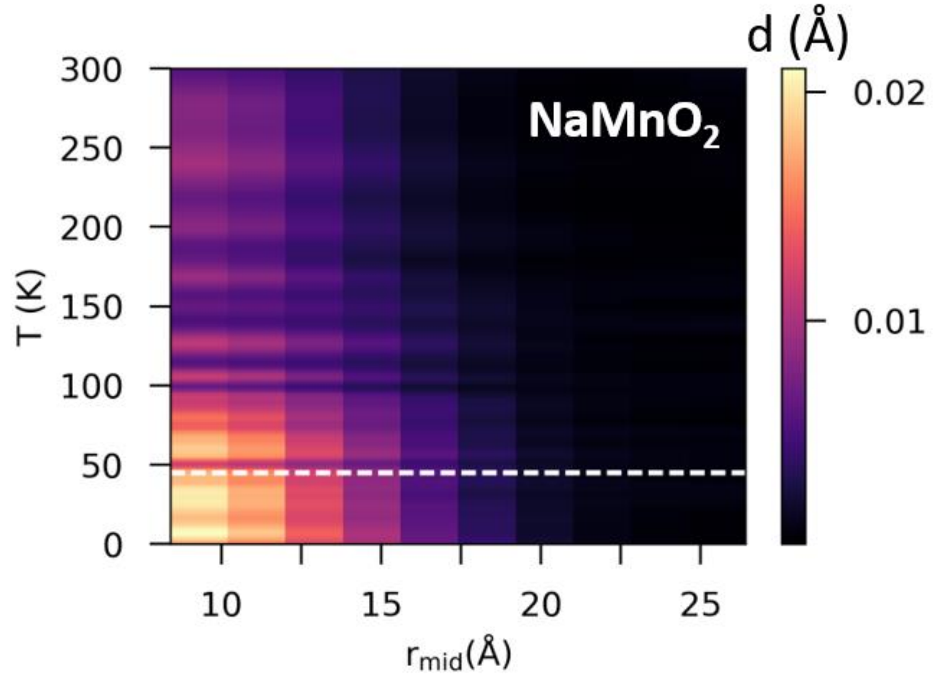
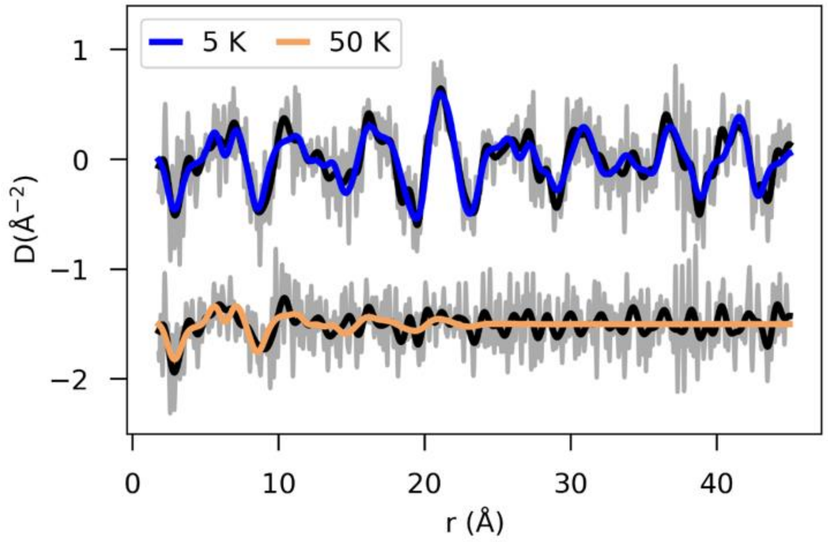
Nanoscale degeneracy lifting in triangular antiferromagnets studied by combined PDF+mPDF



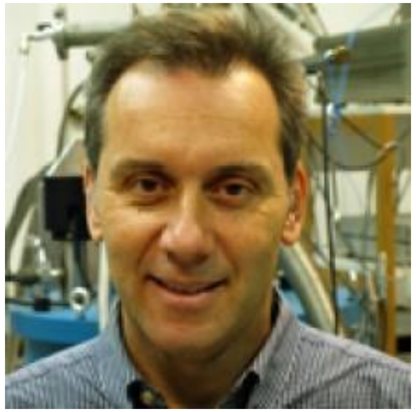


Benjamin Frandsen, Brigham Young University Dept. of Physics and Astronomy

ADD 2019, 21 March 2019

Acknowledgments

Emil Bozin
Brookhaven National Lab



Alex Lappas
The Foundation for Research and Technology—Hellas

Sample synthesis and characterization (FORTH-IESL)
- Eleni Aza
- Antonio Fernandez Martinez

Beamtime assistance
- Mikhail Feygenson (ORNL/Jülich)
- Kate Page (ORNL)
- Dave Keen (ISIS/RAL)
- Eric Dooryhee, Milinda Abeykoon (NSLS-II)

SPALLATION NEUTRON SOURCE

NSLS-II NATIONAL SYNCHROTRON LIGHT SOURCE II

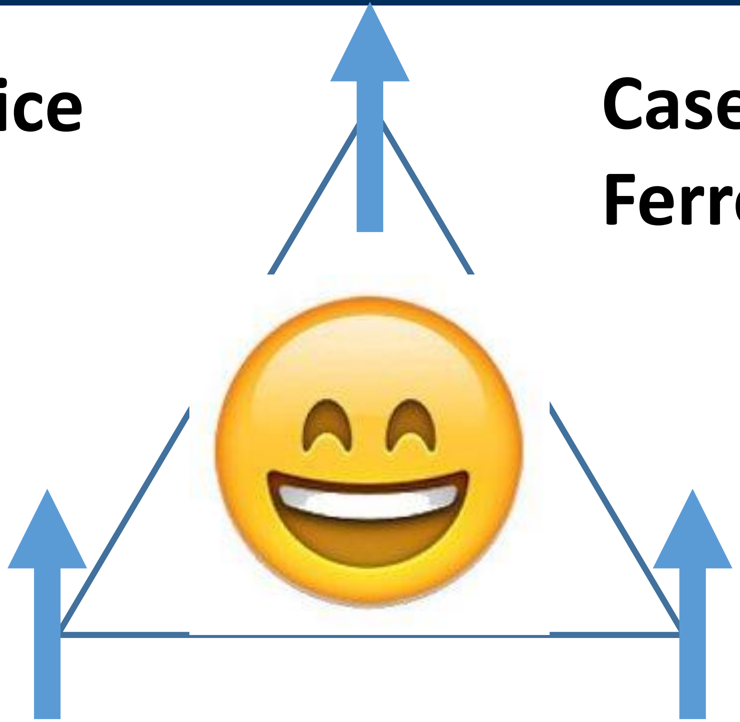
Science & Technology Facilities Council ISIS

BRIGHAM YOUNG UNIVERSITY FOUNDED BYU 1875 PROVO, UTAH

Reference: Frandsen, Bozin, Lappas, et al; under review.

Geometrically Frustrated Magnetism

Spins on a triangular lattice

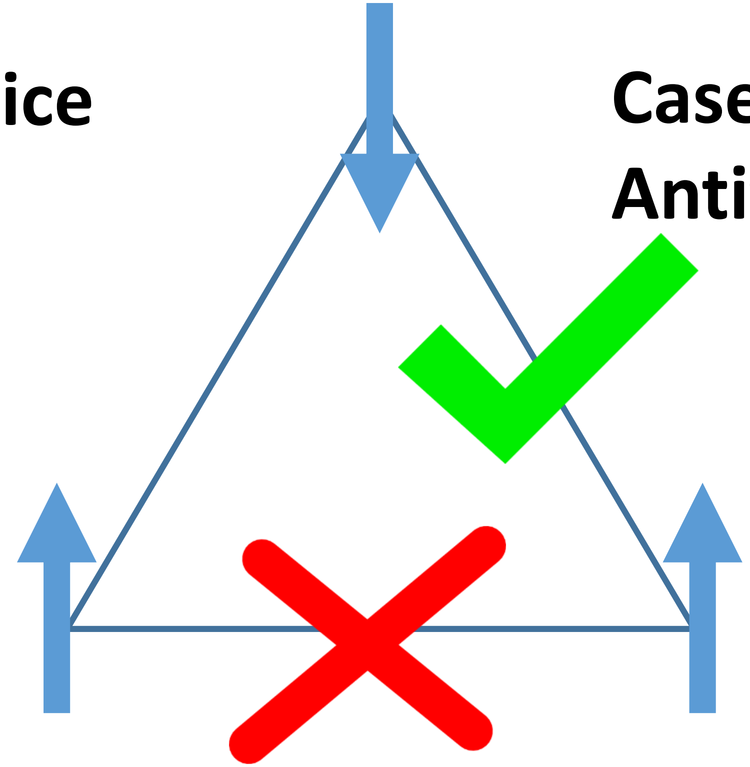


Case 1:

