivation
  - Neel antiferromagnetism and spin waves in single crystals
- $CoAl_2O_4$
  - Existing work and exotic predictions
  - Elastic scattering and novel interpretations
  - Thermal and cold neutron inelastic data
  - *Proceedings of the National Academy of Science USA* 108, 15693 (2011)
- Conclusions and implications for other systems

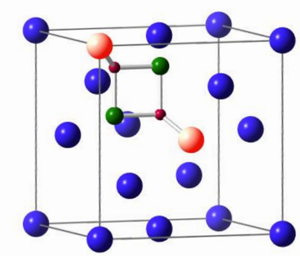
A-site spinels

- Spinels with magnetic cations residing solely on the diamond sublattice



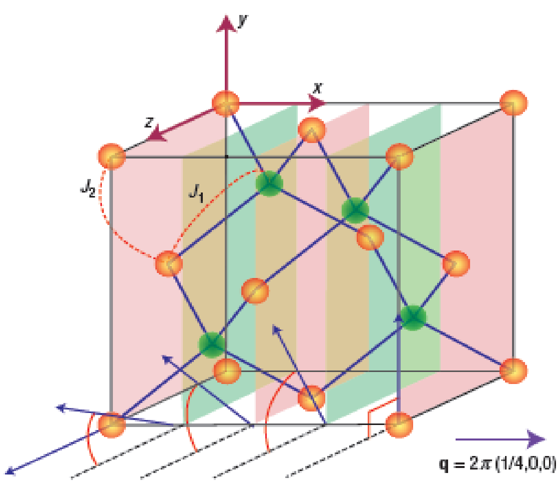
- NOT *geometrically* frustrated
  - Ground state is collinear AF, if only n.n. exchange (J_1) is considered
  - e.g. Co_3O_4, $MnAl_2O_4$
- However, J_1 is typically weak
  - 4 n.n., each connected through 6 A-X-B-X-A 'exchange chains'
  - 12 next n.n., each connected through 2 similar paths
  - The condition $J_2 \sim J_1$ leads to ***frustration***



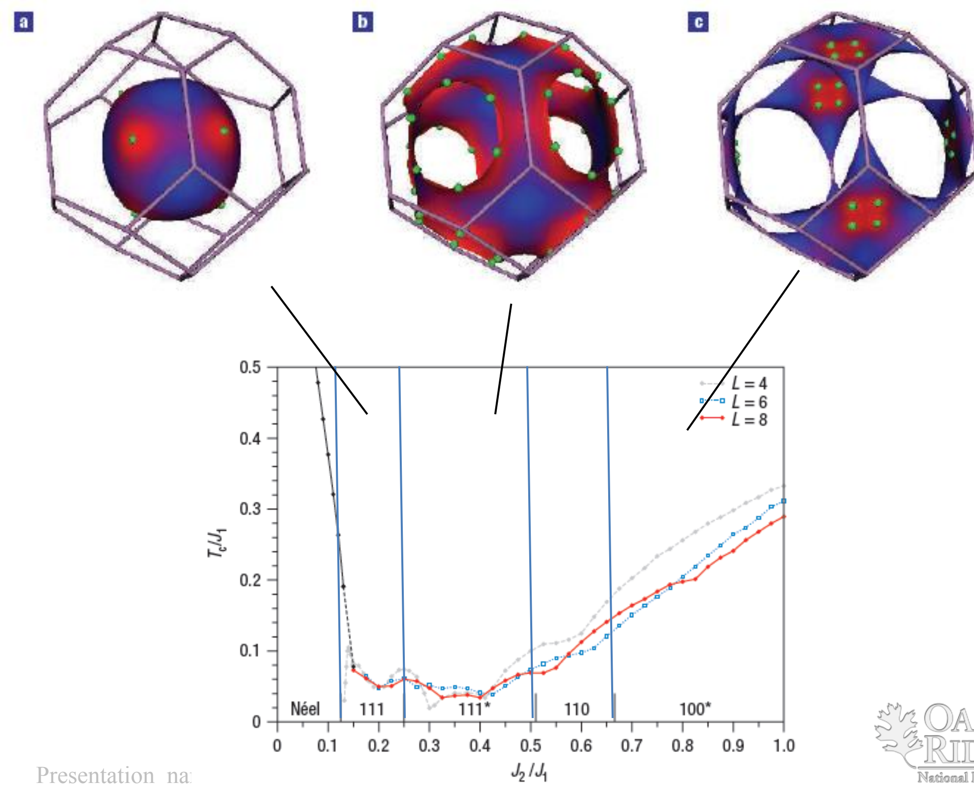


Exotic predictions for A-site spinels

- Bergman *et al.* considered the minimal model of n.n. and n.n.n exchange on a diamond lattice
  - Neel state energetically favourable only for $J_2 / J_1 < 1/8$
  - Infinitely degenerate ground state for larger $J_2 \rightarrow$ ‘spin-spiral correlations’
  - Possible transition at lower temps to a state selected by thermal fluctuations (classical order-by-disorder)

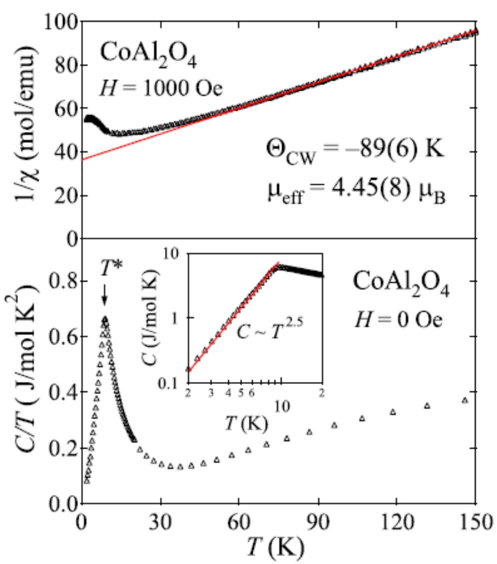


Bergman *et al.*, Nature Physics **3**, 487 (2007).
Order-by-disorder and spiral spin-liquid in frustrated diamond-lattice antiferromagnets



