Disorder and Magnetism: An Examination of Some Spinel and Perovskite Systems

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Spinels: The motivation [Brent Melot]

Spinel $CuMn_2O_4$ [Daniel Shoemaker]

Perovskite (Ba/Sr)(Ti,Nb)O_3 [Katharine Page]

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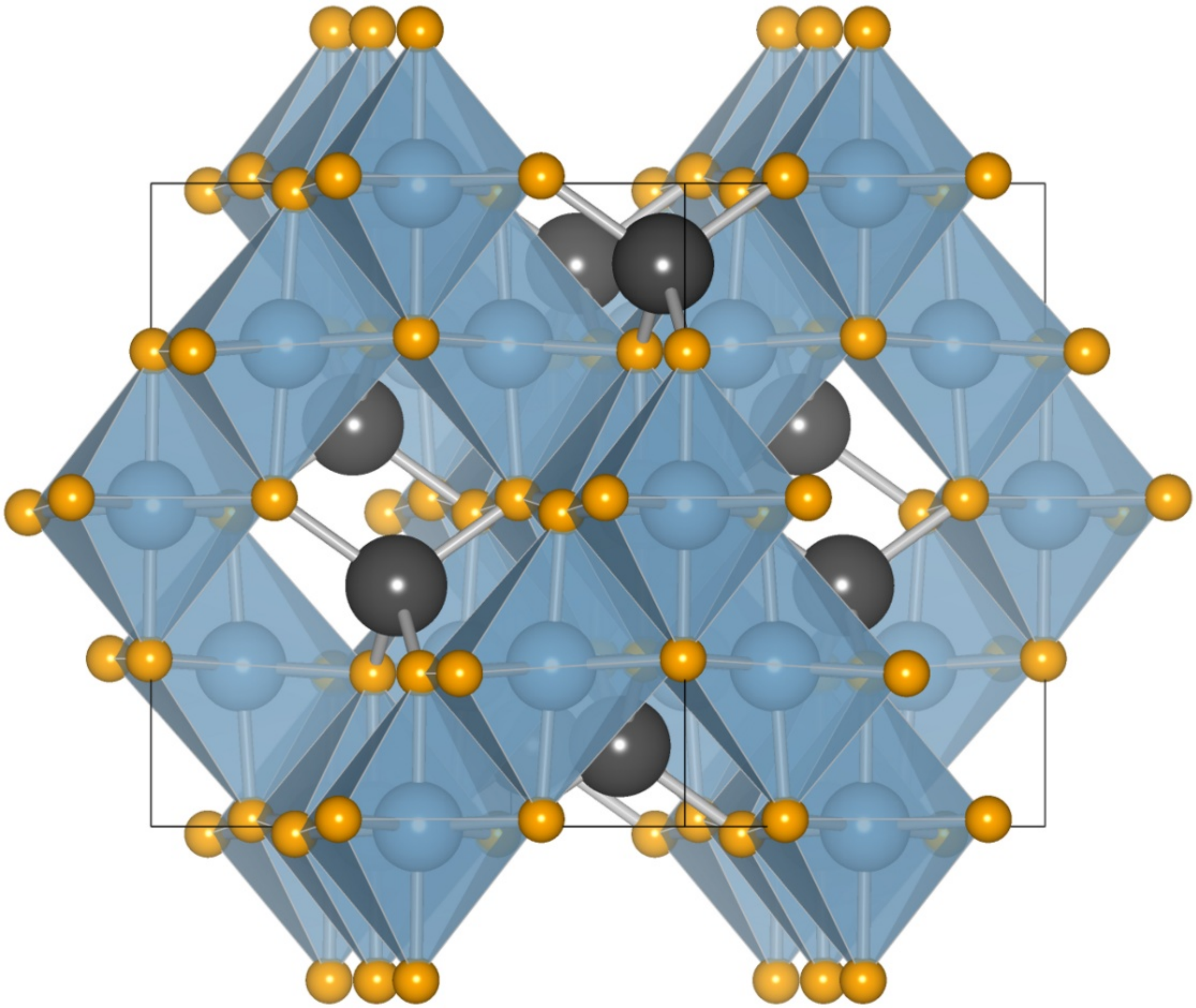
Spinels: The Motivation

Thanks: A. P. Ramirez, G. Lawes

The spinel structure



Edge-shared AO_6octahedra, with tetrahedral B ions connecting the octahedra.

A-B is the principle magnetic interaction, and it is usually uncompensated antiferromagnetic.

B-B and A-B are also important

The spinel structure

The AB_2O_4 palette: Almost all ions are closed magnetic shells.
Exceptions: ■ Strong *B*-site tendency: (s)

A	Magn.	JT	B	Magn.	JT	Aniso.
Mn^{2+}	Y	N	V^{3+}(s) ■	Y	Y	N/Y
Fe^{3+}	Y	N	Cr^{3+}(s)	Y	N	N
Co^{2+}	Y	N	Mn^{3+}(s) ▨	Y	Y	N/Y
Ni^{2+} ■	Y	Y	Fe^{2+}	Y	N	Y
Cu^{1+}	N	N	Fe^{3+} ■	Y	N	Y
Cu^{2+} ■	Y	Y	Co^{2+}	Y	N	Y
Zn^{2+}	N	N	Co^{3+}	N	N	N
Ga^{3+}	N	N	Rh^{3+}(s)	N	N	N
			Ni^{2+}	Y	N	N
			Cu^{2+} ▨	Y	N	N
			Al^{3+}	N	N	N

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Insulating oxide spinel magnets: New magnetoelectrics

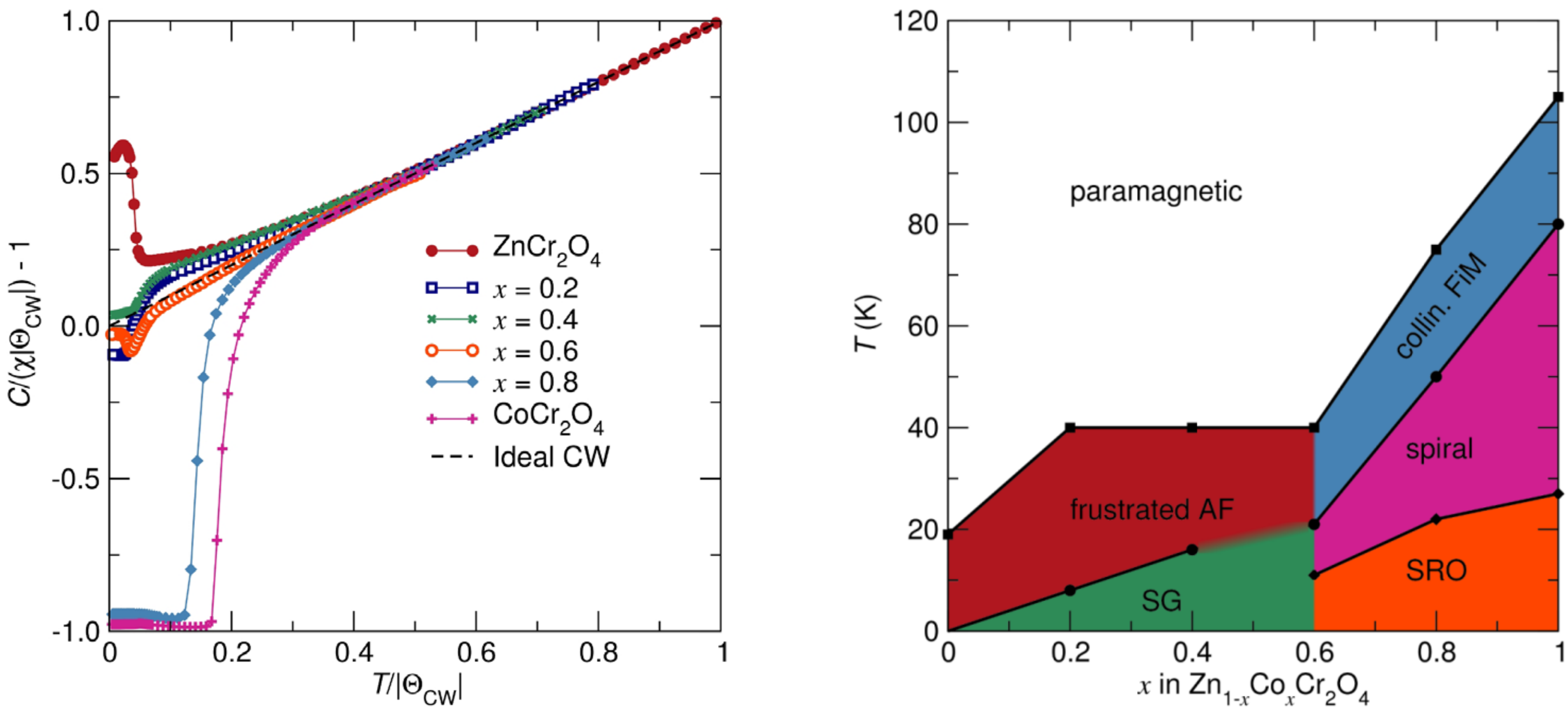
$CoCr_2O_4$: Lawes, Melot, Page, Ederer, Proffen, Hayward, Seshadri, *Phys. Rev. B* **74** (2006) 024413(1-6).

Mn_3O_4: Tackett, Lawes, Melot, Grossman, Toberer, Seshadri, *Phys. Rev. B* **76** (2007) 024409(1-6).

Inhomogeneous magnetism (exchange biasing)

$ZnMn_2O_4$: Shoemaker, Rodriguez, Seshadri, Abumohor, Proffen, *Phys. Rev. B* **80** (2009) 144422(1-9).

$Zn_{1-x}Co_xCr_2O_4$



Rich magnetic phase diagram obtained by increasing A-B magnetic interactions whilst preserving B-B. "*Morphotropic*" *magnetoelectrcs?*

Melot, Drewes, Seshadri, Stoudenmire, Ramirez,
J. Phys. Condensed Matter **21** (2009) 216007(1-7).