Ferromagnetic interactions

Geometrically Frustrated Magnetism

Spins on a triangular lattice



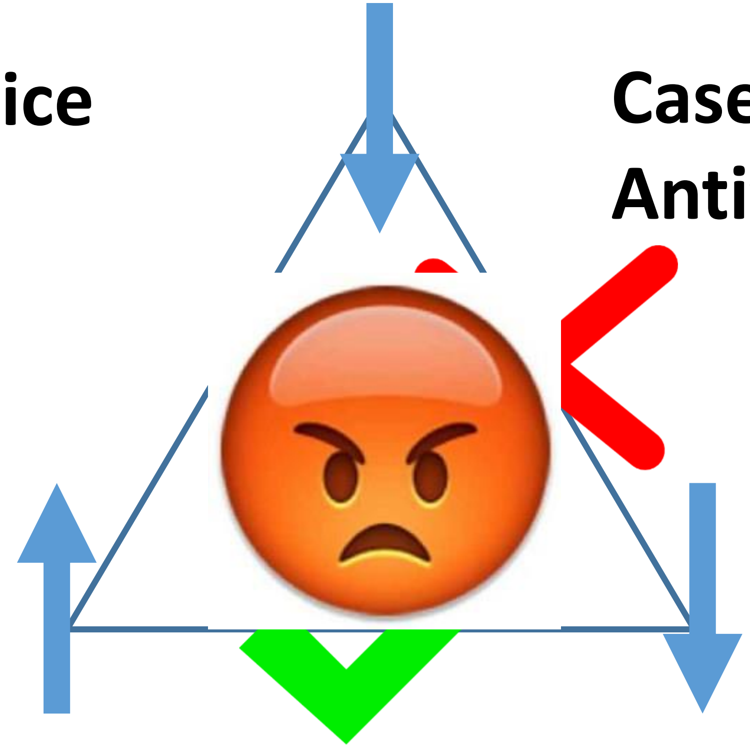
Case 2:

Antiferromagnetic interactions

Geometrically Frustrated Magnetism

Spins on a triangular lattice

Case 2:
Antiferromagnetic interactions

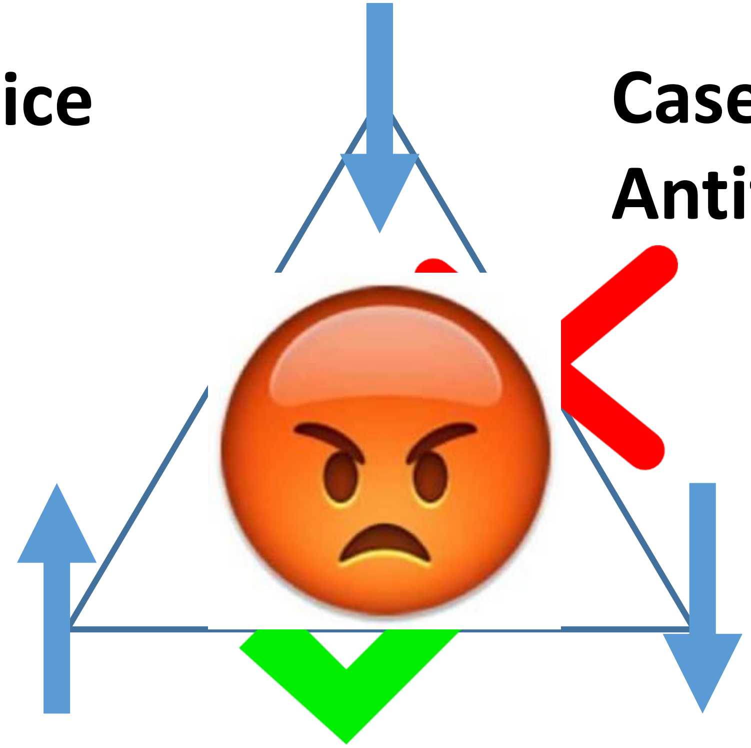


Geometrically frustrated magnets: The geometry of the lattice prevents competing magnetic interactions from being simultaneously satisfied, often with surprising consequences!

Geometrically Frustrated Magnetism

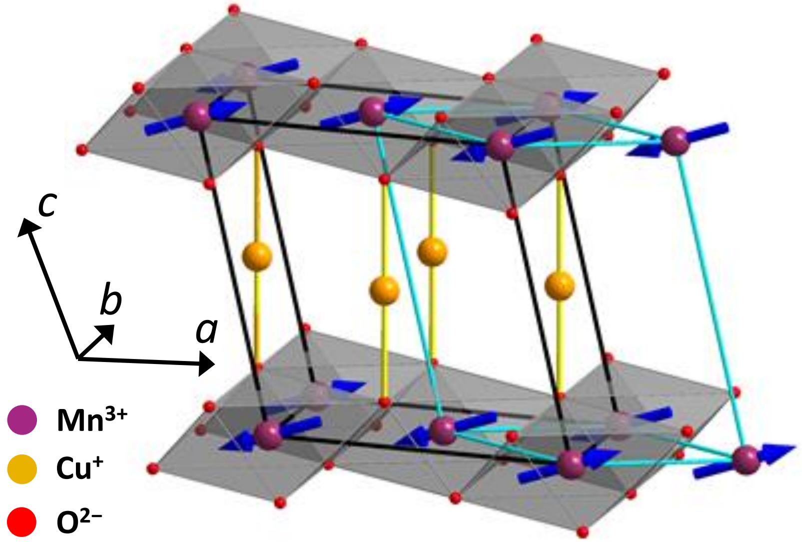
Spins on a triangular lattice

Case 2:
Antiferromagnetic interactions

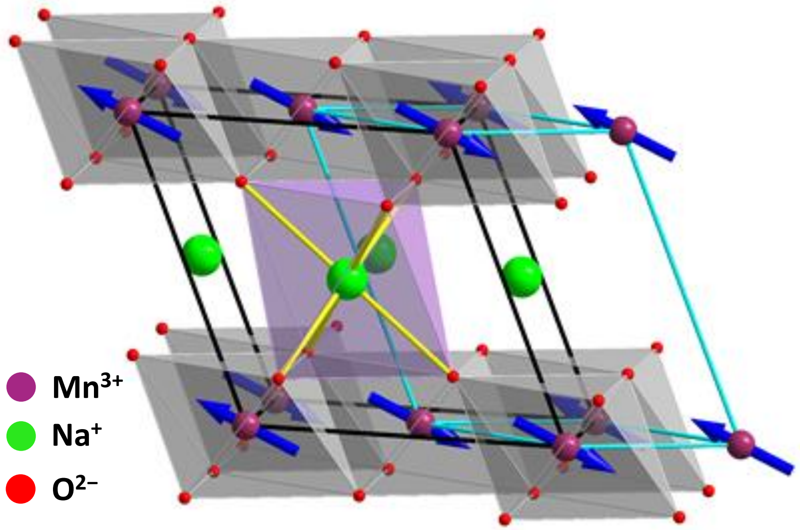


Macroscopic ground-state degeneracy; ground states lacking long-range order; quantum spin liquids; unconventional transition mechanisms; extreme sensitivity to perturbations

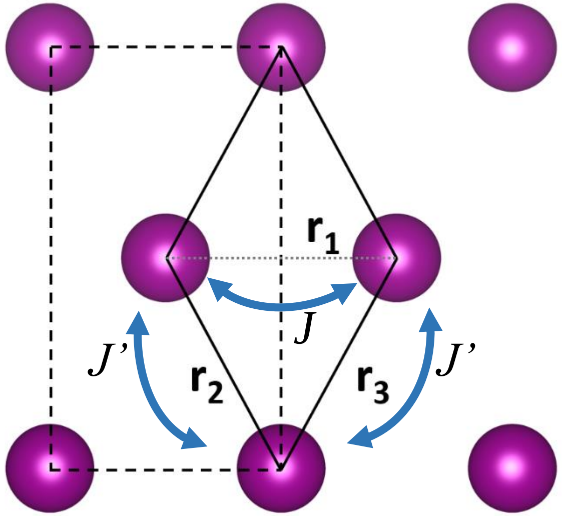
$CuMnO_2$ and $NaMnO_2$: Case studies of frustrated magnetism in strongly correlated TMOs



$CuMnO_2$



$NaMnO_2$



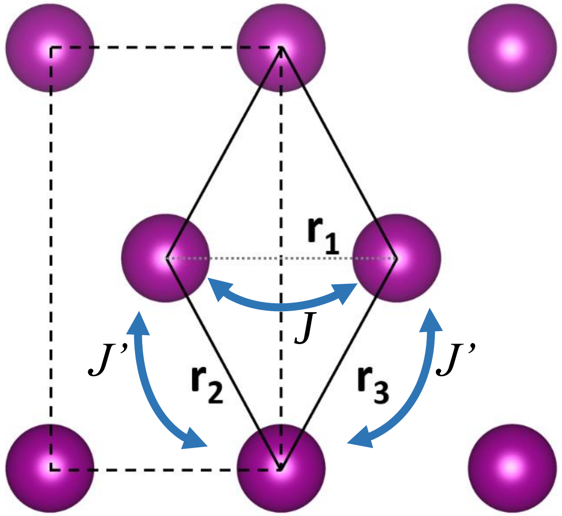
- Triangular network of Mn^{3+} $S = 2$ spins hosted by monoclinic lattice
- Geometrical frustration is partially relieved at ambient conditions
  - $r_1 < r_2 = r_3$
  - J’/J = 0.27 for Cu, 0.44 for Mn
- Both achieve long-range antiferromagnetic order (T_N = 65 K for Cu, 45 K for Na)
- Transition mechanisms show interesting differences

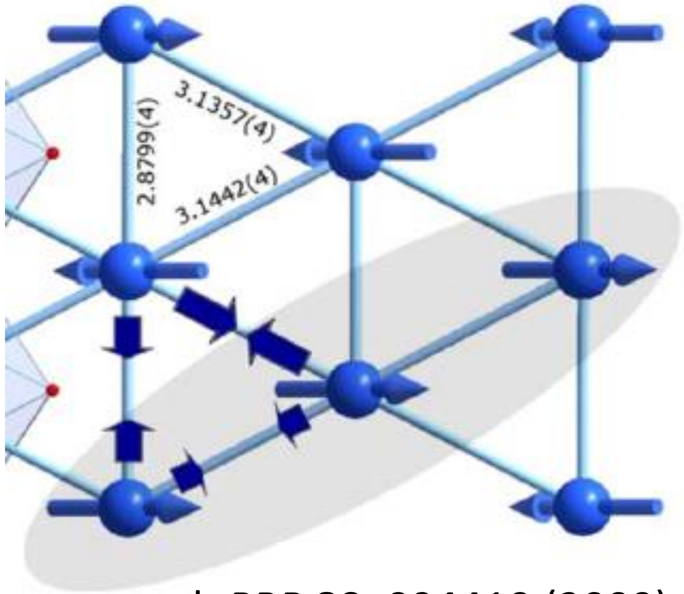
BRIGHAM YOUNG UNIVERSITY FOUNDED BYU 1875 PROVO, UTAH

Achieving LRO in $CuMnO_2$

A conventional magnetoelastic mechanism leads to long-range AF order in $CuMnO_2$

- Monoclinic-to-triclinic structural phase transition further distorts the triangles such that r1 < r2 < r3, fully lifting the degeneracy
- AF alignment along short bonds, ferro alignment along long bond





Damay et al, *PRB* **80**, 094410 (2009)

How about $NaMnO_2$?