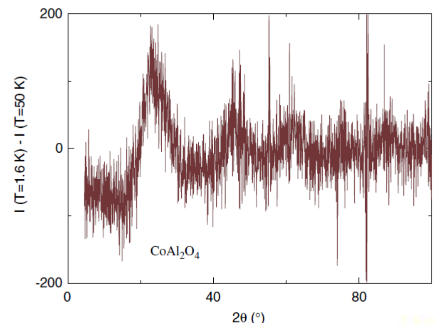
$CoAl_2O_4$

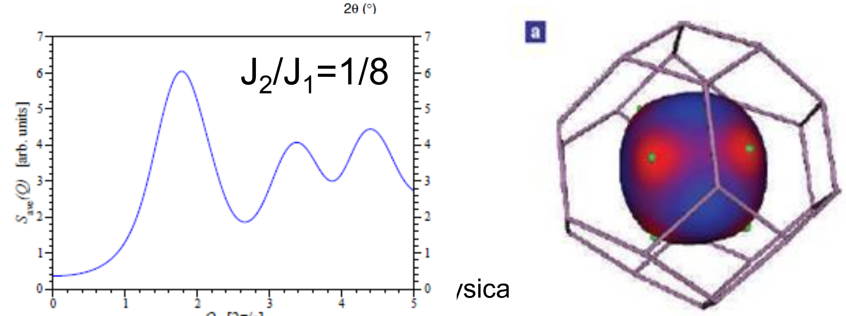
- Well-known compound, long used as a *pigment*
- Spinel structure with A-site (diamond lattice) occupied by Co^{2+} ($3d^7$) ions in tetrahedral environment → $S=\frac{3}{2}$, L=0
- Previous work suggests frustration, short-range correlations at low T and an “anomalous spin glass” transition at T^*~4-9K, well below $|\Theta_{CW}|$~100K



Suzuki *et al*., J. Phys: Condens. Matt. **19**, 145265 (2006)

Krimmel *et al*., Physica B **378**, 583 (2006)





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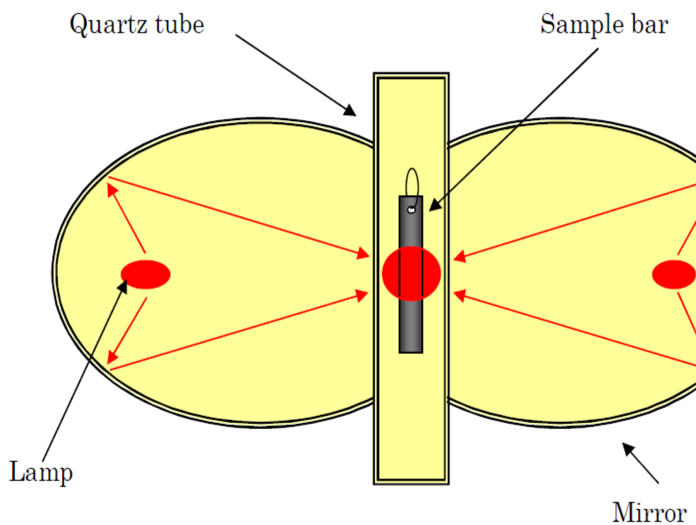
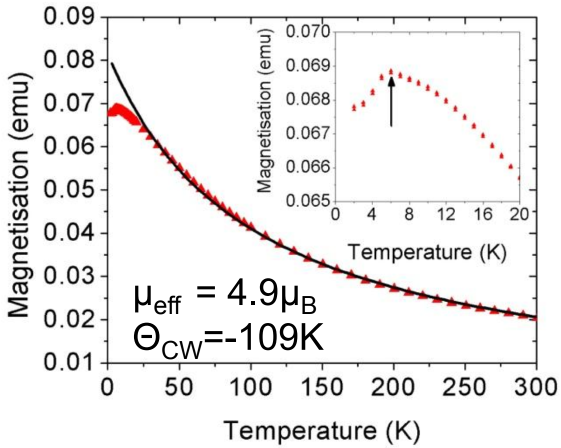
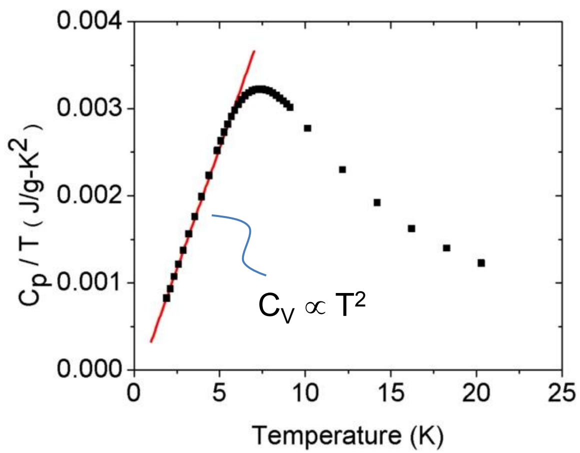
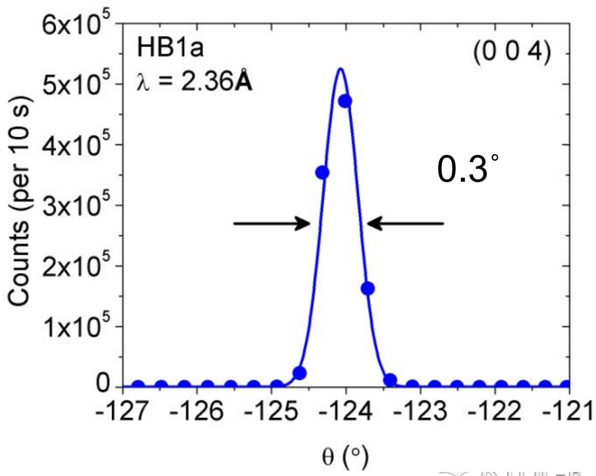
Bergman *et al*., Nature Physics **3**, 487 (2007).