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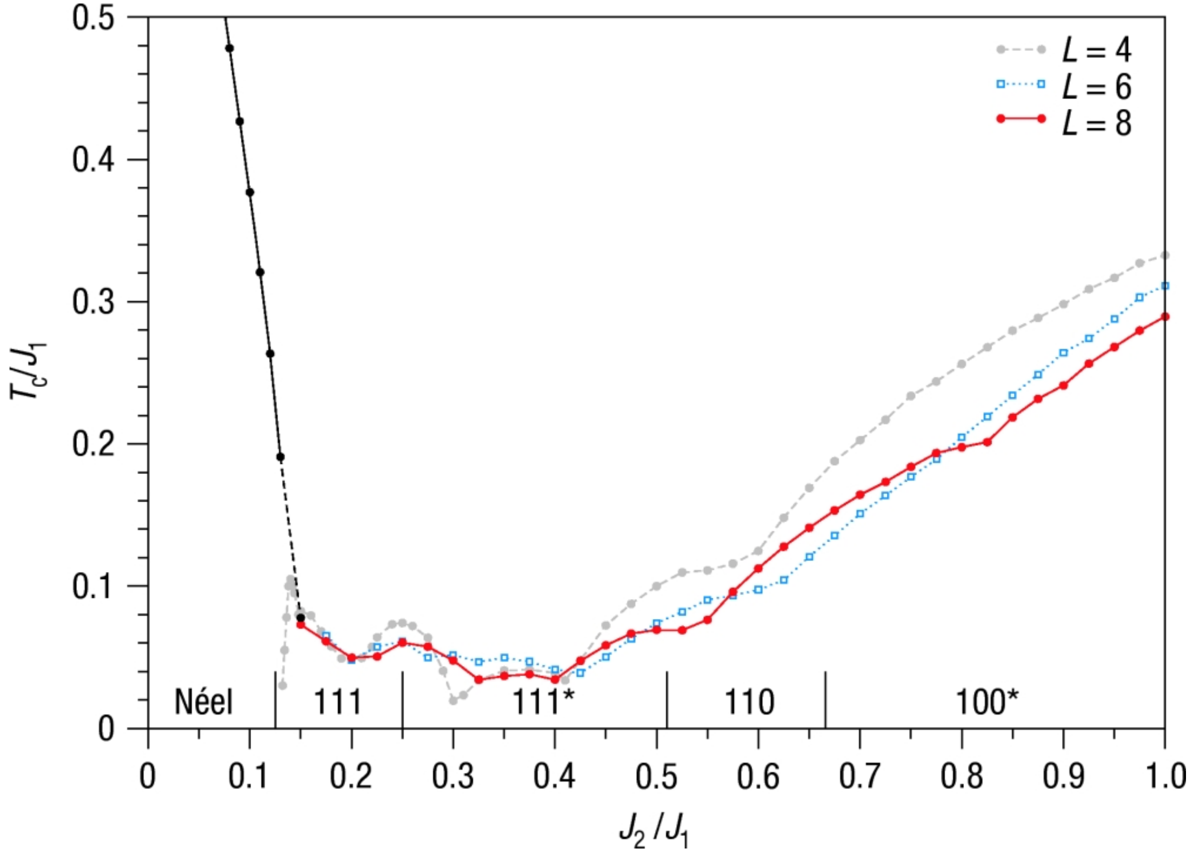
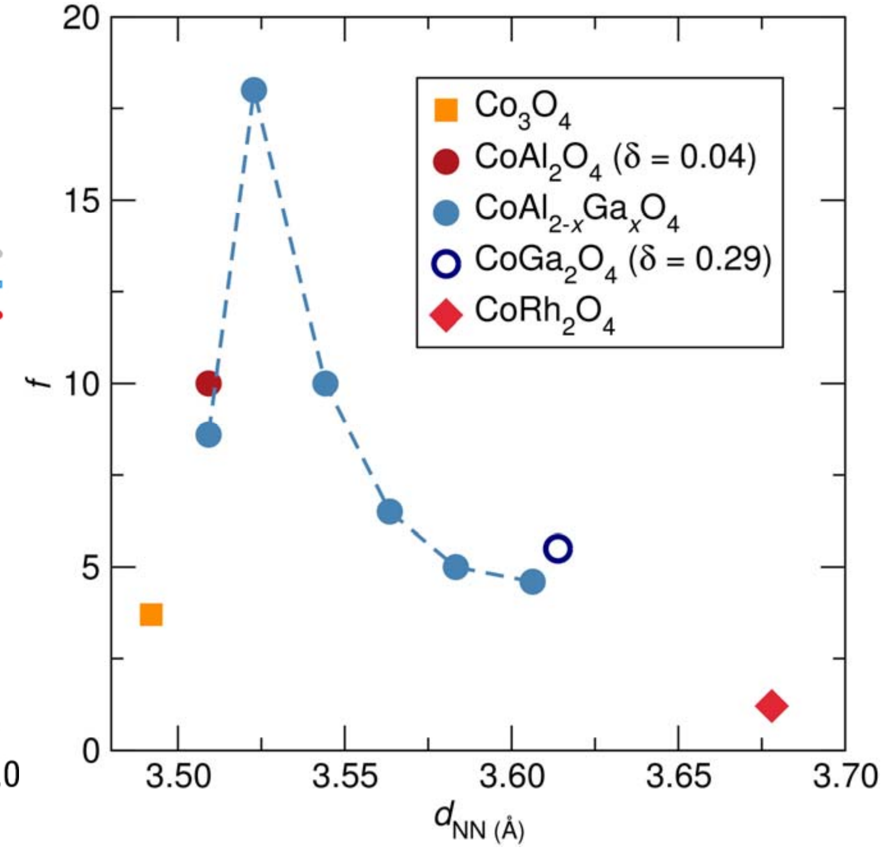
$CoAl_{1-x}Ga_xO_4$: A site-only magnetism





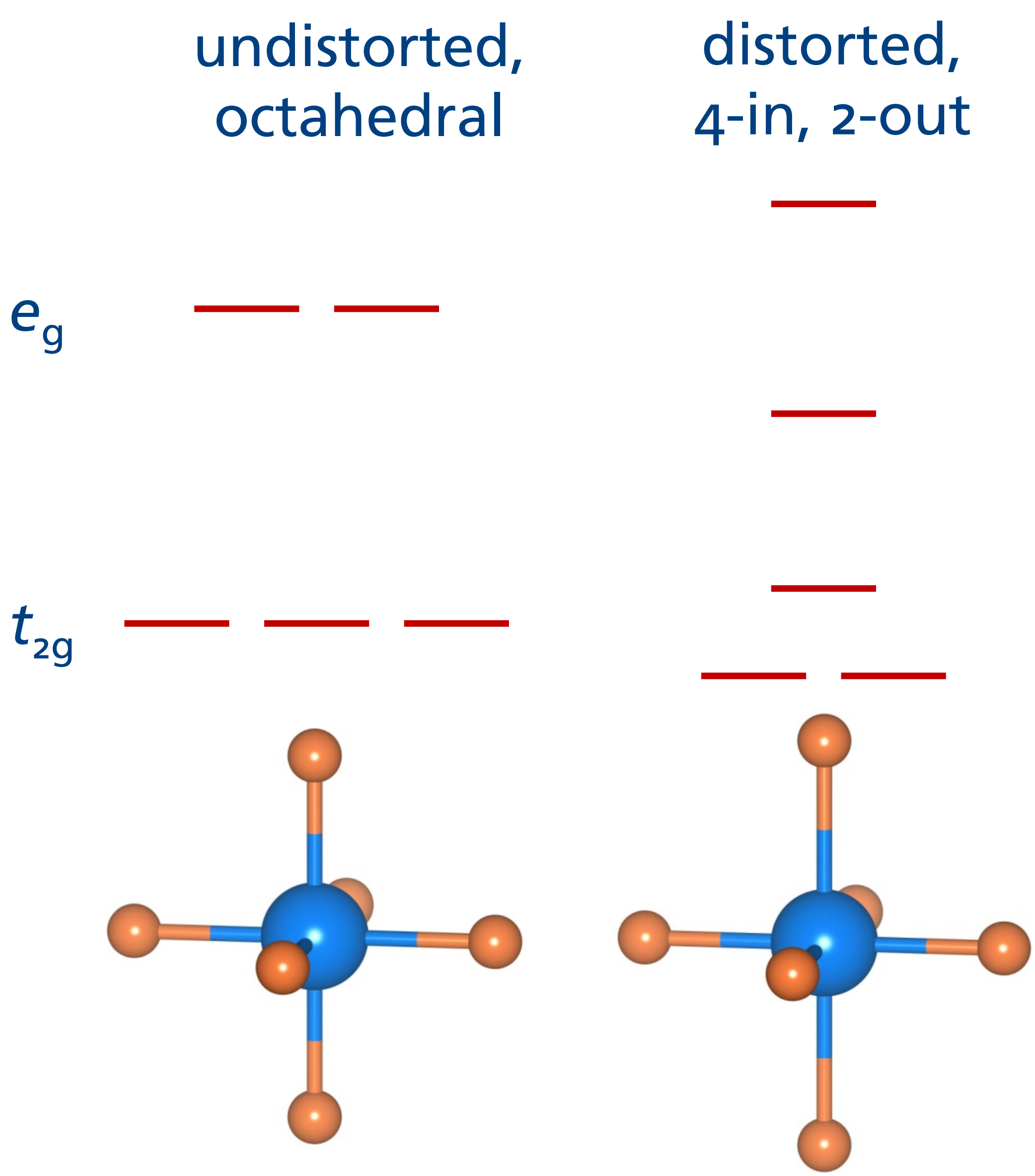
Bergman, Alicea, Gull, Trebst,Balents, *Nature Phys*. **3** (2007) 487-491.

Melot, Page, Seshadri, Stoudenmire, Balents, Bergman, Proffen, *Phys. Rev. B.* **80** (2009) 104420(1-8).