Long-range AF order occurs below T_N = 45 K, but no long-range structural transition occurs.

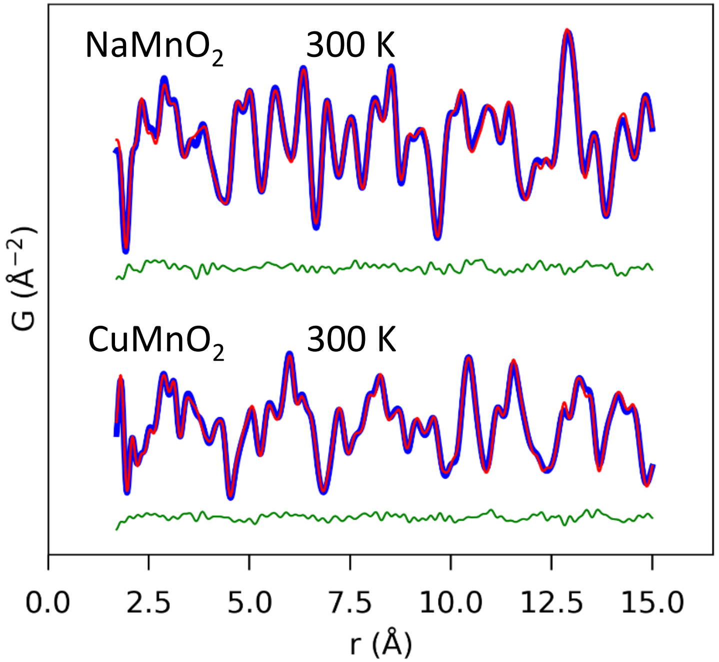
By what mechanism is the triangular degeneracy lifted if the average structure remains monoclinic at all temperatures?

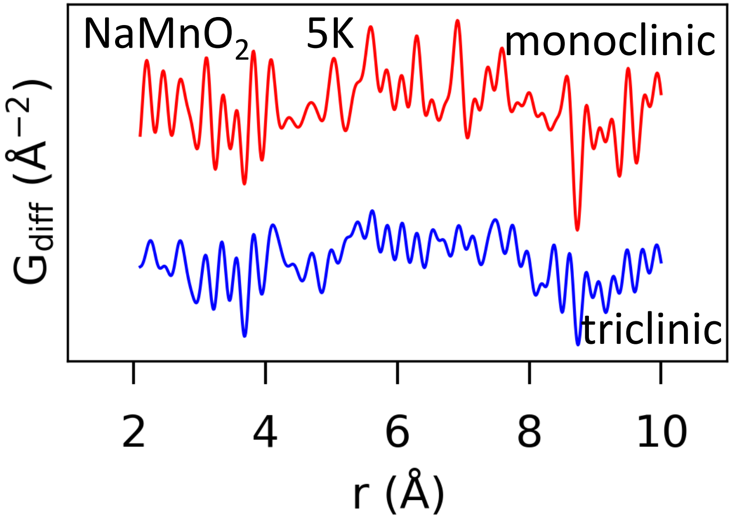
Potentially relevant experimental facts:

- Strong diffuse magnetic scattering survives into the paramagnetic state
- Bragg peaks show subtle anisotropic broadening at low T
- Significant disorder in the form of Na vacancies and planar defects

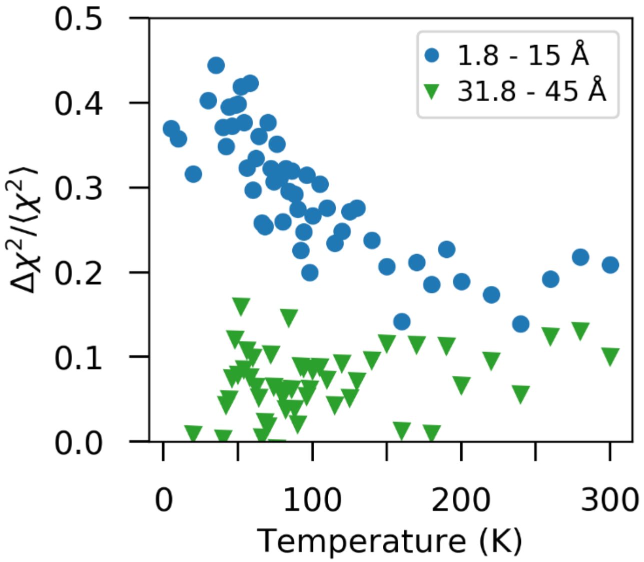
Perhaps PDF can solve the riddle!

Results of atomic PDF analysis



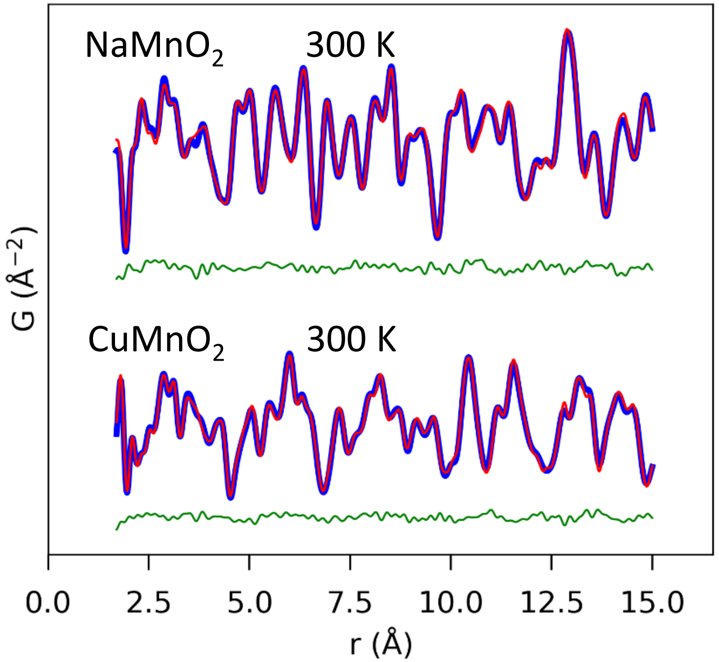


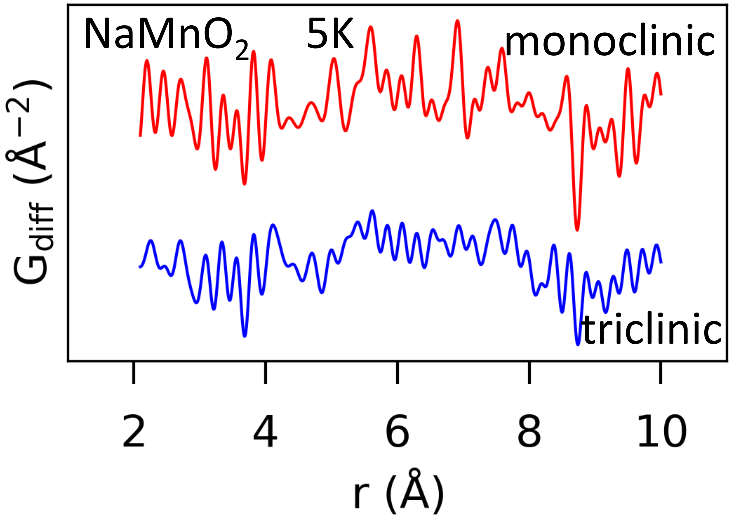
Triclinic model is significantly better



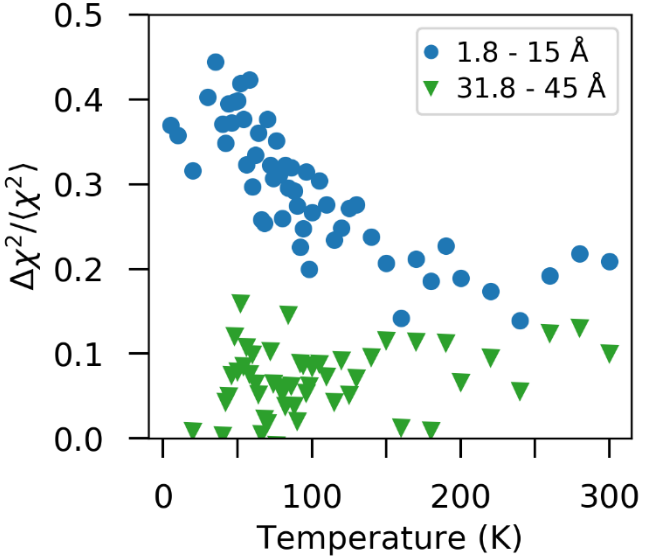
$$\frac{\chi^2_{\mathrm{mono}} - \chi^2_{\mathrm{tri}}}{\frac{1}{2}(\chi^2_{\mathrm{mono}} + \chi^2_{\mathrm{tri}})}$$