$CoAl_2O_4$ - single crystals

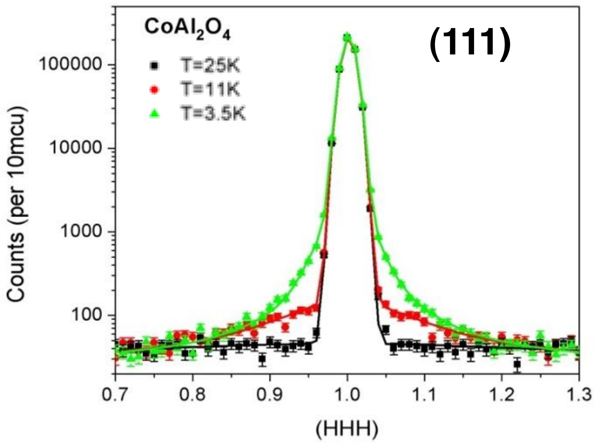


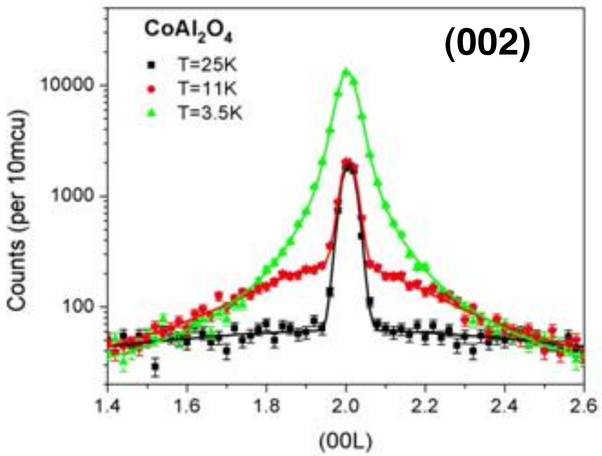


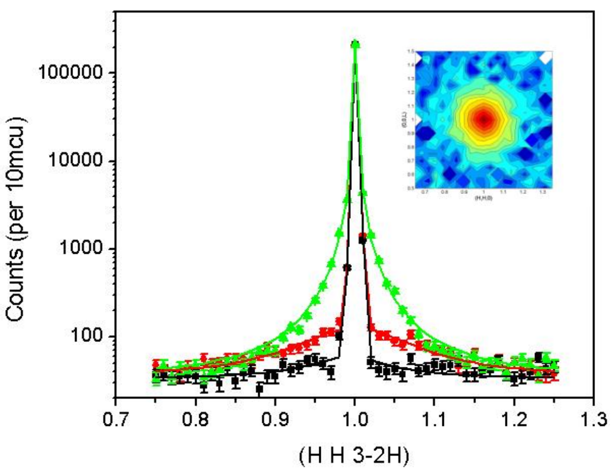


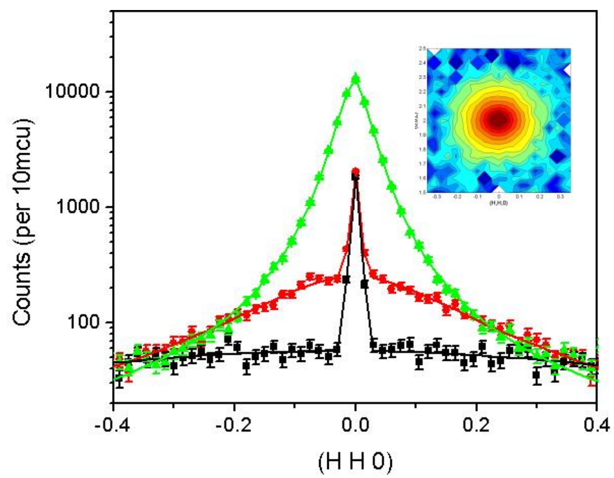


Enormous diffuse scattering in *single crystals* at low T

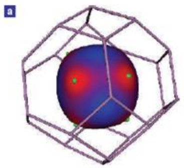




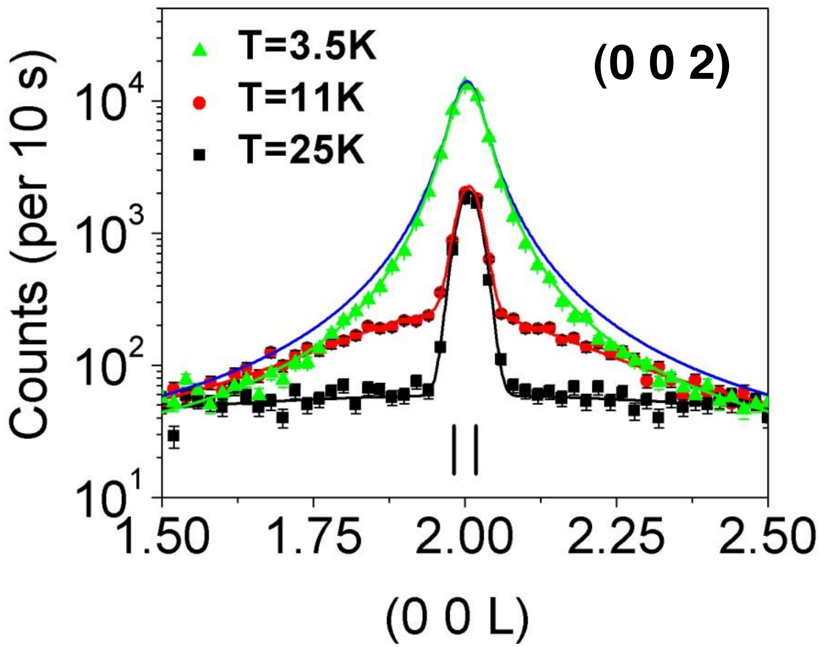




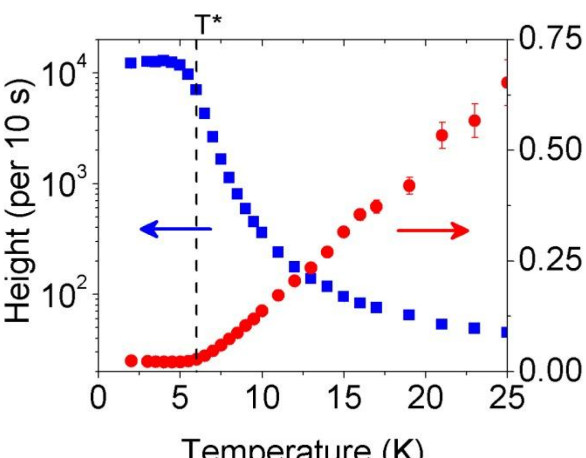
- Diffuse scattering observed at (1,1,1), (0,0,2), (1,1,3), (1,1,5), (2,2,2), (3,3,3), (2,0,4)
- Diffuse scattering absent at (2,2,0), (4,4,0), (0,0,4)
- Selection rules: (H,K,L) all odd OR H+K+L=4n+2: →antiferromagnetic points
- Not consistent with spin spiral