Disorder in Jahn-Teller-active $CuMn_2O_4$

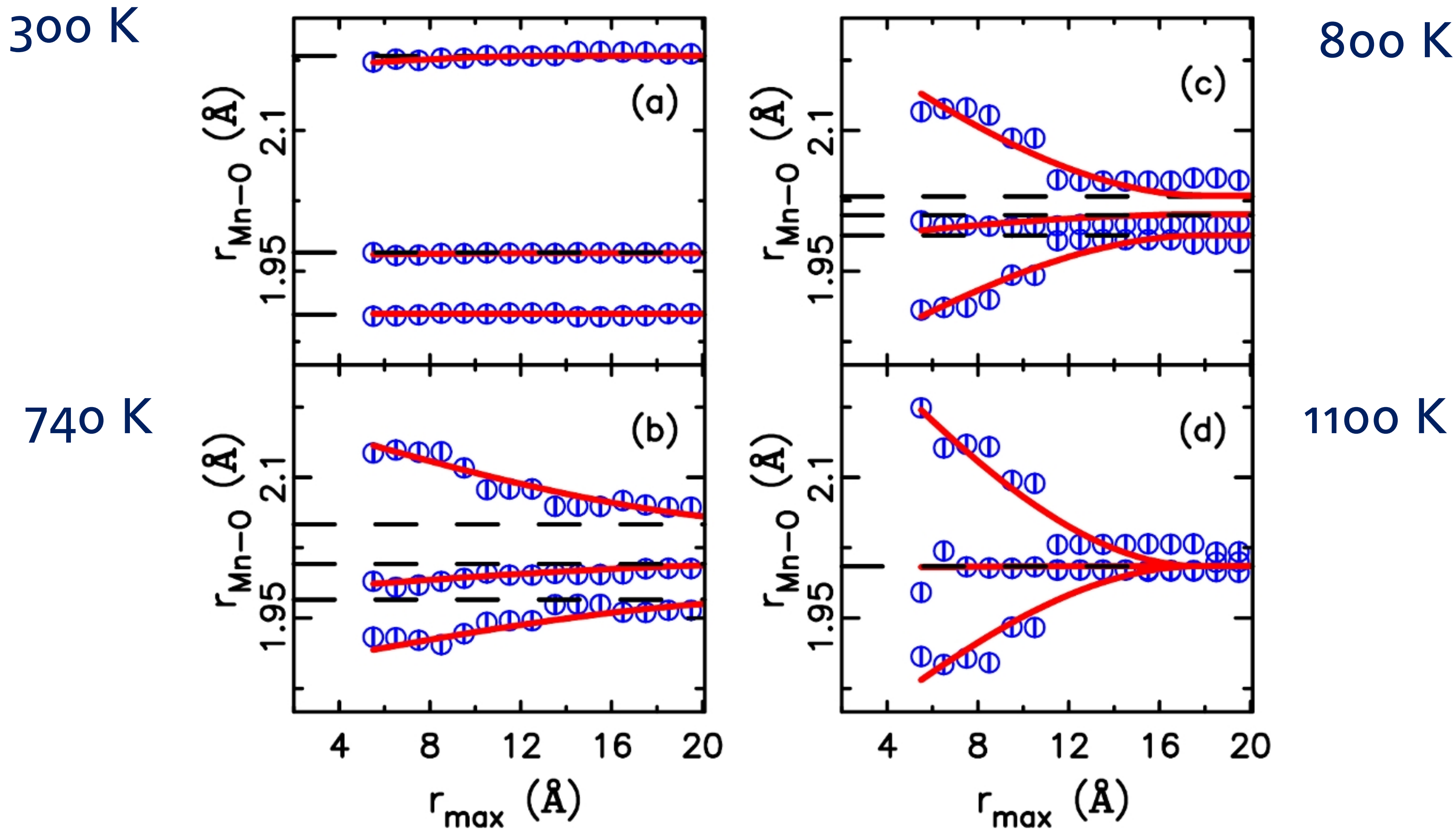
Shoemaker, Li, Seshadri, *J. Am. Chem. Soc.* **131** (2009) 11450–11457.

Disorder in Jahn-Teller-active $CuMn_2O_4$



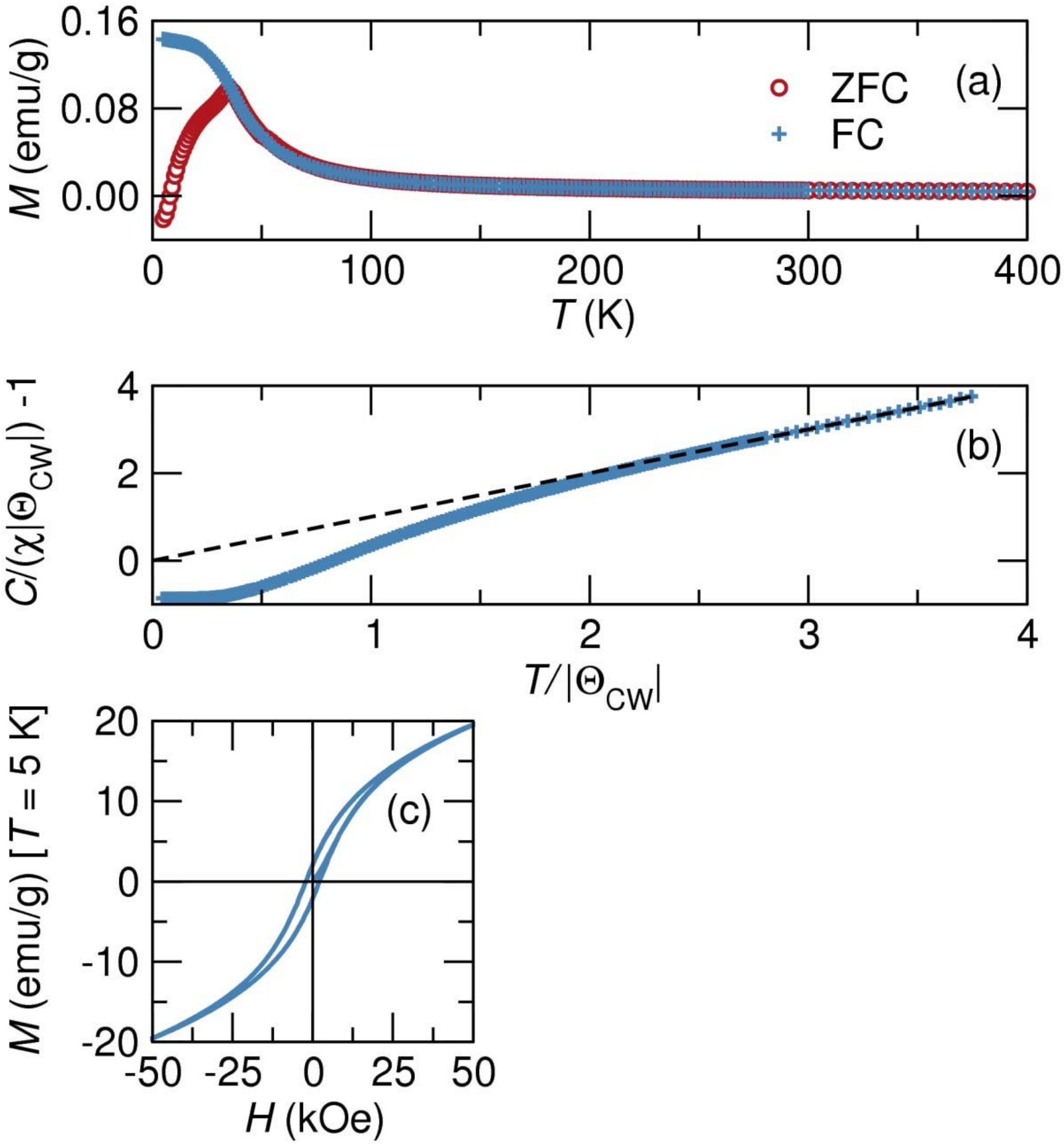
3*d* transition metal ions susceptible to such distortion include Ti^{3+}, Mn^{3+}, Cu^{2+} …

Jahn-Teller effects in $LaMnO_3$



The example of $LaMnO_3$ shows the need for *local* probes for understanding cooperative Jahn-Teller: Qiu, Proffen, Mitchell, Billinge, *Phys. Rev. Lett.* **94** (2005) 177203(1–4).

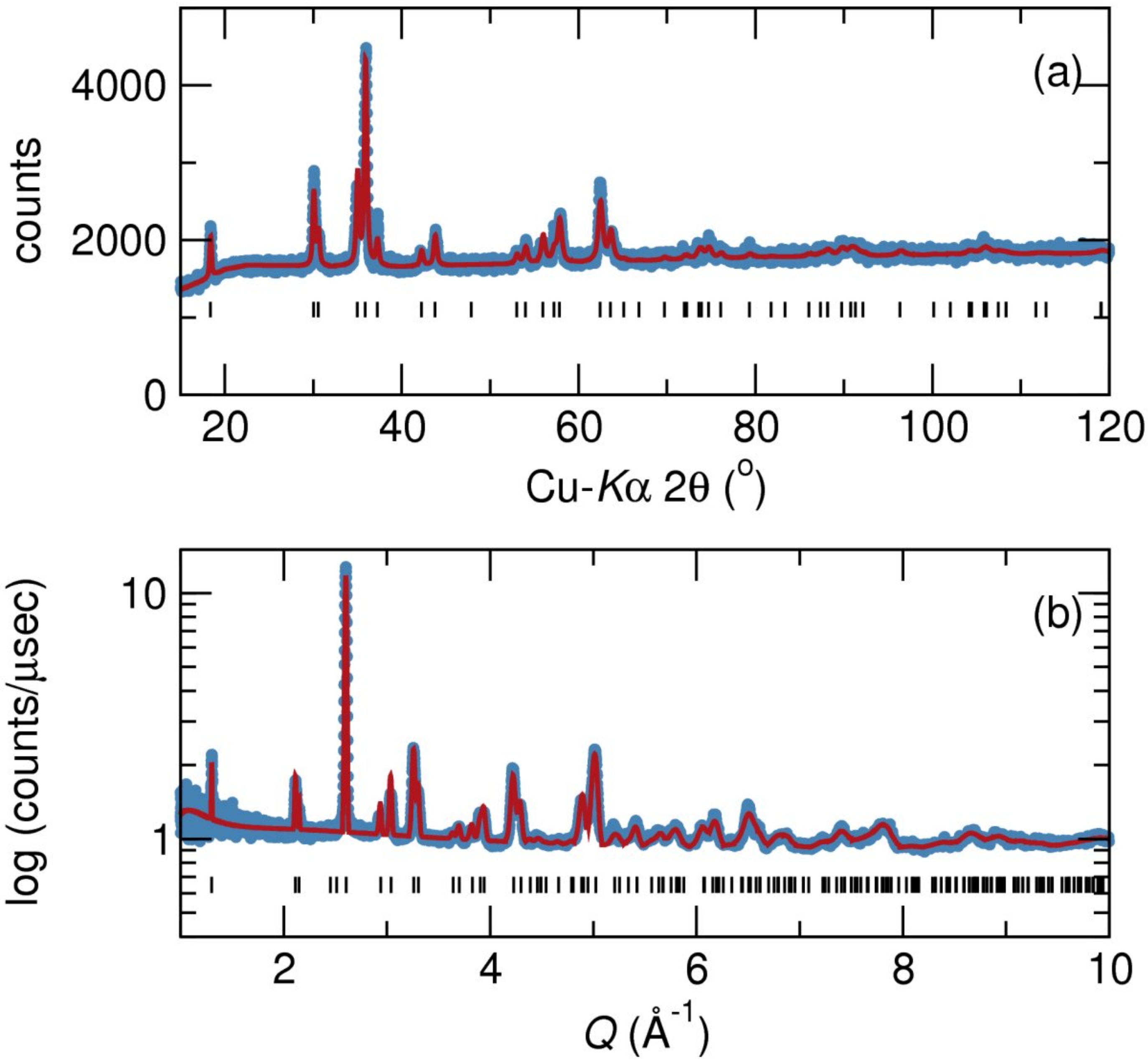
Disorder in Jahn-Teller-active $CuMn_2O_4$



Magnetization acquired under a field of 100 Oe, showing the emergence of a hard ferrimagnet below 40 K.