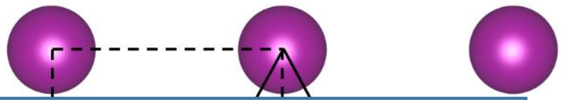
Results of atomic PDF analysis





Triclinic model is significantly better

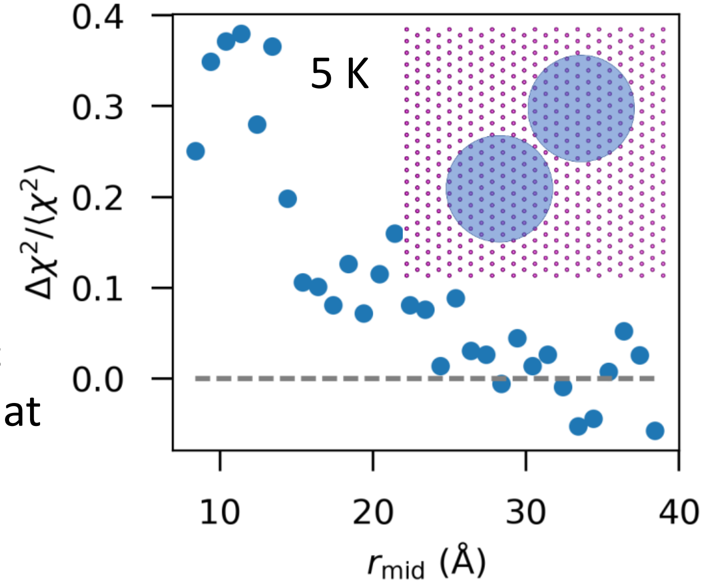




Local structure of $NaMnO_2$ is triclinically distorted, despite persistence of monoclinic symmetry in the average structure.

$r_1 < r_2 < r_3$

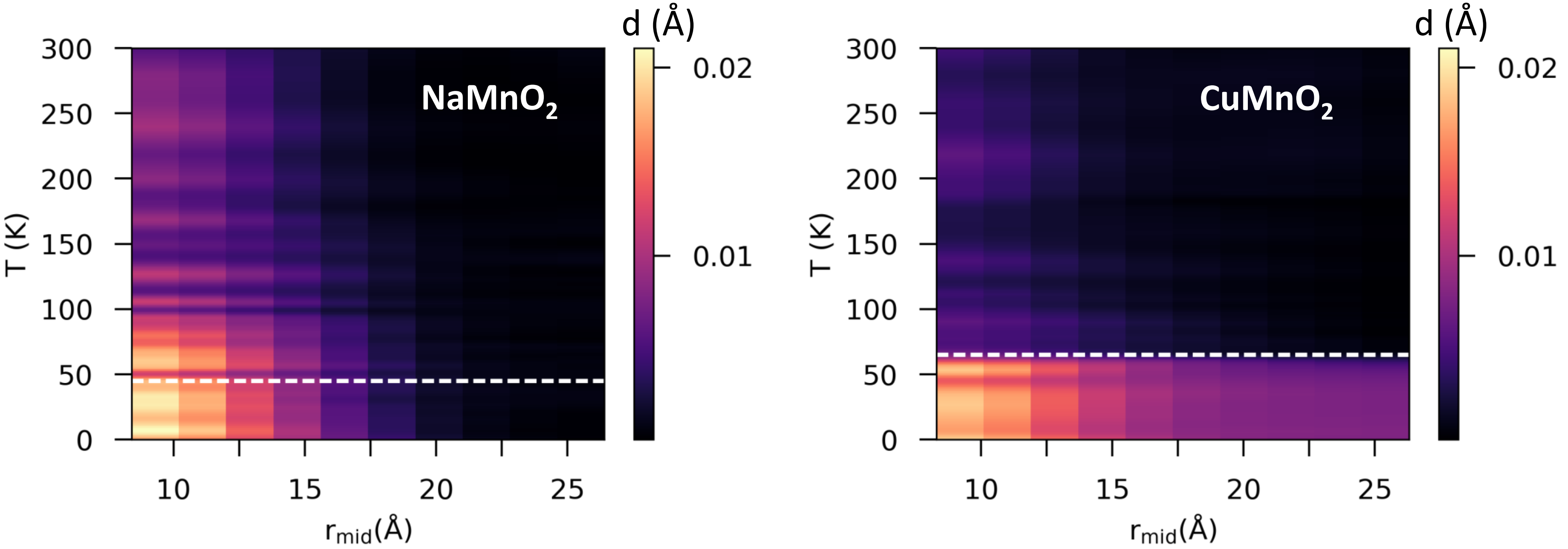
Benefit of triclinic model is greatest at low *r* and low *T*.



Comprehensive *r*- and *T*-dependent fits

- Boxcar fits using the monoclinic and triclinic models were carried out on a dense *r* and *T* grid
- Triclinic splitting $d = r_2 - r_3$ extracted from each refinement