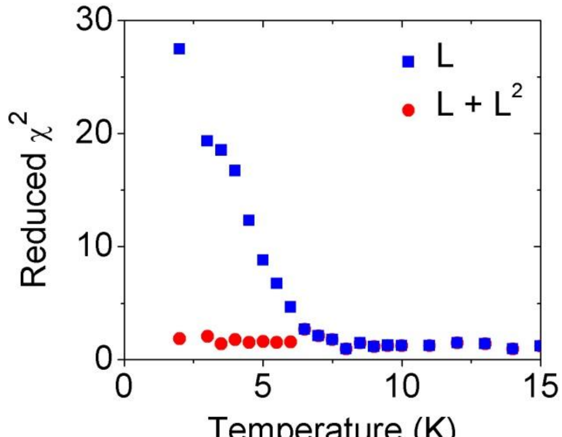


Remarkable lineshape change at low T

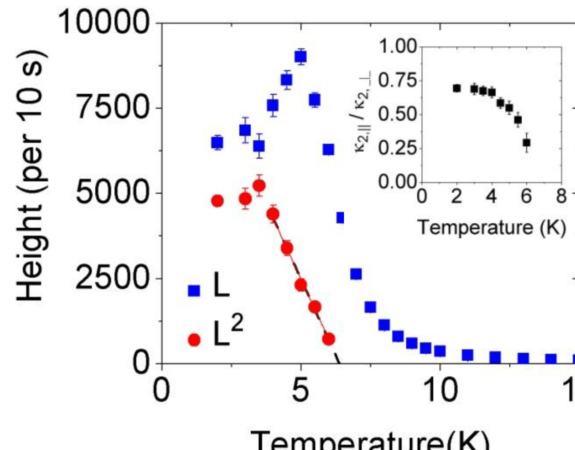


Pure Lorentzian

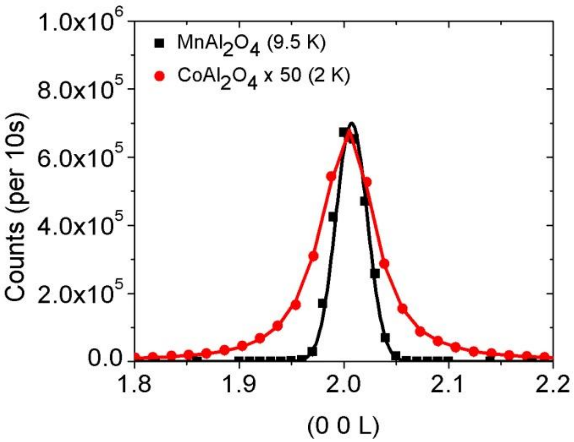


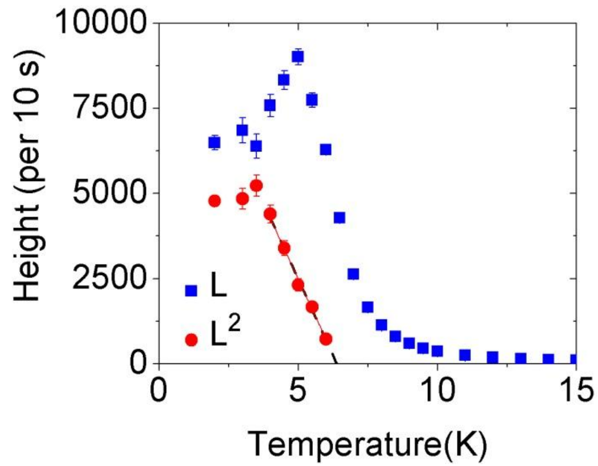


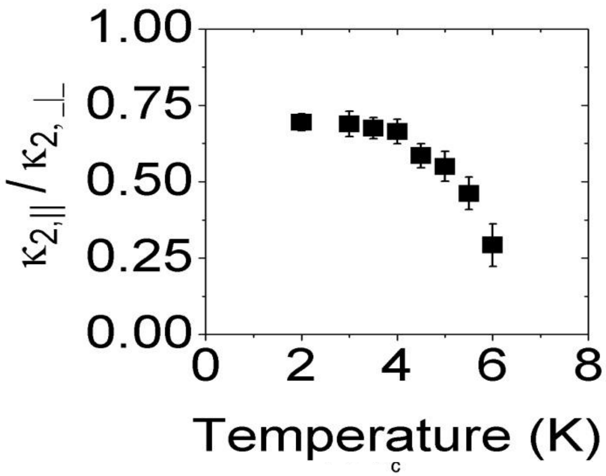
Lorentzian + Lorentzian squared



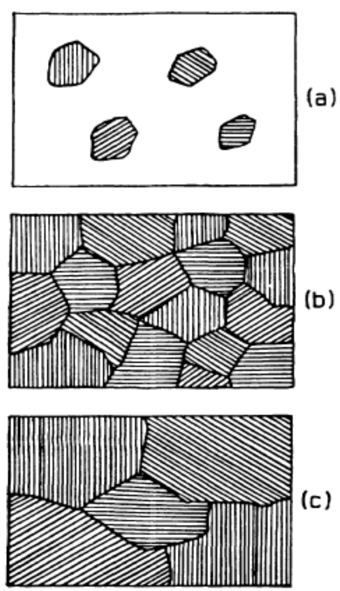
Line shape indicate existence of domains