Θ_{CW} = -107 K.

Disorder in Jahn-Teller-active $CuMn_2O_4$

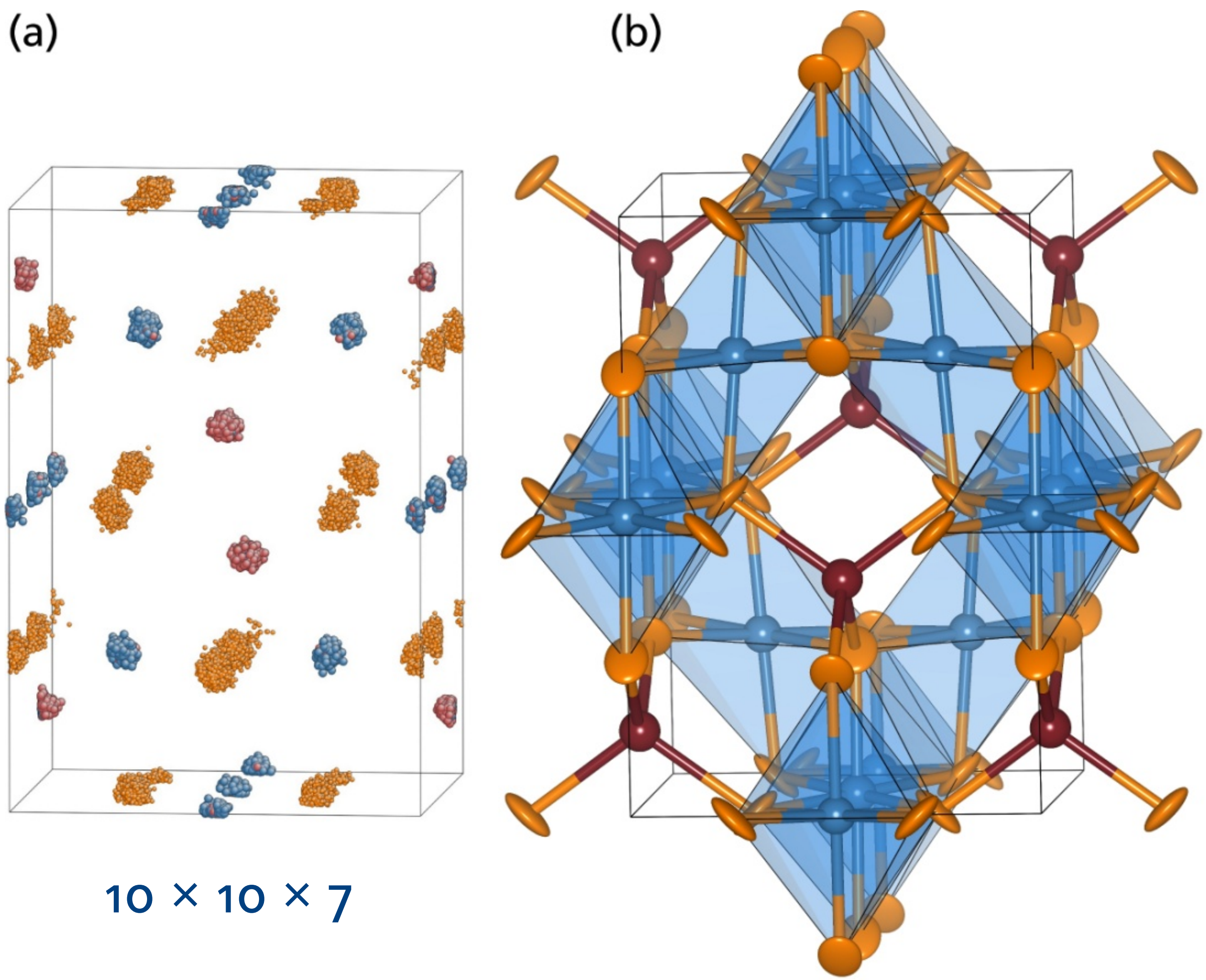


A metastable tetragonal spinel with *two* Jahn-Teller ions. Site mixing as well (close to 30%).

Note the rapid drop in scattering (lab X-ray and NPDF, Los Alamos) intensity, even for neutrons.

$I4_1/amd$ structure does a good job in describing the data.

Disorder in Jahn-Teller-active $CuMn_2O_4$

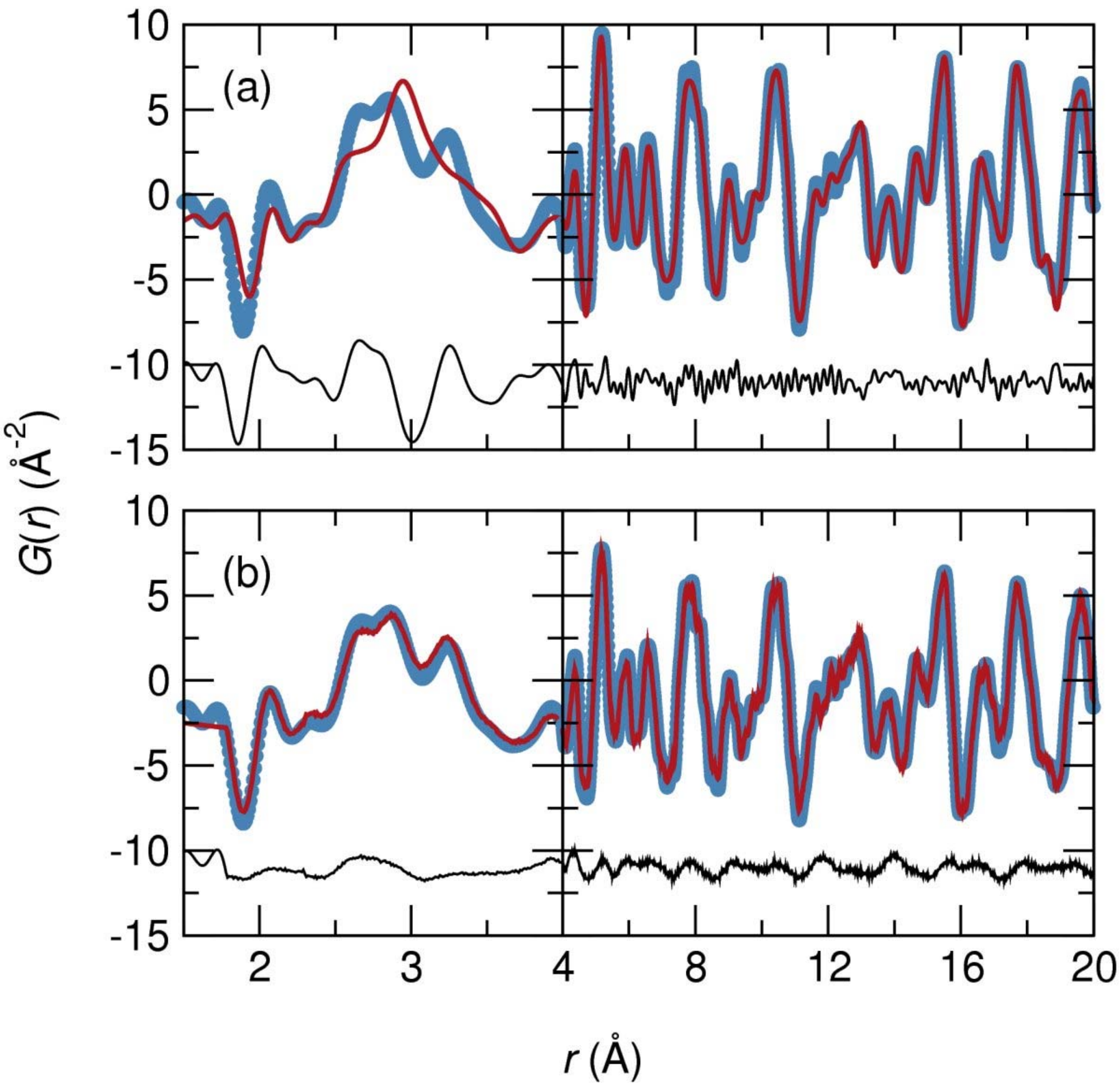


RMC modeling of the total scattering *G*(*r*), using a between 20,000 and 40,000 atom models; ~6 million steps. Hops between A and B sites allowed.

Note smearing of atom positions and contrast the anisotropic thermal parameters from Rietveld.

RMCProfile: Tucker, Keen, Dove, Goodwin, Hui, *J. Phys.: Condens. Matter* **19** (2007) 335218.