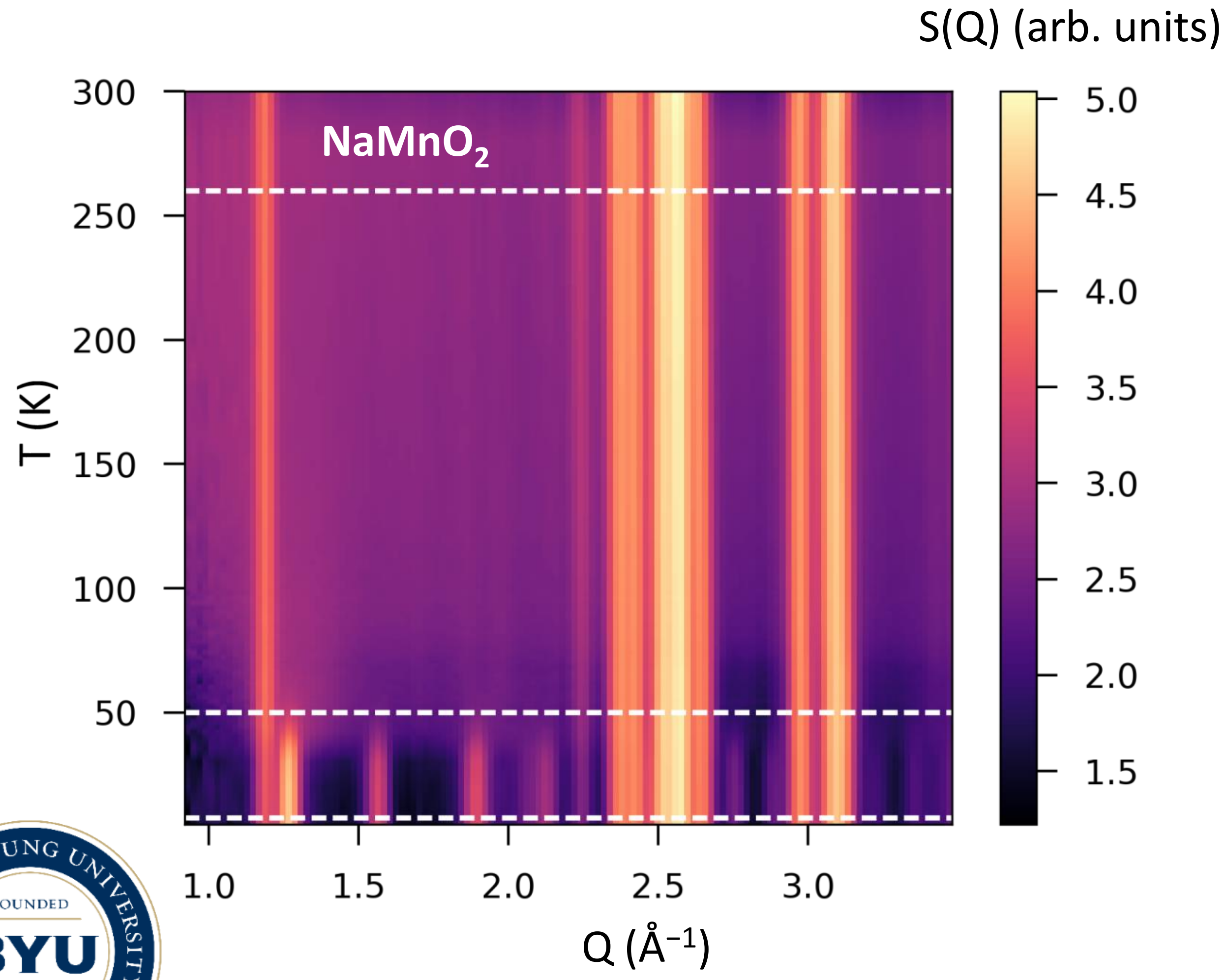
Lifts degeneracy of isosceles triangles

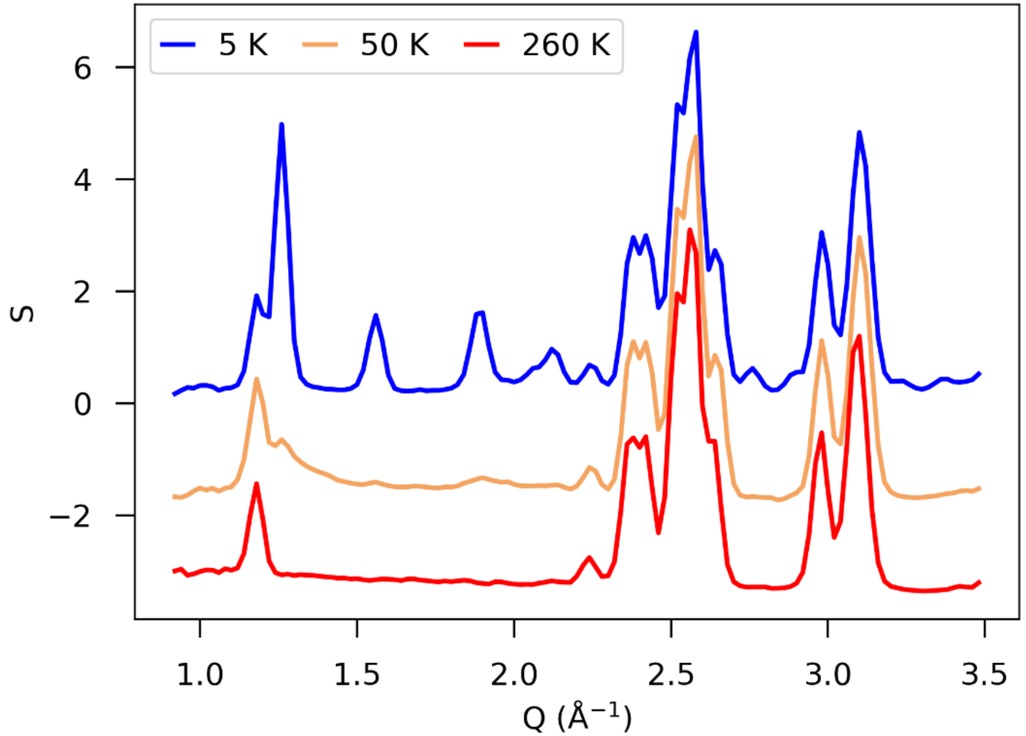


Short-range triclinic distortion on a ~2 nm length scale that grows at low *T*

Enhanced triclinic splitting at low *r*, weak local triclinicity above T_N

Investigating the local magnetic structure





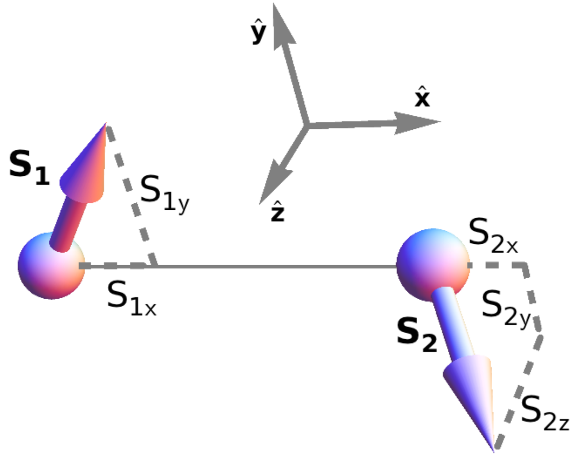
Magnetic PDF

ATOMIC $$f(r) = \frac{1}{N\langle b\rangle^2}\sum_{i\neq j}\frac{b_i b_j}{r}\delta(r-r_{ij})$$

MAGNETIC $$f(r) = \frac{1}{N}\frac{3}{2S(S+1)}\sum_{i\neq j}\left(\frac{A_{ij}}{r}\delta(r-r_{ij}) + B_{ij}\frac{r}{r_{ij}^3}\Theta(r_{ij}-r)\right)$$

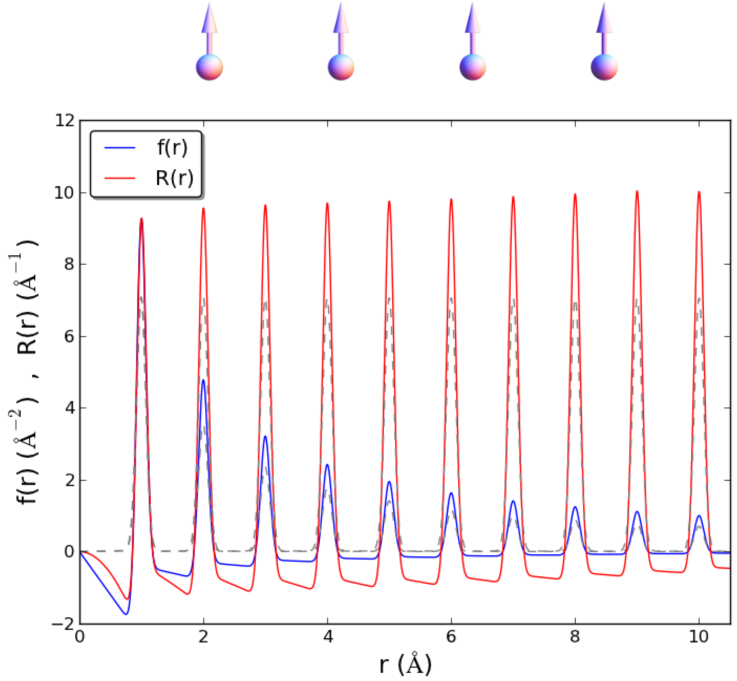
$$A_{ij} = S_i^y S_j^y$$

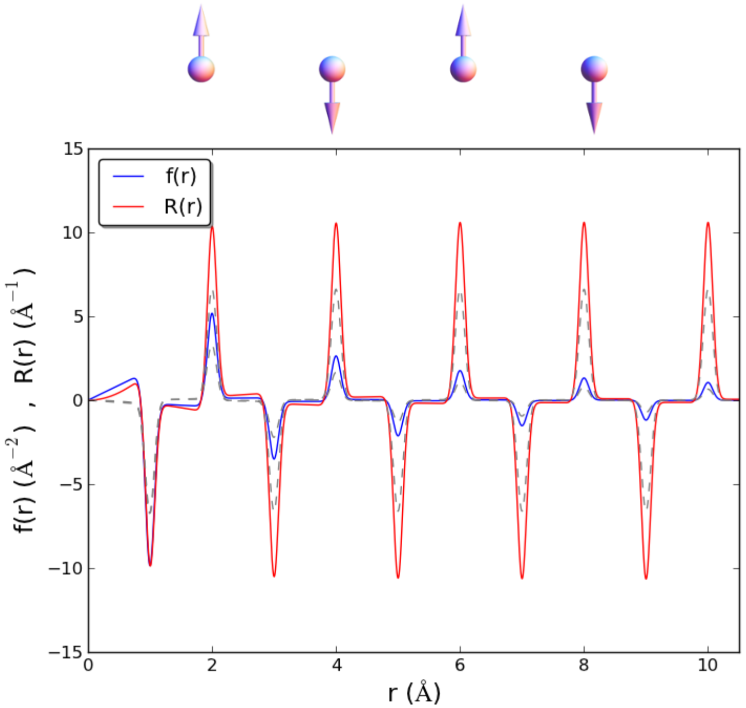
$$B_{ij} = 2S_i^x S_j^x - S_i^y S_j^y$$



Positive peaks for *ferromagnetic* correlations

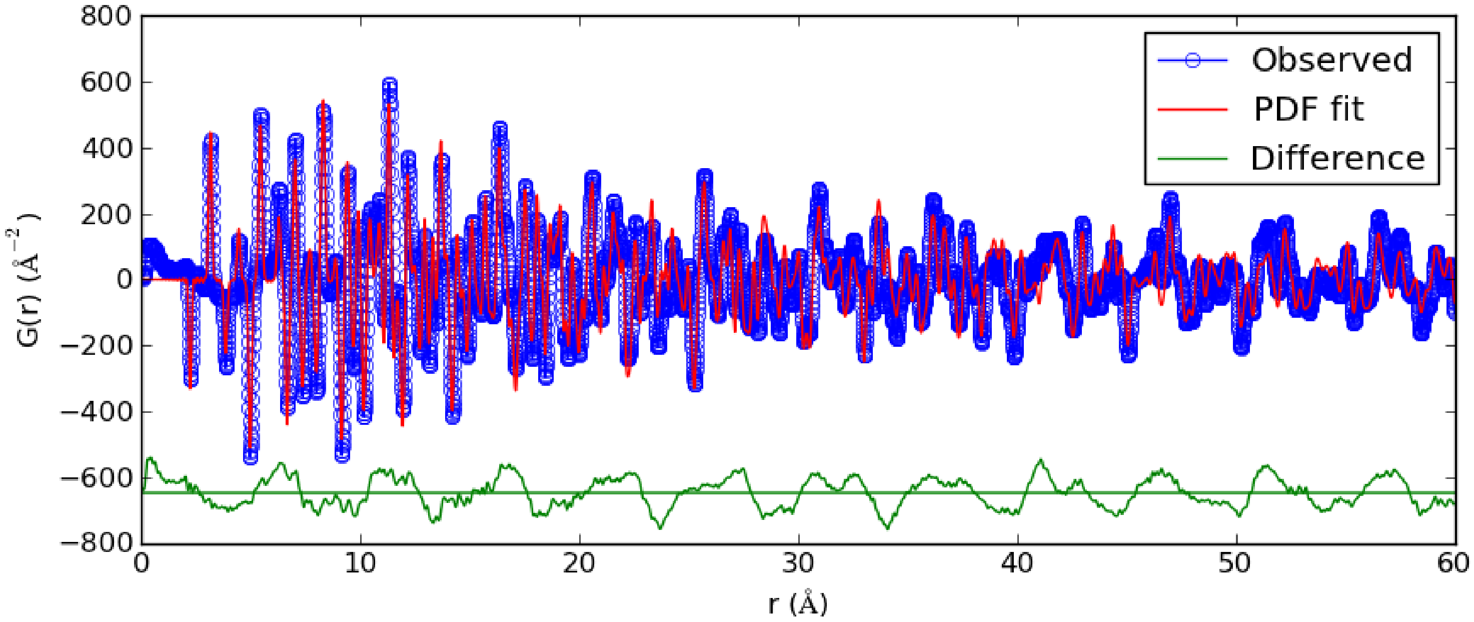
Negative peaks for *antiferromagnetic* correlations