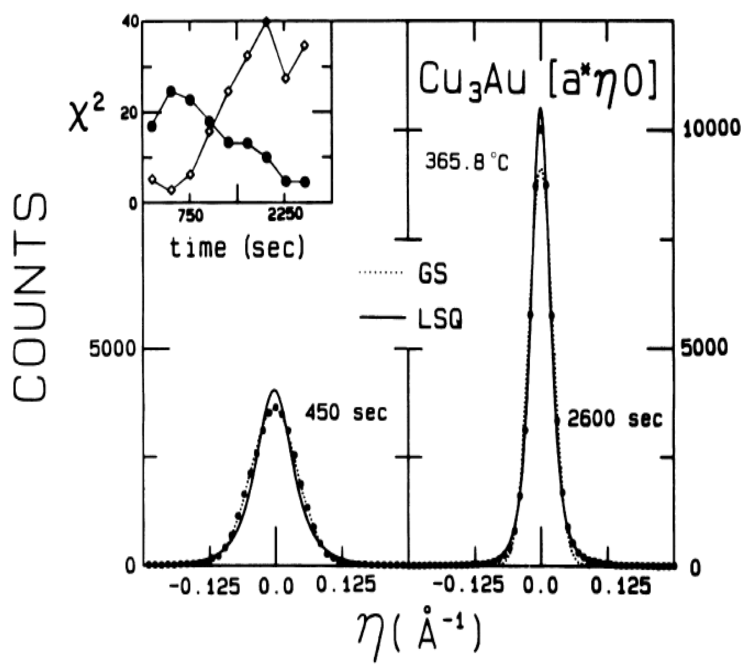






Consistent with 1st order phase transition + anti-phase domain walls

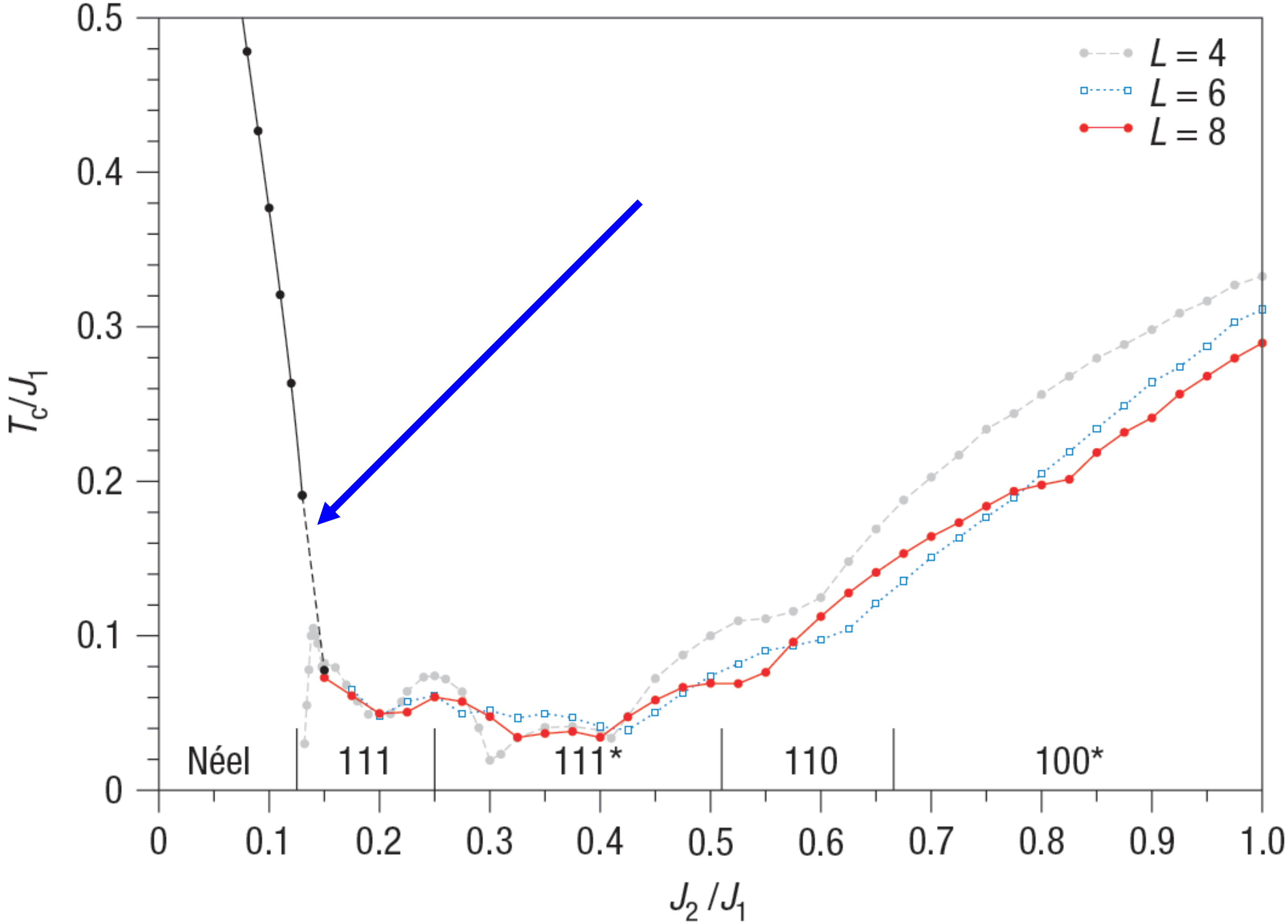




SEN *et al.*, PRL **61**, 718 (1988)

1st order transition to AF order ?

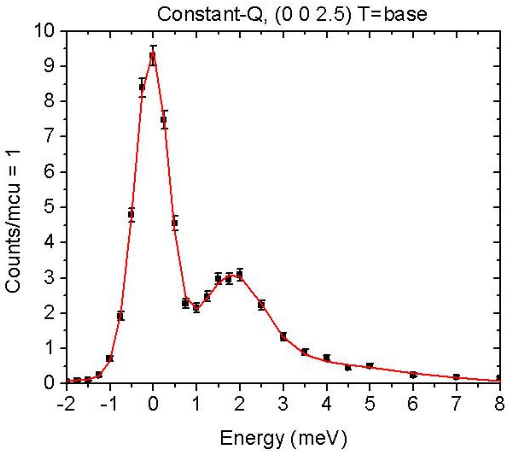
"As an interesting aside, for J_2/J_1 just above 1/8 two ordering transitions appear…This occurs due to thermal stabilization of the Néel phase slightly beyond the value of J_2/J_1=1/8... Throughout this region, the transition is strongly first order."

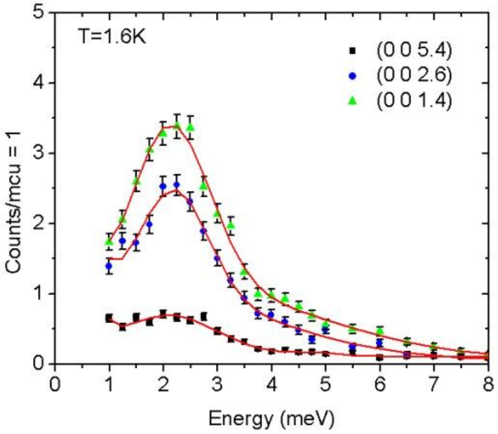


Bergman *et al.*, Nature Physics **3**, 487 (2007).