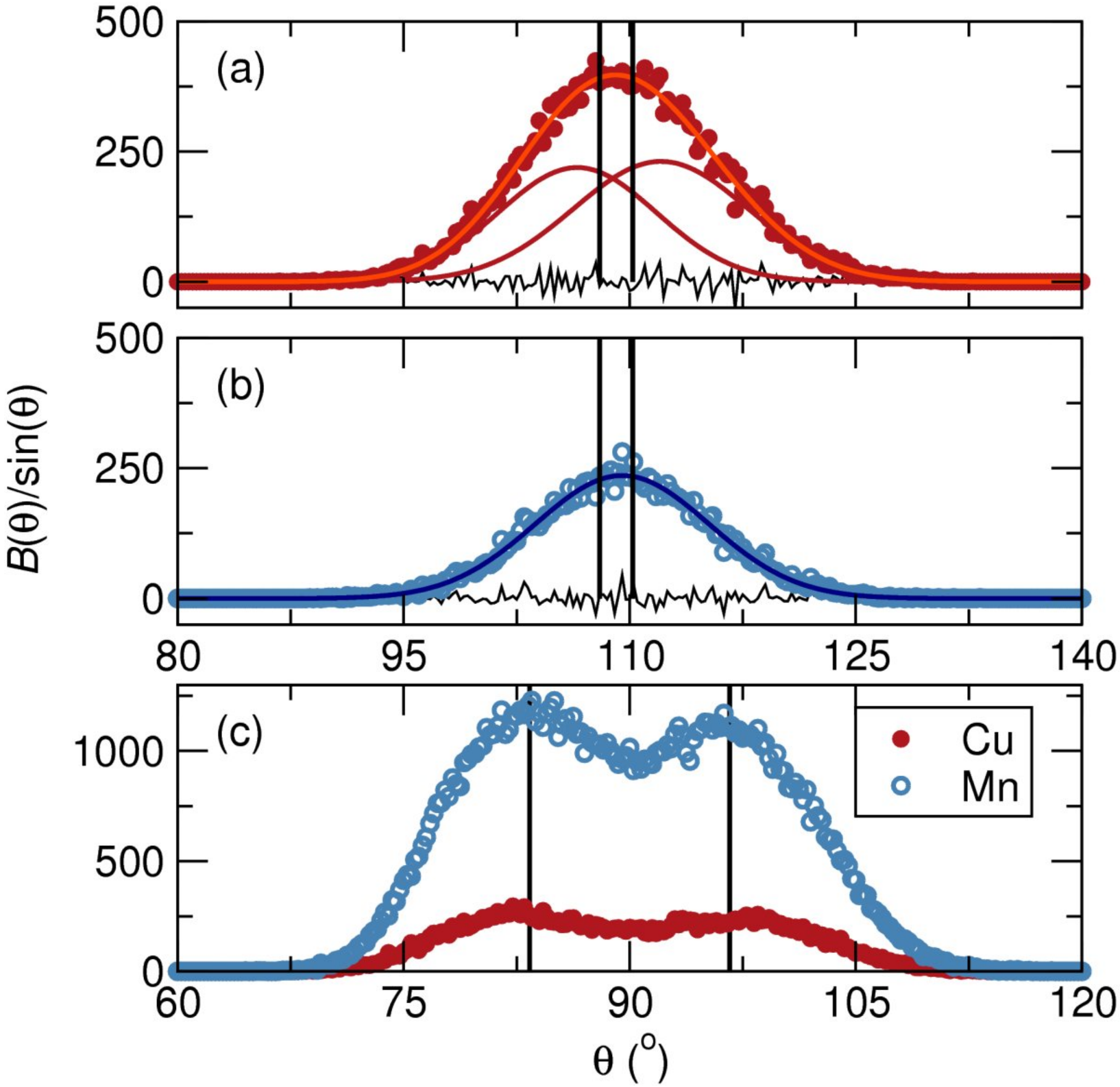
Disorder in Jahn-Teller-active $CuMn_2O_4$



The Rietveld (average) structure fits the *G*(*r*) well beyond the second-near neighbors.

RMC does a much better job all over.

Disorder in Jahn-Teller-active $CuMn_2O_4$



What does a JT active ion do on a tetragonal site?

$Cu^{2+}O_4$ tetrahedra appear flattened, with deviations from 109°28′

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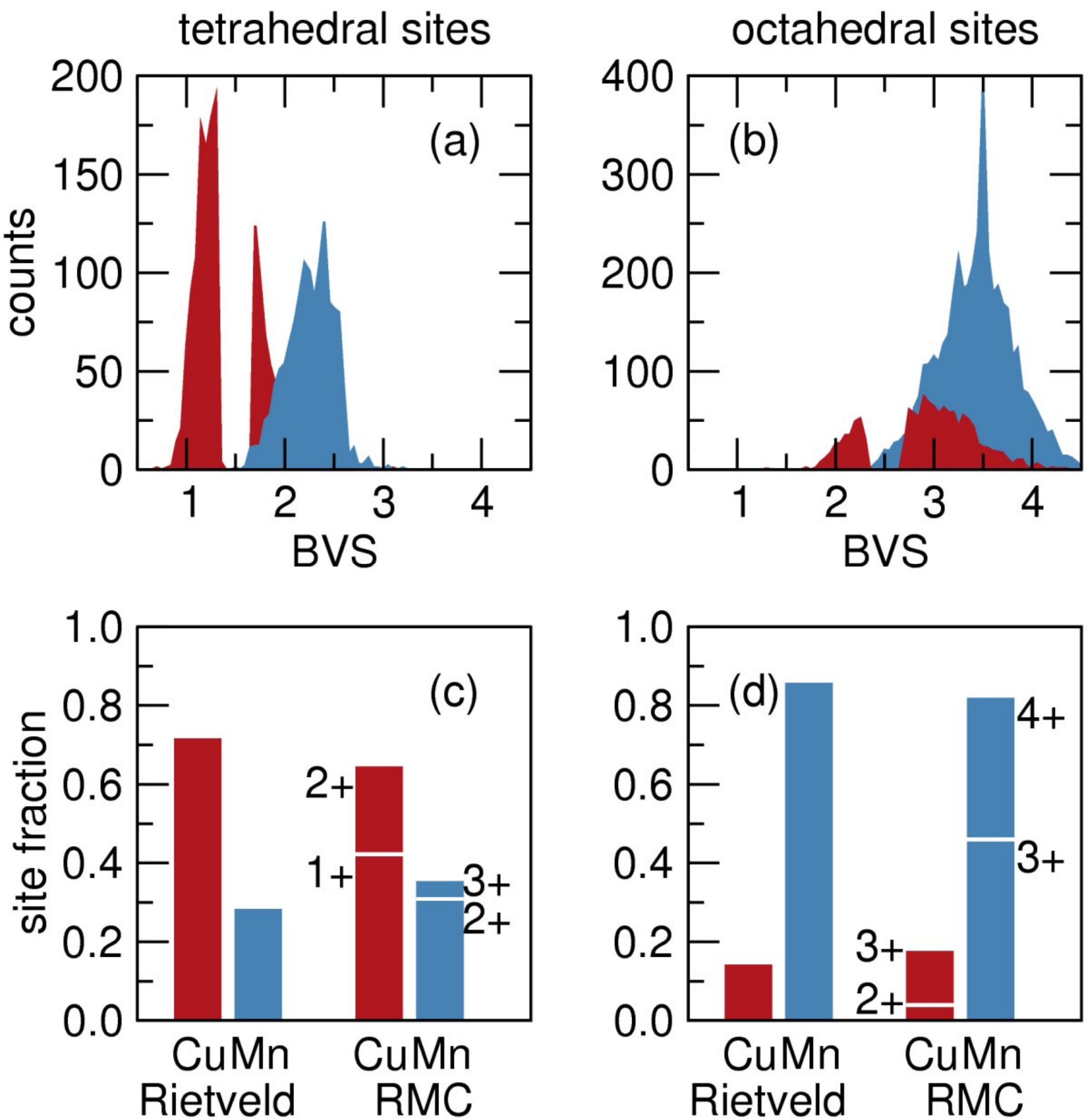
Disorder in Jahn-Teller-active $CuMn_2O_4$



The explicit atom-by-atom description allows bond valence sums to be employed to determine oxidation state, separately on the two sites.

The big surprise: Cu^{3+}

The system disproportionates charge to avoid Jahn-Teller:

$2Cu^{2+} \rightarrow Cu^{1+} + Cu^{3+}$

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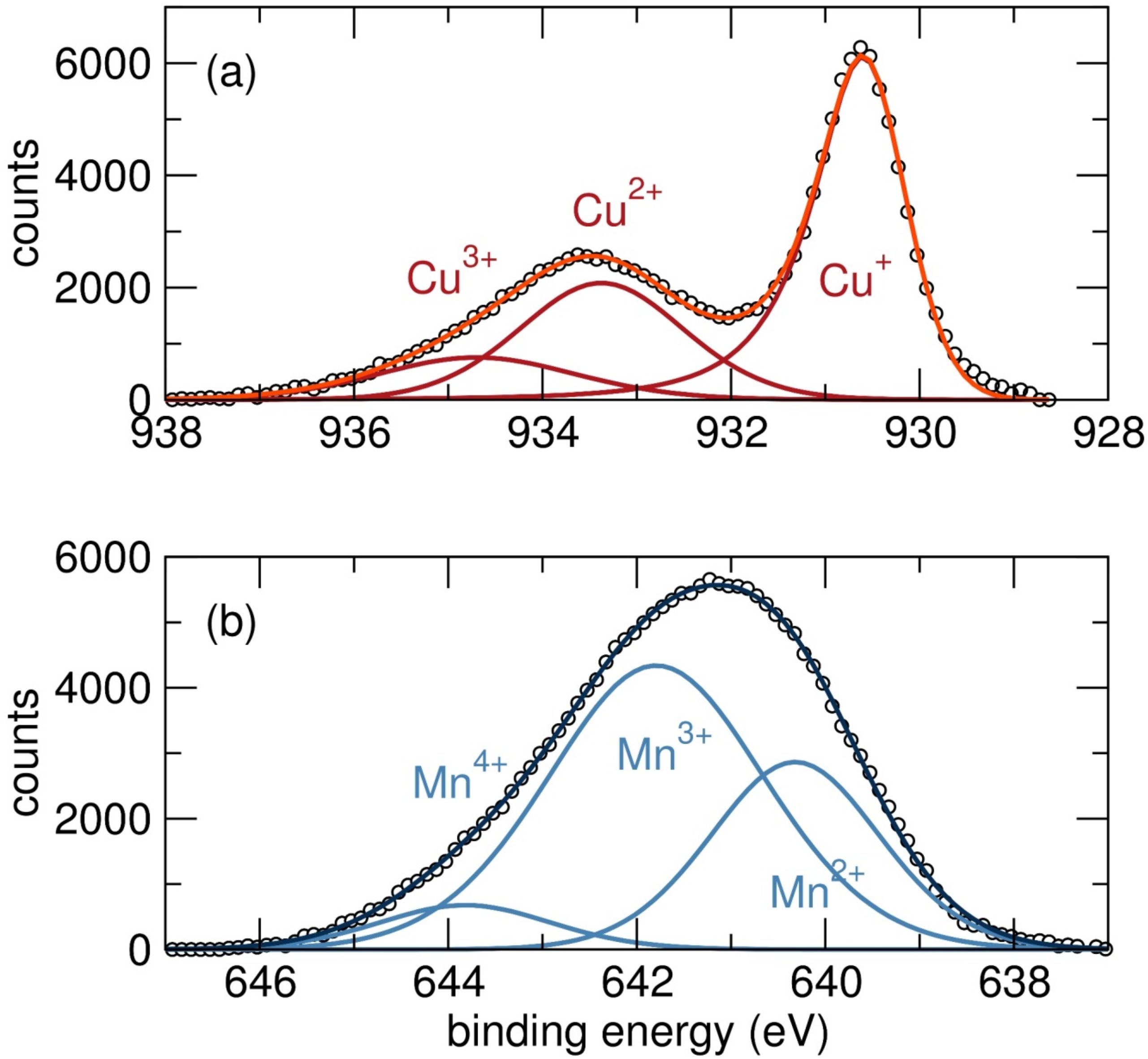
Disorder in Jahn-Teller-active $CuMn_2O_4$



XPS shows up Cu^{3+} as well.