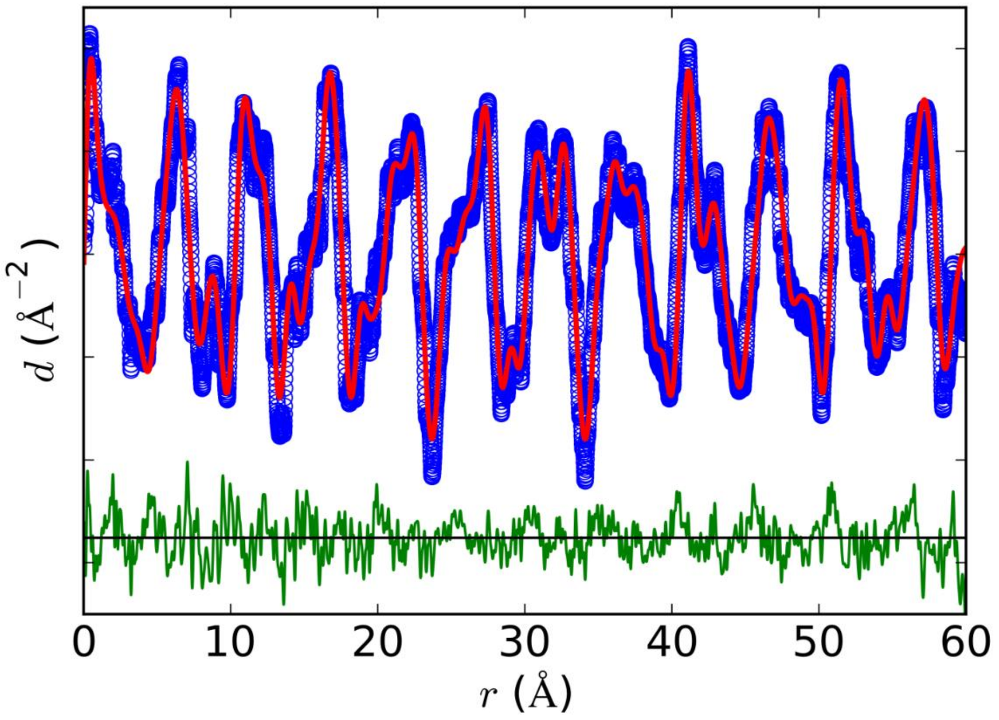




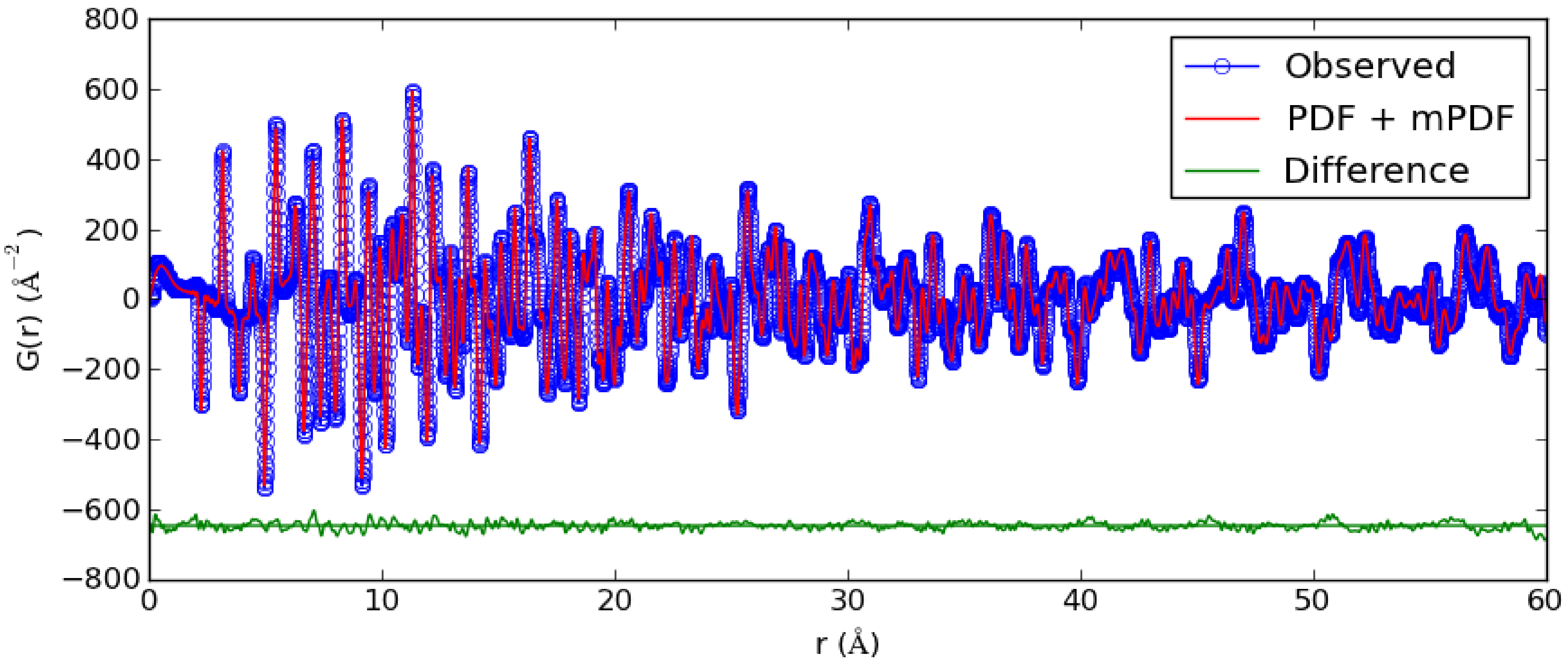
Frandsen et al, *Acta A* **70**, 3-11 (2014)