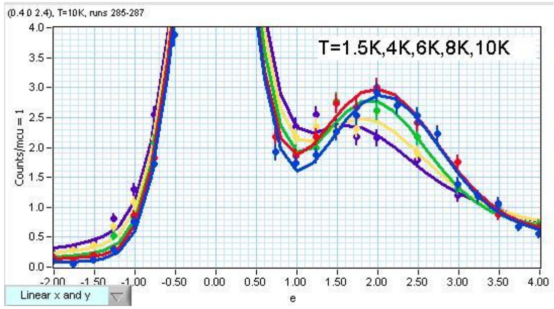
Excitations in crystals

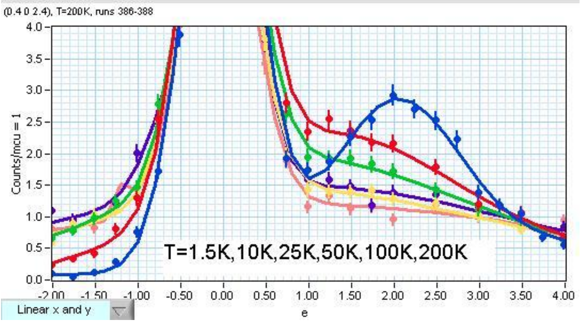
- **Well defined excitations at all Q, with intensity decreasing with increasing Q:**



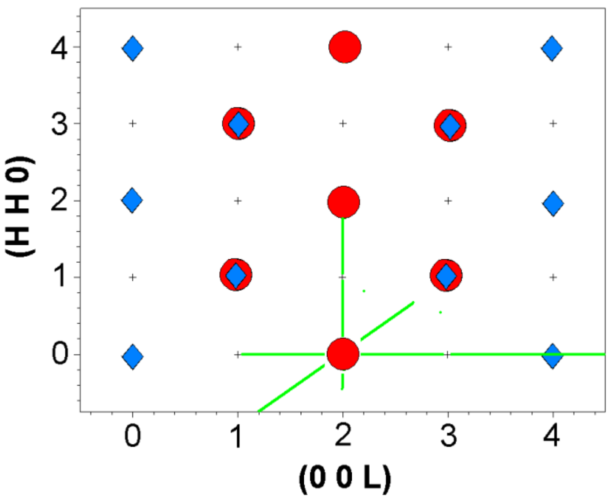


- **Intensity decrease with increasing T, characteristic of magnetic order:**



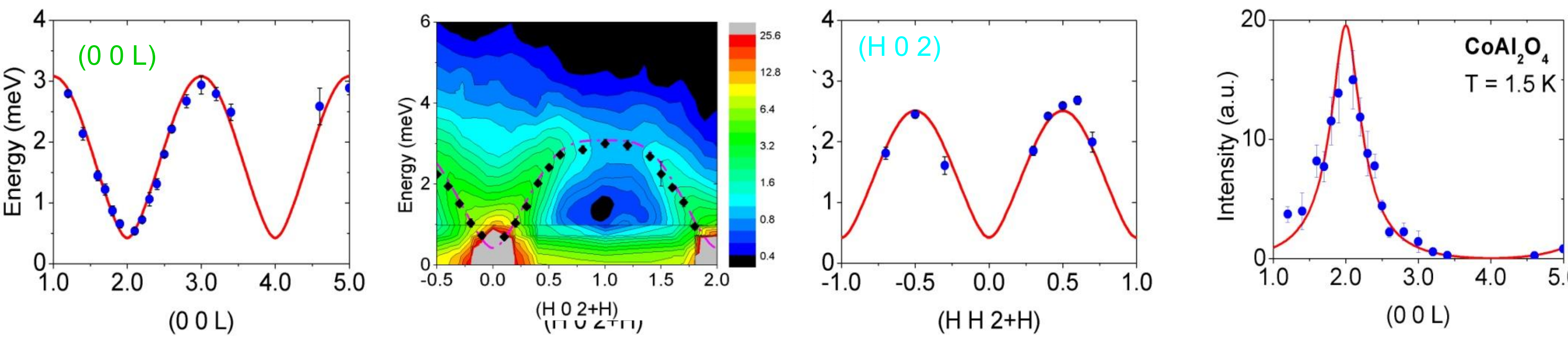


Simple AF model again fits excitations

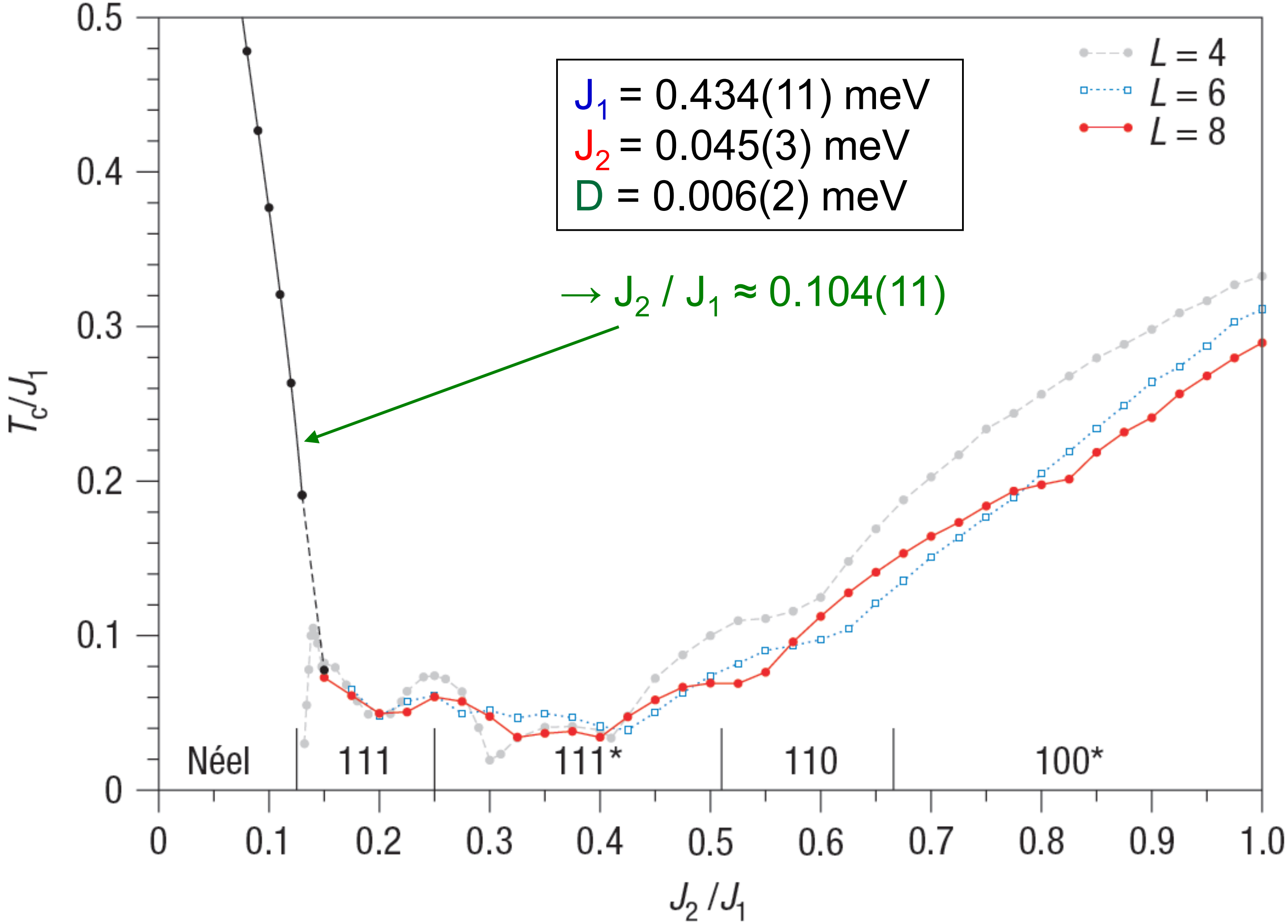


$$\hat{H} = \sum_{\vec{r}} \left\{ J_1 \vec{S}_{\vec{r}} \cdot \vec{S}_{\vec{r}+\vec{\delta}_1} + J_2 \vec{S}_{\vec{r}} \cdot \vec{S}_{\vec{r}+\vec{\delta}_2} + D(S^z_{\vec{r}})^2 \right\}$$