Assignment not previously made.

Disorder in Jahn-Teller-active $CuMn_2O_4$

	Cu			Mn		
charge	tet.	oct.	XPS	tet.	oct.	XPS
1+	0.42 (42%)		47%			
2+	0.20 (20%)	0.10 (10%)	35%	0.34 (17%)		35%
3+		0.28 (28%)	18%	0.05 (2%)	0.80 (44%)	47%
4+					0.72 (36%)	18%

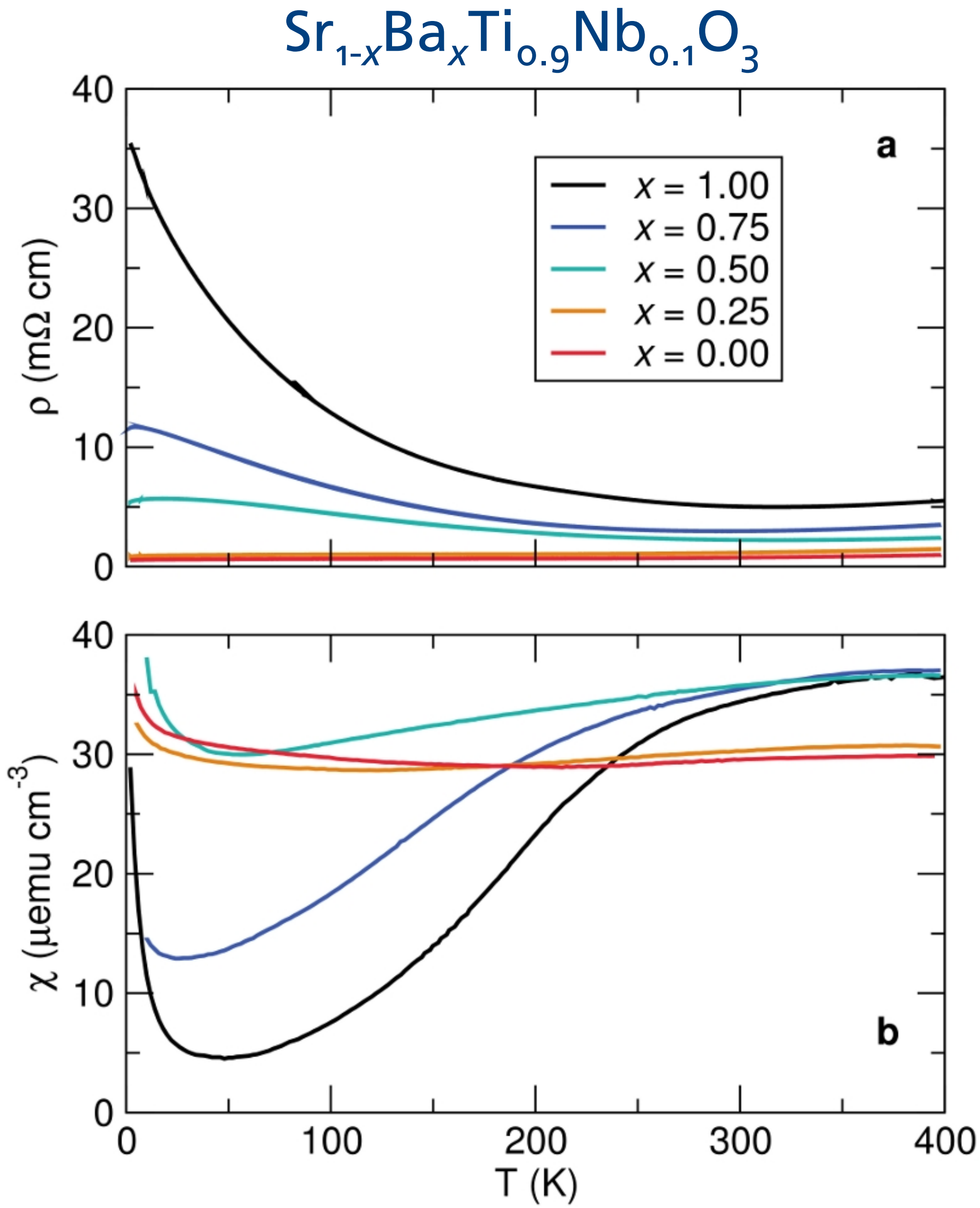
2 sites, 2 cations, and 4 oxidation states.

Charge disproportionation seems to be driven by a tendency to avoid Jahn-Teller states (Cu^{2+} and Mn^{3+} on the tetrahedral site)

Perovskite $(Ba/Sr)(Ti,Nb)O_3$

Page, Kolodiazhnyi, Proffen, Cheetham, Seshadri, *Phys. Rev. Lett.* **101** (2008) 205502.

Perovskite (Ba/Sr)(Ti,Nb)O_3



$SrTiO_3$ and $BaTiO_3$ are band insulators.

Nb^{4+}-substitution (even small amounts) make $SrTiO_3$ metallic and even superconducting.

Not so $BaTiO_3$

Samples from T. Kolodiazhnyi, NIMS, Tsukuba

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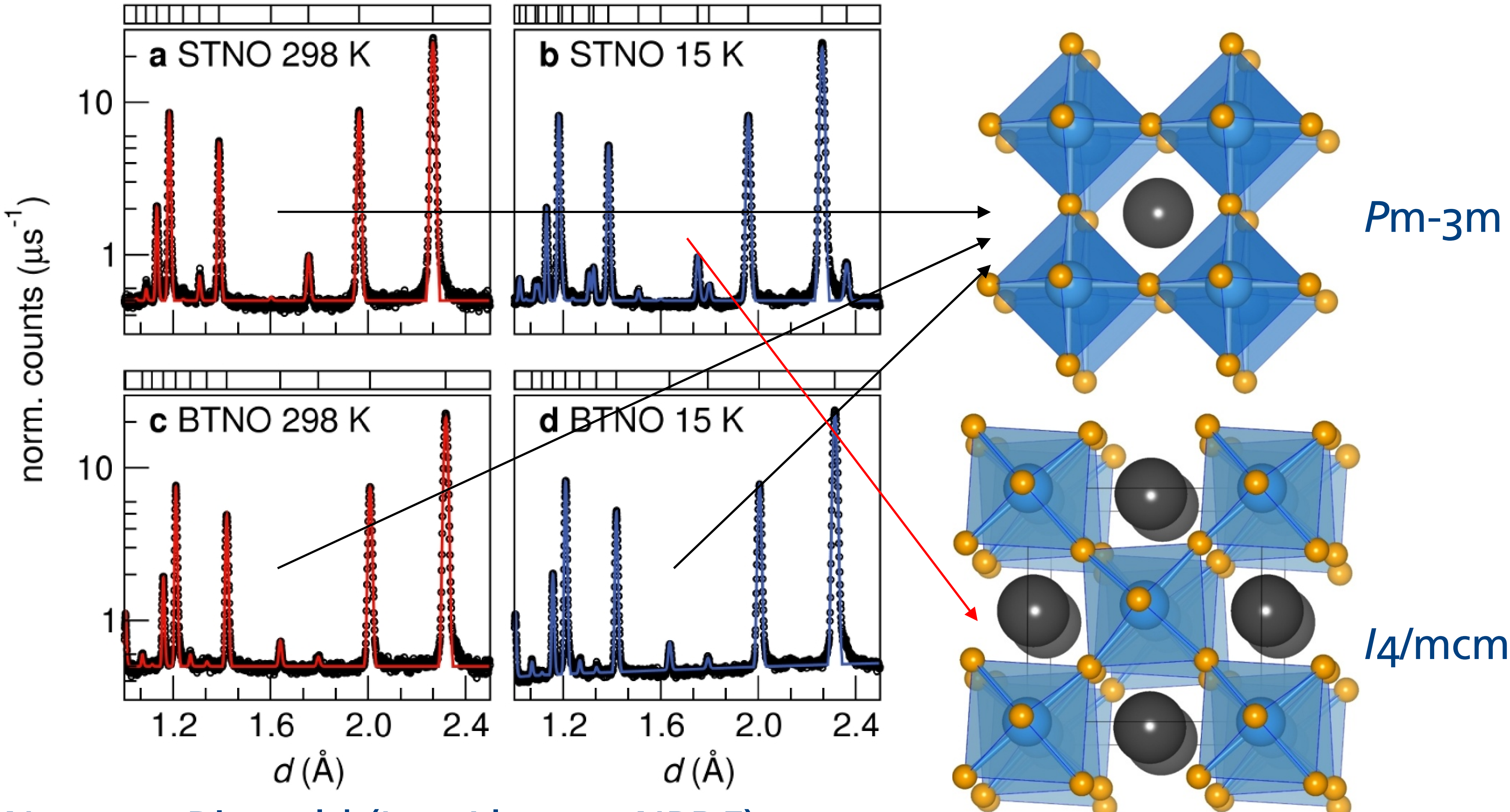
Perovskite (Ba/Sr)(Ti,Nb)O_3