Example: Antiferromagnetic MnO



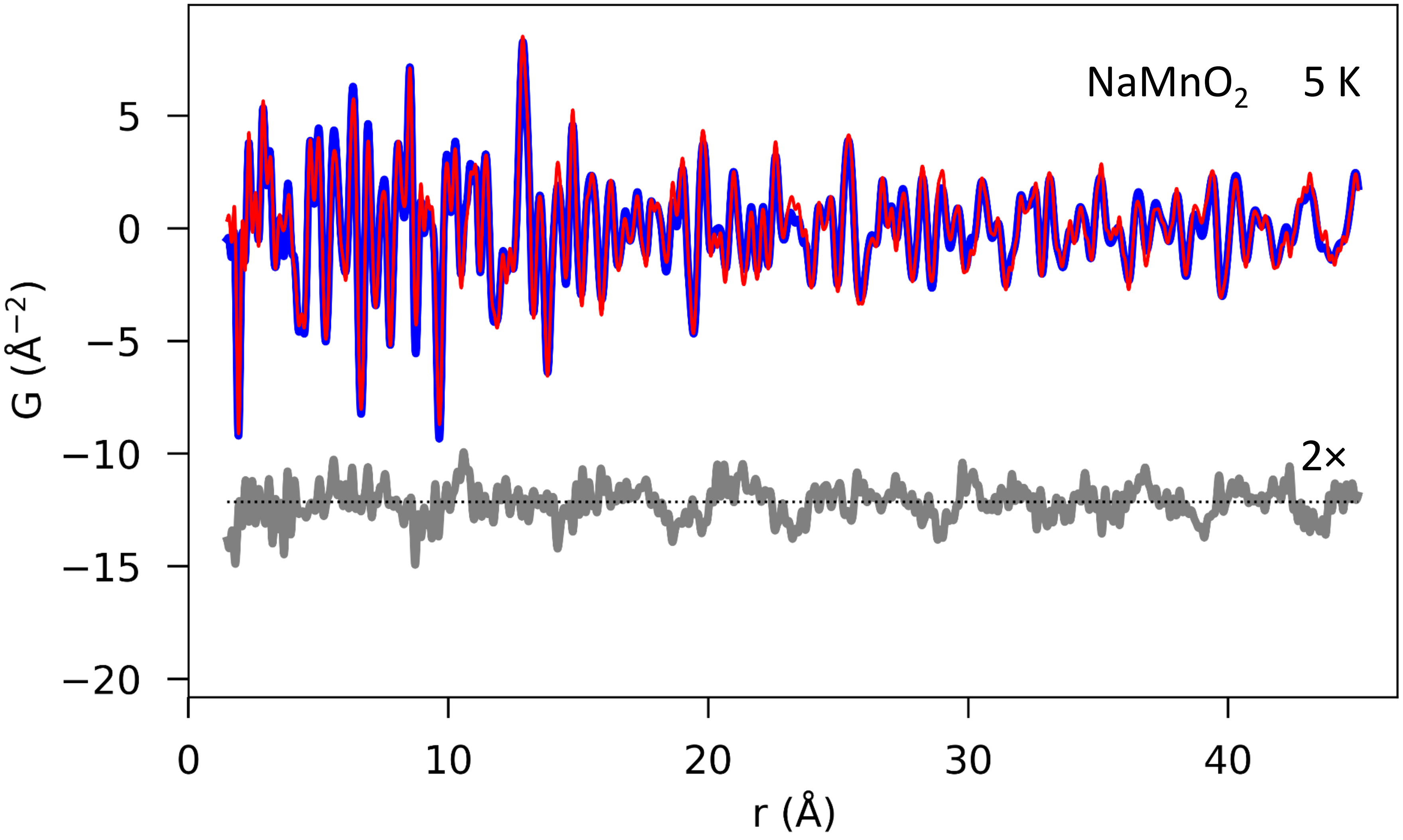


Example: Antiferromagnetic MnO

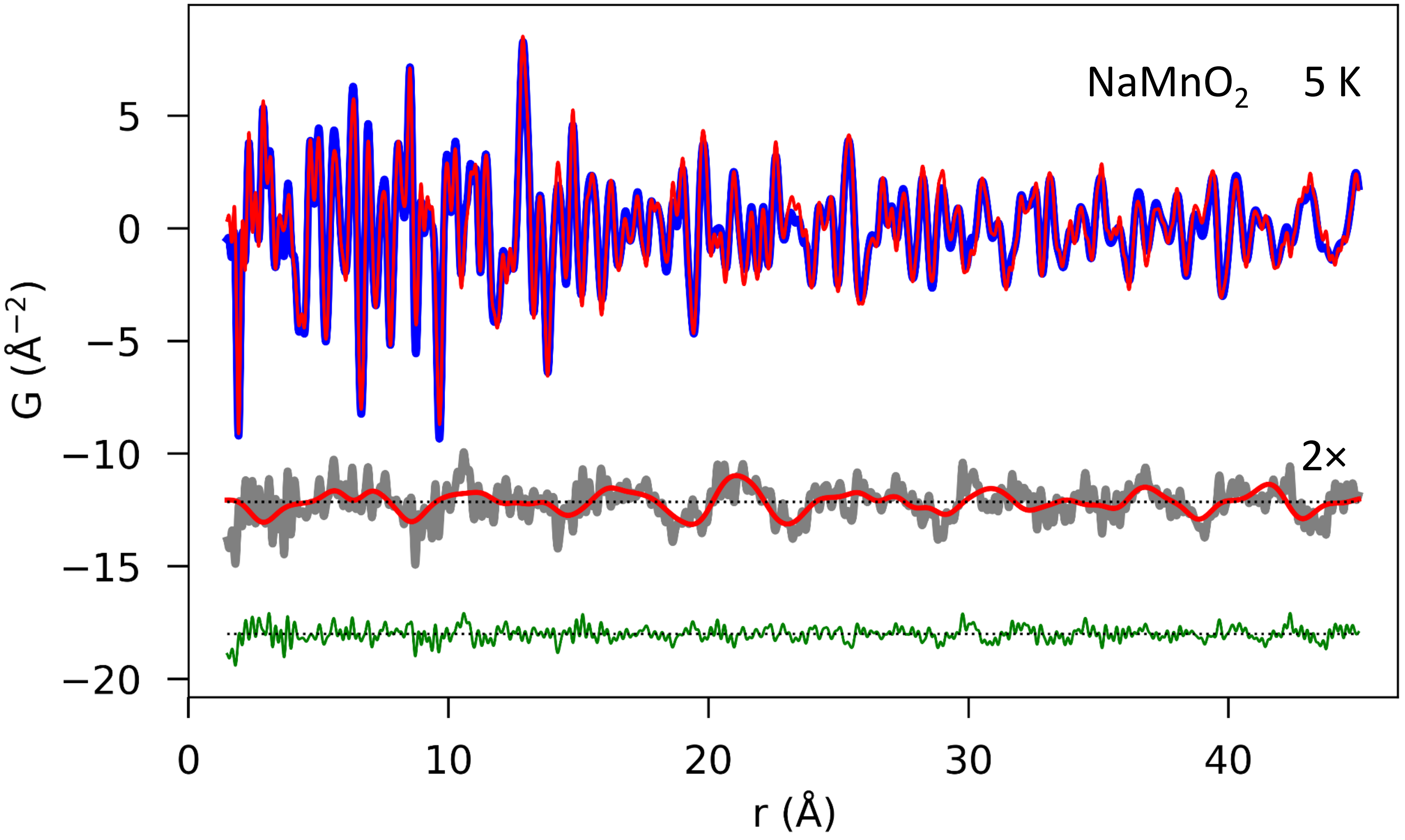


Total PDF fit (atomic + magnetic)

Magnetic PDF refinements for $NaMnO_2$



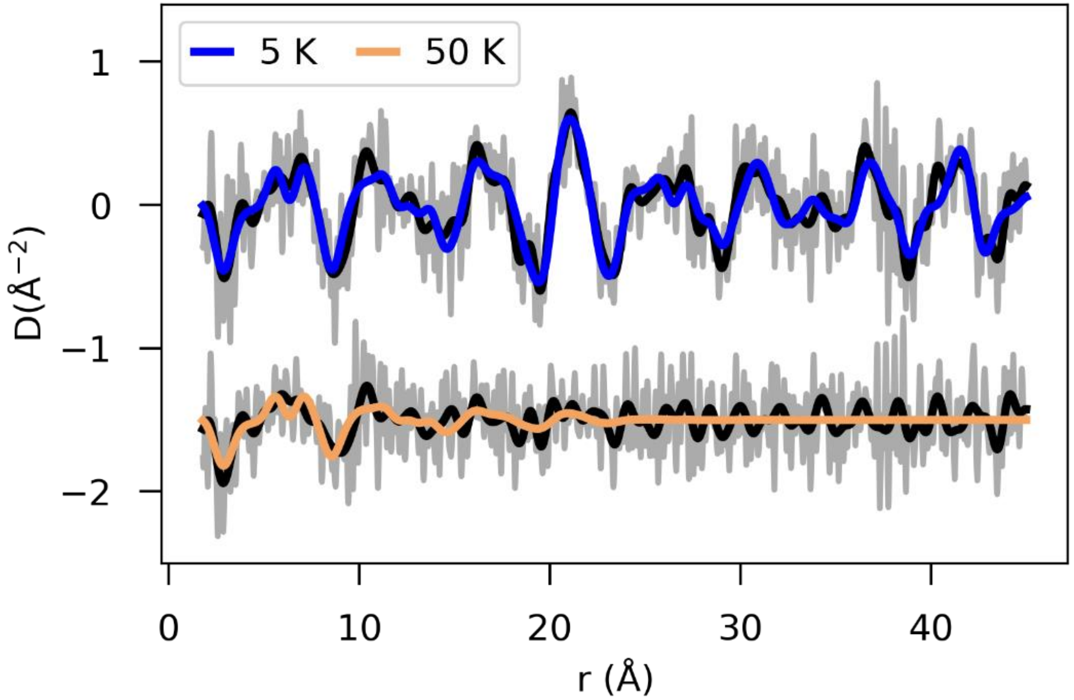
Magnetic PDF refinements for $NaMnO_2$

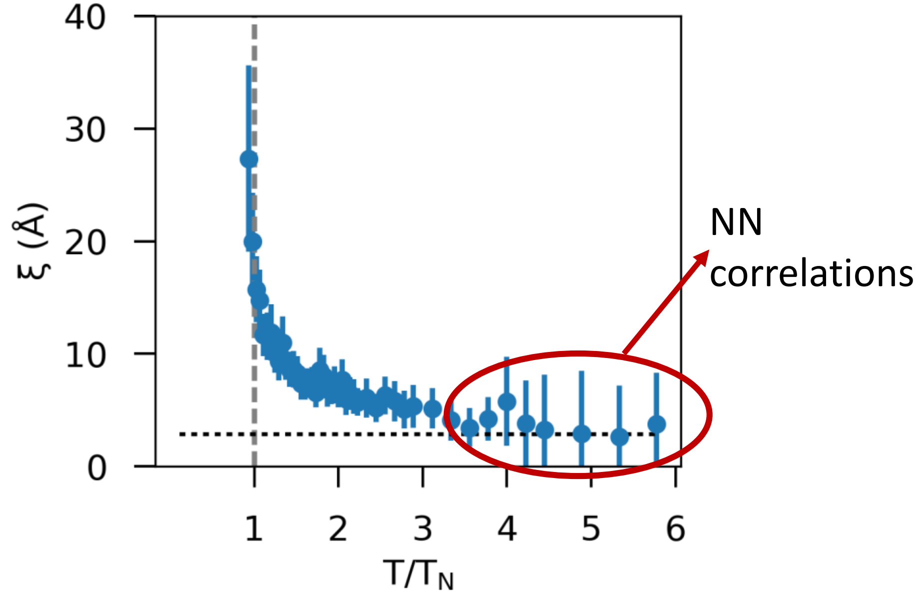


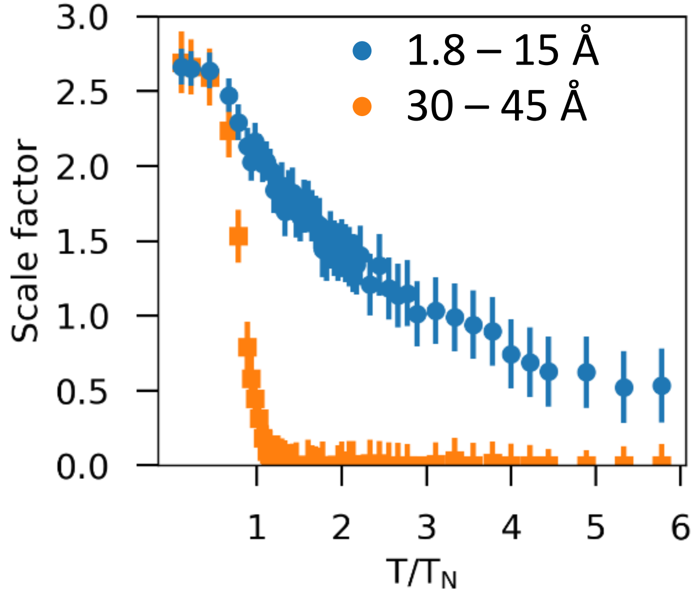
Magnetic PDF refinements

Magnetic model parameters:

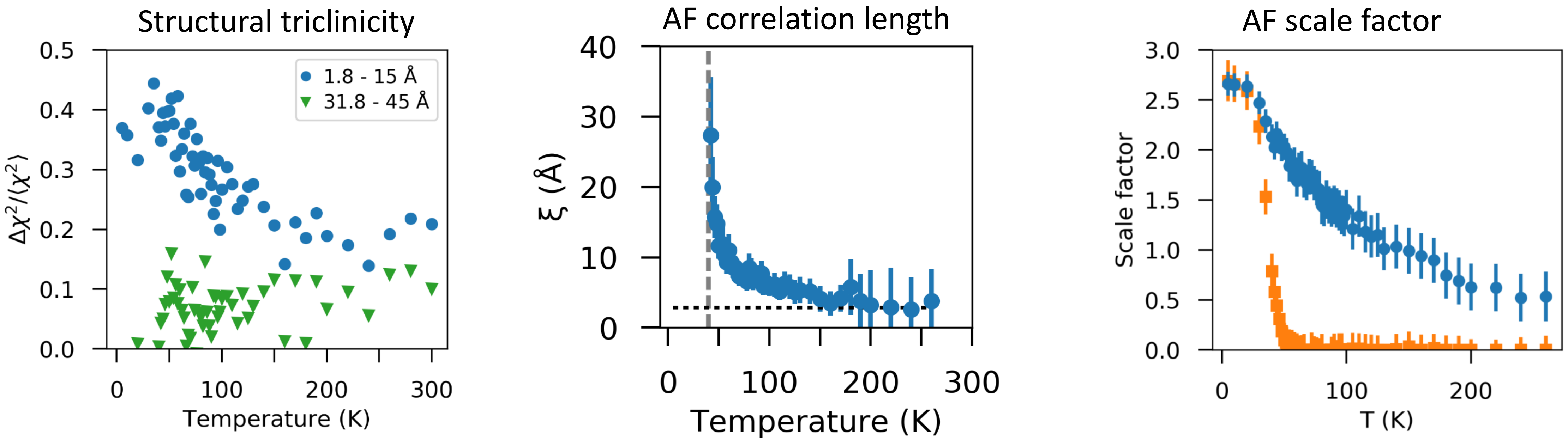
- Scale factor
- Exponential damping envelope
- Two polar angles to define spin direction







Connection to atomic PDF results: Pinning down the transition mechanism



- Local triclinicity and AF correlations share identical temperature dependence
- Long-range AF order triggered once AF correlations reach length scale of local triclinic distortion (~2 nm)
- **Novel transition mechanism:** *Short-range* triclinic distortion lifts triangular degeneracy on the nanoscale, enabling *long-range* antiferromagnetic order

Comparison to $CuMnO_2$: Whence the difference?

$CuMnO_2$ achieves magnetic LRO through a *global* degeneracy-lifting structural distortion; $NaMnO_2$ does the same through a *local* distortion

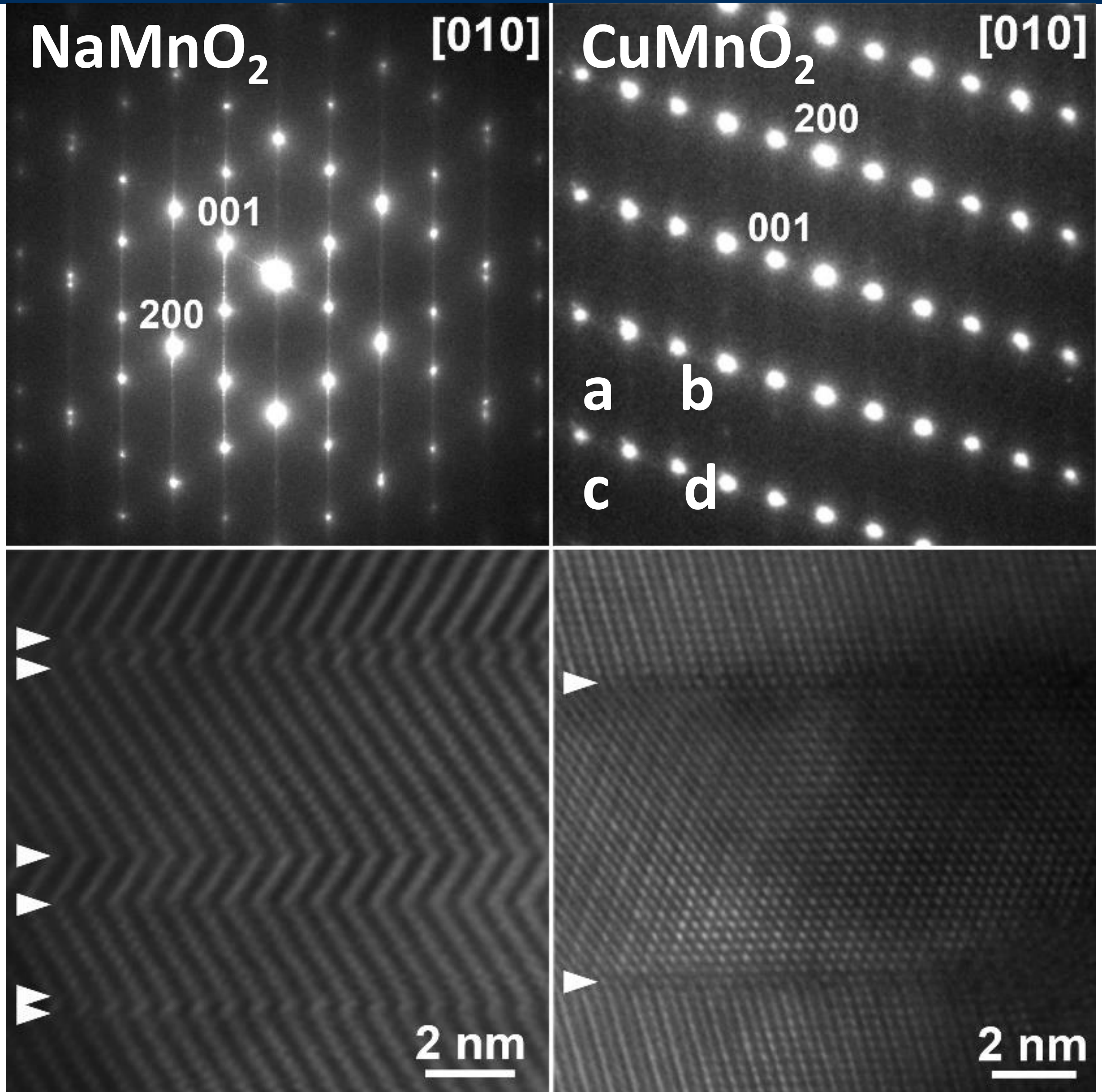
Key Difference: $NaMnO_2$ has significantly more structural disorder

→ Na vacancies (8%)
Mn^{3+} (S=2) → Mn^{4+} (S=3/2)

→ Stacking faults

Stacking faults in $NaMnO_2$ and $CuMnO_2$

TEM data



Comparison to $CuMnO_2$: Whence the difference?

$CuMnO_2$ achieves magnetic LRO through a *global* degeneracy-lifting structural distortion; $NaMnO_2$ does the same through a *local* distortion

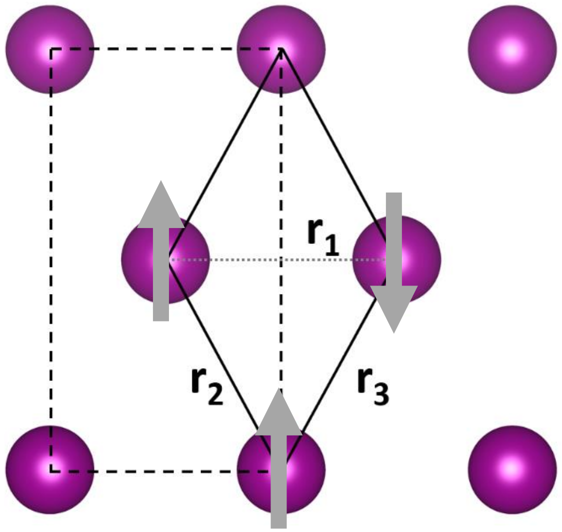
Key Difference: $NaMnO_2$ has significantly more structural disorder

Na vacancies (8%)
Mn^{3+} (S=2) → Mn^{4+} (S=3/2)

Stacking faults

Magnetic Exchange Disorder

Theoretical prediction of NN Heisenberg model with magnetoelastic coupling: Beyond a critical level of exchange disorder, a global structural transition will NOT occur



Conclusions

- $NaMnO_2$ displays a well-defined local triclinic distortion correlated over a 2 nm length scale that increases at low temperature
- Short-range AF correlations persist above T_N and track with the local triclinic distortion
- Local triclinic distortion lifts the magnetic degeneracy on the nanoscale, enabling long-range AF order below 45 K
- Rare example of short-range structural distortion coupling to long-range AF order
- Combined atomic and magnetic PDF analysis was key to understanding this system