J_1 = 0.434(11) meV (1st neighbor)
J_2 = 0.045(3) meV (2nd neighbor)
D = 0.006(2) meV (anisotropy)

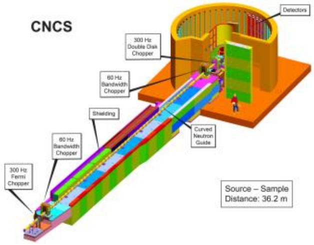


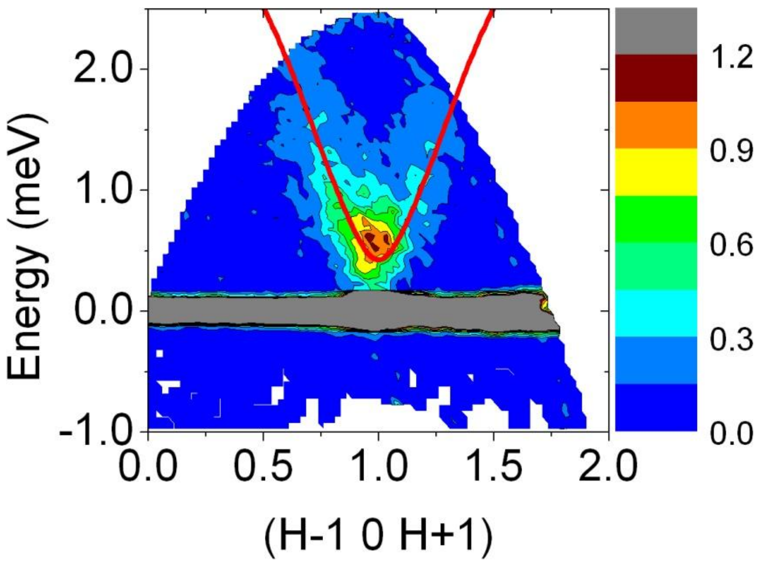
Results suggest system lies in the vicinity where a 1st order transition expected

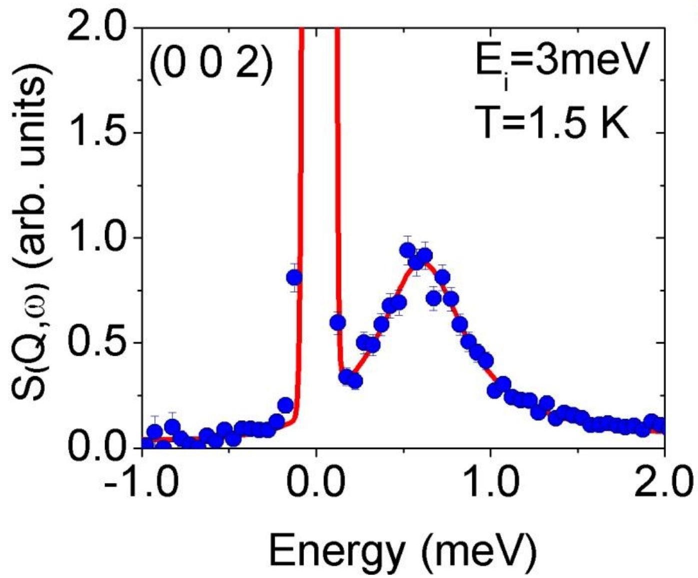


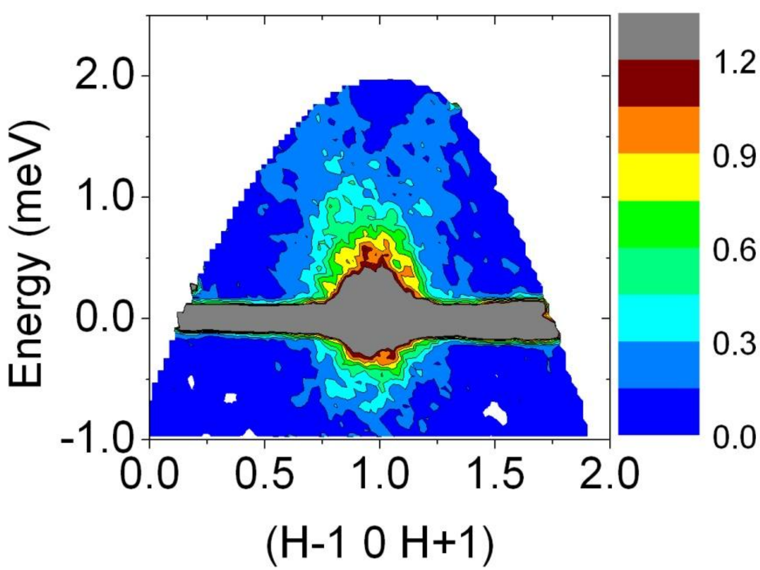
Bergman *et al.*, Nature Physics **3**, 487 (2007).