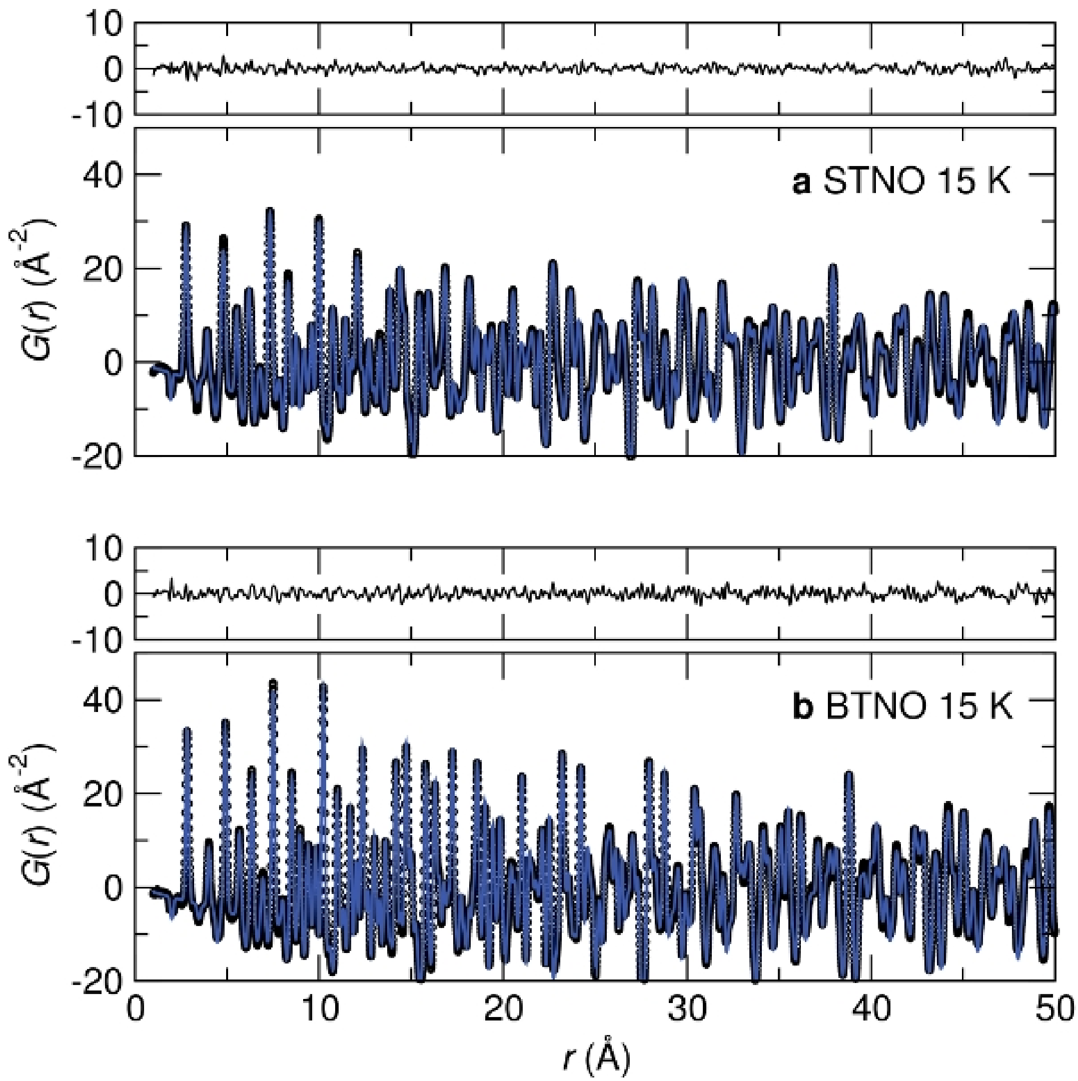
What does structure tell us? Compare $SrTi_{0.875}Nb_{0.125}O_3$ (STNO) and $BaTi_{0.875}Nb_{0.125}O_3$ (BTNO): 1/8th substitution to aid modeling



Neutron Rietveld (Los Alamos, NPDF)

Perovskite (Ba/Sr)(Ti,Nb)O_3

Pair distribution functions fit the average structure out to rather long vectors, very well !



The implication is that the average structure is a good approximation of the real structure.

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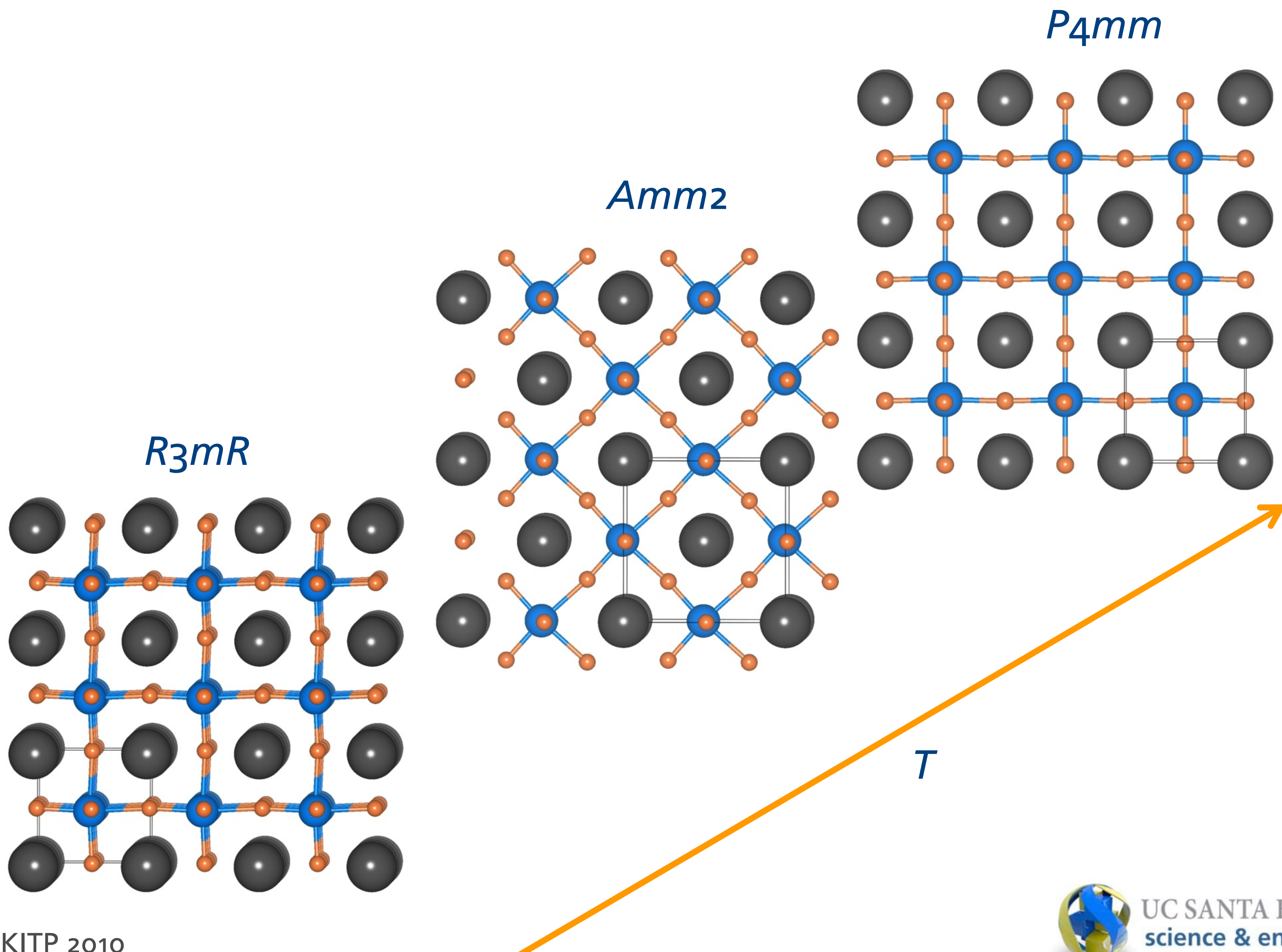
Perovskite (Ba/Sr)(Ti,Nb)O_3



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Perovskite $(Ba/Sr)(Ti,Nb)O_3$

	$SrTi_{0.875}Nb_{0.125}O_3$ 300 K, $Pm\bar{3}m$ Rietveld	PDF	15 K, $I4/mcm$ Rietveld	PDF
a (Å)	3.9237(1)	3.9255(1)	5.5391(2)	5.5418(4)
c (Å)			7.8312(4)	7.835(1)
U_{iso} (Sr)	0.0098(1)	0.0076(2)	0.0053(1)	0.0034(1)
U_{iso} (Ti/Nb)	0.0056(3)	0.0050(2)	0.0042(3)	0.0028(1)
U_{iso} (O)	0.0098(1)	0.0084(1)	0.0054(1)	0.0042(1)
x (O2)			0.2349(1)	0.2350(1)
Occupancy (Nb)	0.127(2)	1/8	0.123(2)	1/8
R_w (%)	3.6	7.7	3.8	7.7
	$BaTi_{0.875}Nb_{0.125}O_3$ 300 K, $Pm\bar{3}m$ Rietveld	PDF	15 K, $Pm\bar{3}m$ Rietveld	PDF
a (Å)	4.0147(1)	4.0165(1)	4.0084(1)	4.0100(1)
U_{iso} (Ba)	0.0061(1)	0.0052(3)	0.0028(1)	0.0021(1)
U_{iso} (Ti/Nb)	0.0093(3)	0.0080(2)	0.0070(2)	0.0059(1)
U_{iso} (O)	0.0077(1)	0.0061(1)	0.0053(1)	0.0040(1)
Occupancy (Nb)	0.131(1)	1/8	0.132(1)	1/8
R_w (%)	3.0	7.4	3.4	8.5