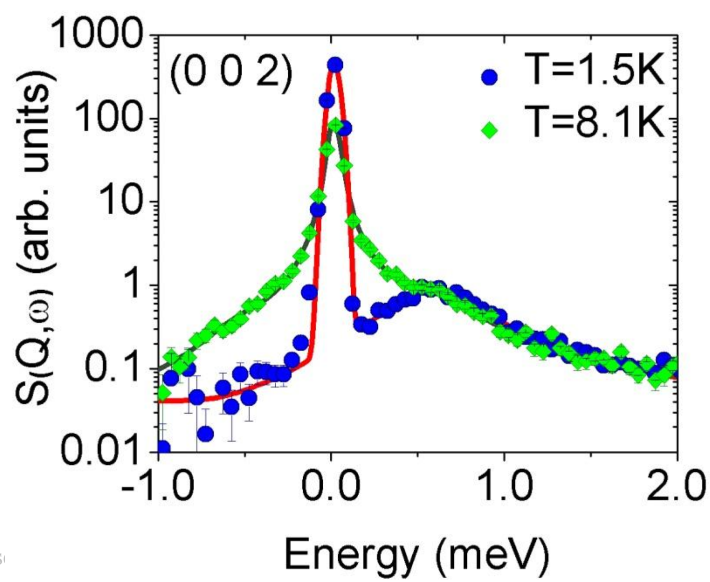
Low T gap is real – gone above 6 K



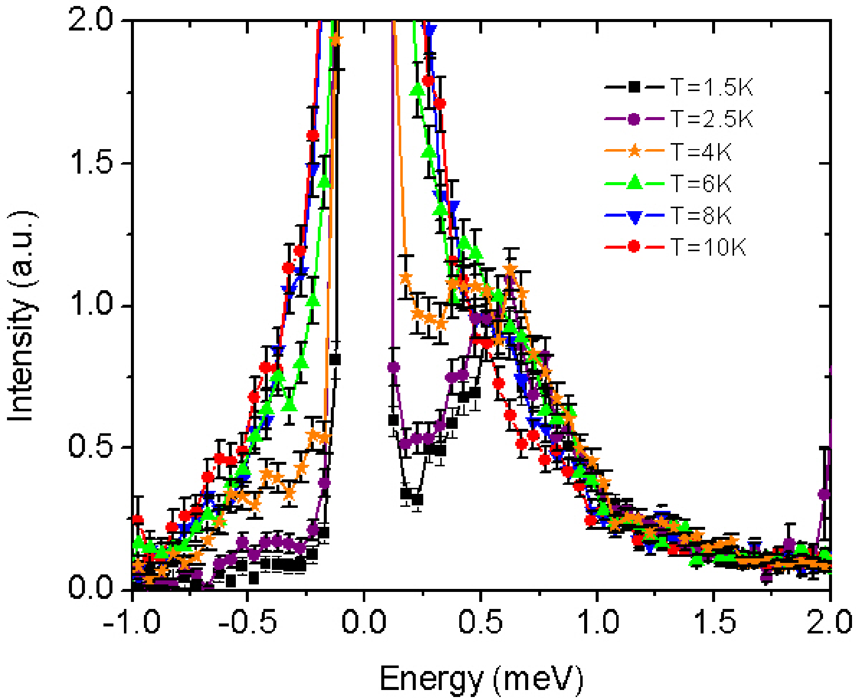


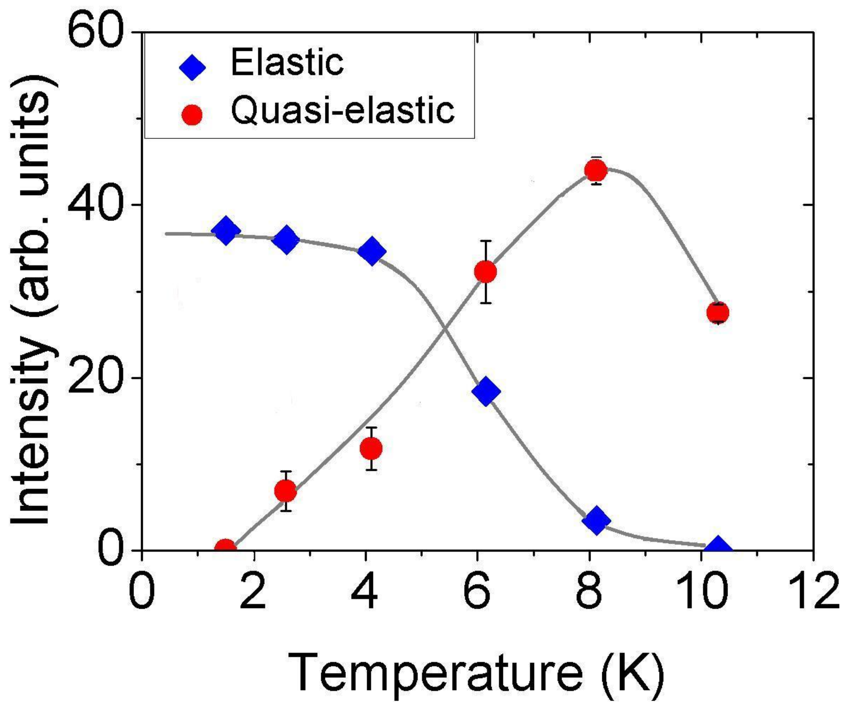






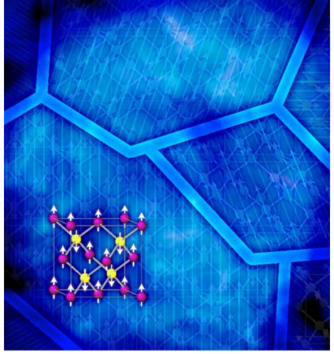
Also a remarkable quasi-elastic component above T_N





- The mode at ordering wavevector is another indicator of actual magnetic order
- The quasi-elastic scattering seems related to the Lorentzian component of the elastic lineshape, but demands more investigation

Kinetically inhibited order



- Neutron scattering data supports the existence of a first-order phase transition at in $CoAl_2O_4$, with true long-range order inhibited by the freezing in of domains
- Such *kinetically inhibited* order explains reports of glassiness in this system, and in particular reports of
  1. Diffuse scattering in powder neutron scattering data
  2. ZFC-FC divergence in magnetisation measurements
  3. Signatures of local AF order in ESR data
  4. The lack of a strong anomaly in heat capacity measurements which employ the time relaxation technique
- Similar behaviour might be expected in other frustrated systems which contain a first-order phase transition

Summary

- The A-site spinels are prototypical systems for frustration via competing interactions in 3 dimensions
- Elastic and inelastic neutron scattering indicates that $MnAl_2O_4$ acts largely as a classical Heisenberg AF
- $CoAl_2O_4$ is much more strongly frustrated:
  - Elastic scattering is consistent with a *first-order* phase transition to Neel order at T_N = 6.5 K, with small domain sizes
  - Measured J_1, J_2 further imply material is in vicinity of 1^{st} order phase transition
  - Cold neutrons confirm existence of long-wavelength excitation which disappear at T^*
  - The achievement of true long-range order is inhibited by the freezing of domain walls due to low temperature of transition relative to magnetic exchange
  - *Proceedings of the National Academy of Science* USA 108, 15693 (2011)

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