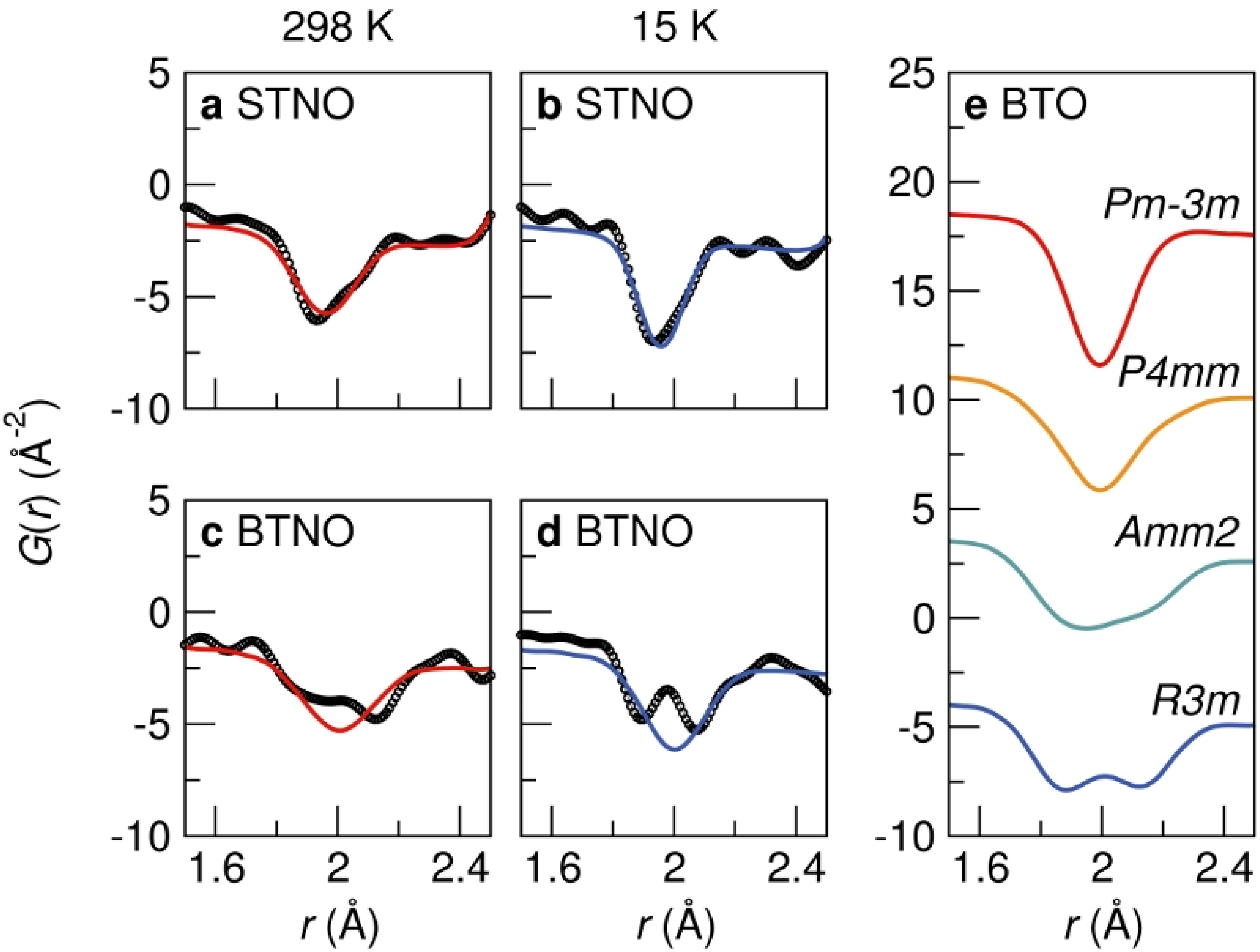
However …

Suggest a tendency to tilt

Suggests a tendency to off-center

Perovskite (Ba/Sr)(Ti,Nb)O_3

What about the very short range ? $BaTi_{0.875}Nb_{0.125}O_3$ displays distortions in the first (Ti/Nb)-O neighbor:



Simulations of the first peak of $BaTiO_3$ for the different crystal structures.

Perovskite (Ba/Sr)(Ti,Nb)O_3

Findings:

$SrTi_{0.875}Nb_{0.125}O_3$:

Nb-substitution (on the perovskite *B* site) does not frustrate tilting. The ground state is tetragonal (with enhanced tilting compared with $SrTiO_3$).

Tilting distortions *do not* influence the ground state, which is metallic (*Cf.* $SrRuO_3$, $LaNiO_3$ …)

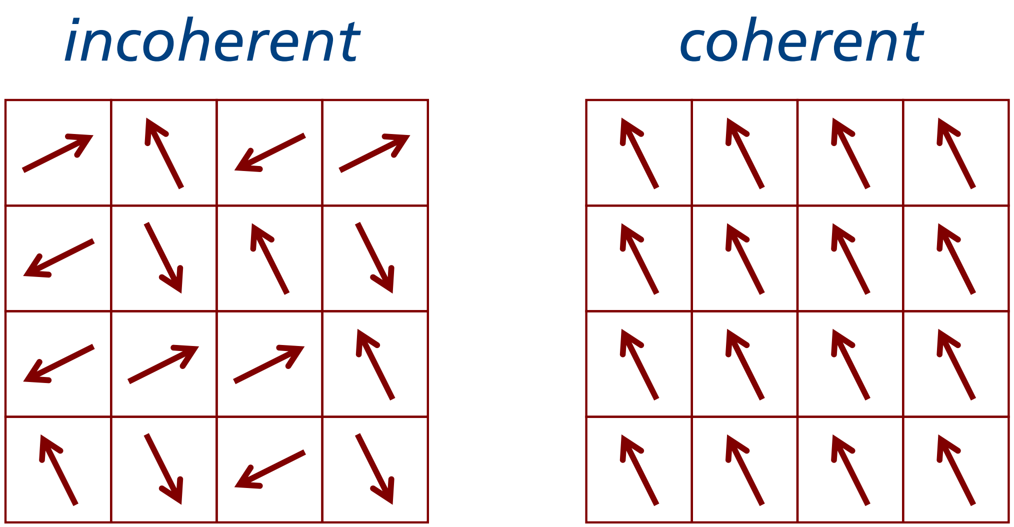
$BaTi_{0.875}Nb_{0.125}O_3$:

Nb-substitution (on the perovskite *B* site) frustrates long-range ordering of dipoles; additionally helped by dipole-dipole screening due to charge carriers. Average structure is cubic.

Dipoles exist locally however. Incoherent off-centering might aid the insulating ground state.

Summary

In many functional materials, modes of disordering exist which may or may not be coherent, and when they are not, special tools are required to see them.

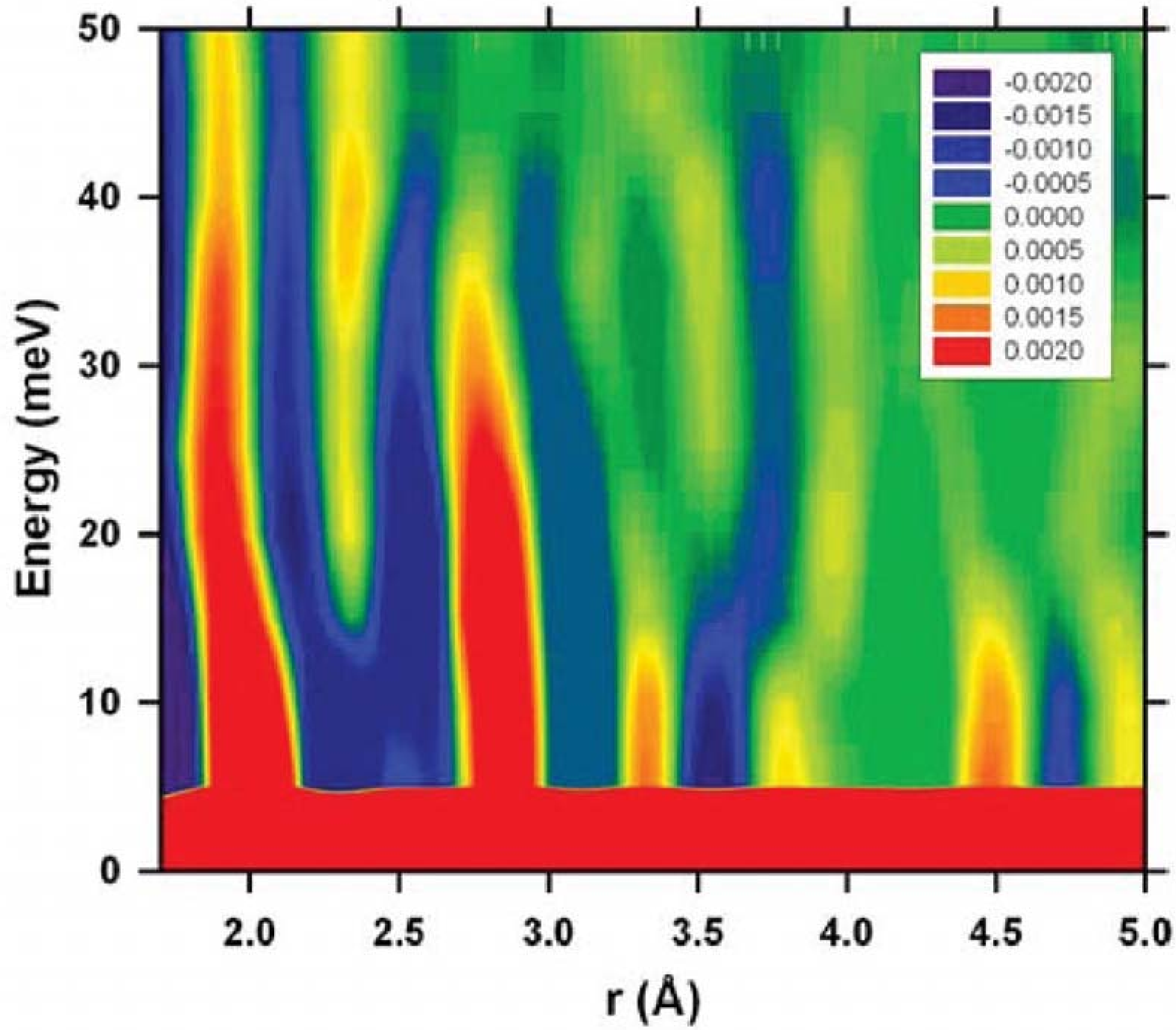


Post scriptum

PRL **100**, 137602 (2008) PHYSICAL REVIEW LETTERS week ending 4 APRIL 2008

Local Lattice Dynamics and the Origin of the Relaxor Ferroelectric Behavior

W. Dmowski,[1] S. B. Vakhrushev,[2] I.-K. Jeong,[3] M. P. Hehlen,[4] F. Trouw,[4] and T. Egami[1,5,6]



Dynamic PDF: $Pb(Mg_{1/3}Nb_{2/3})O_3$, Pharos diffractometer at Los Alamos, 100 g sample, 1 day per temperature.

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