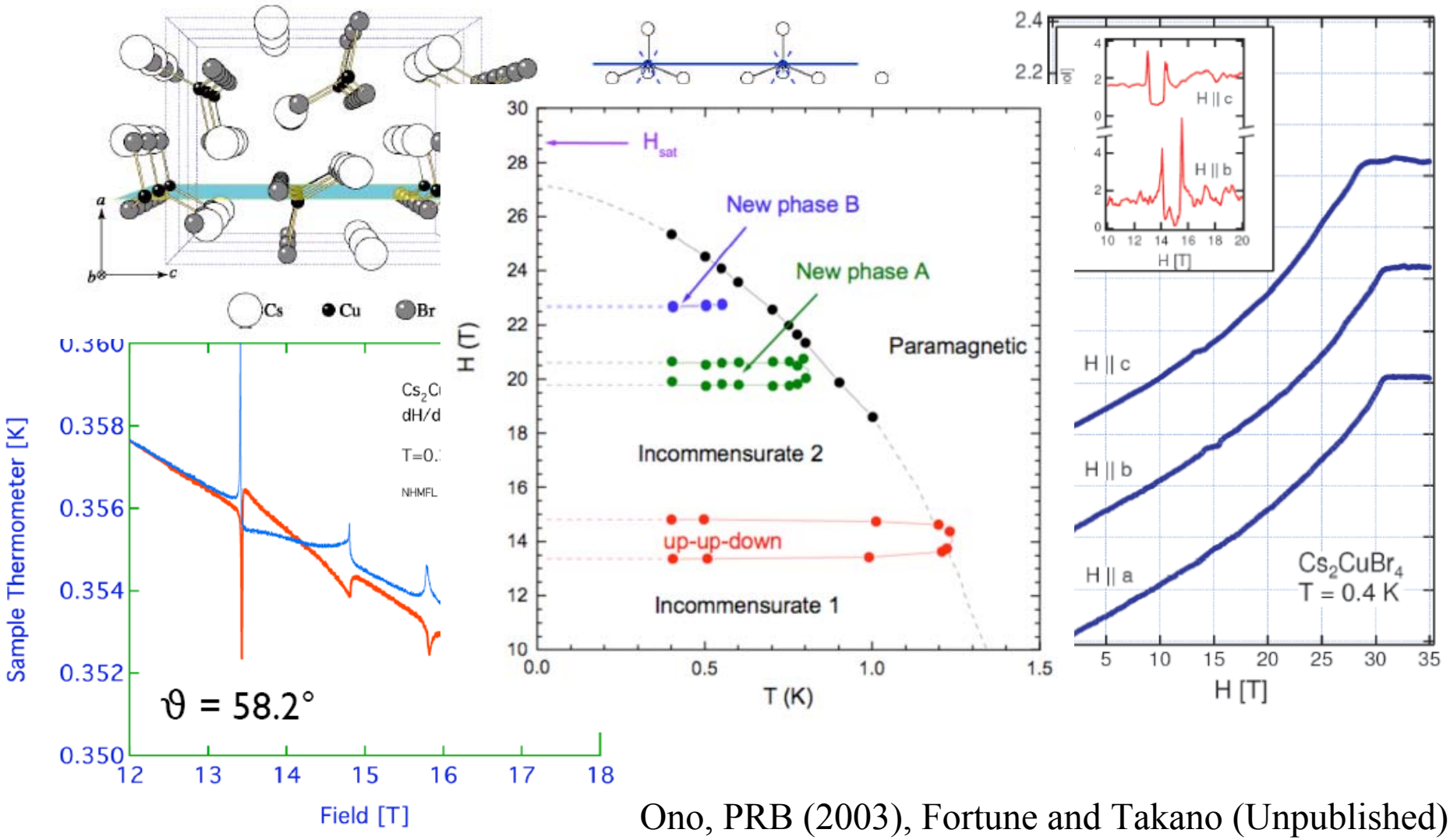
MagnetoElastic Interactions in Multiferroic Materials: An Experimental Point of View

Jan Musfeldt, University of Tennessee

- Several Short Examples to Check What the Lattice is Doing
- Microscopic vs. Bulk Property Measurements
- Things that α Tells Us; Limitations on α
- Searching for Symmetry Breaking, Spin-Phonon Coupling, Using Applied Field to Modify Phonons
  - $DyMn_2O_5$
  - $Ni_3V_2O_8$
- Hope to convince you that lattice is very important in multiferroic materials

MagnetoCalorimetry in Cs_2CuBr_4: an S = ½ 2D Quantum Antiferomagnet



Ono, PRB (2003), Fortune and Takano (Unpublished)

The Lattice is Important

$$C = k_B \beta^2 \frac{d^2(Z)}{d\beta^2}$$

Structural distortions and ferroelectricity in RMn_2O_5

Space group Pbam:

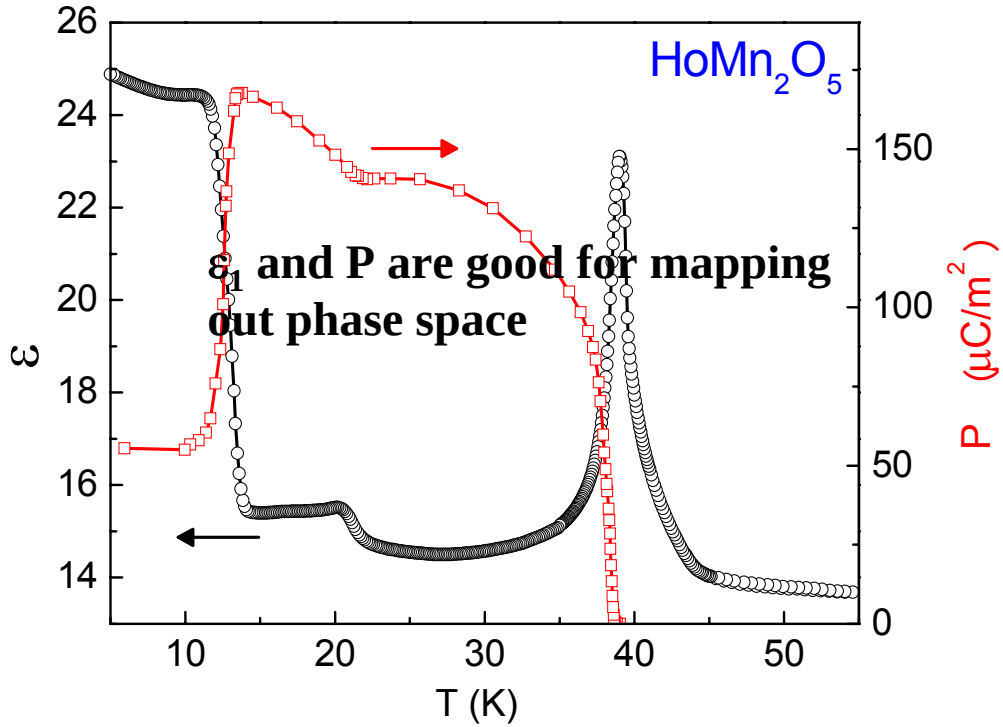
MnO_6 octahedra form ribbons || c and a linked by MnO_5 bi-pyramids

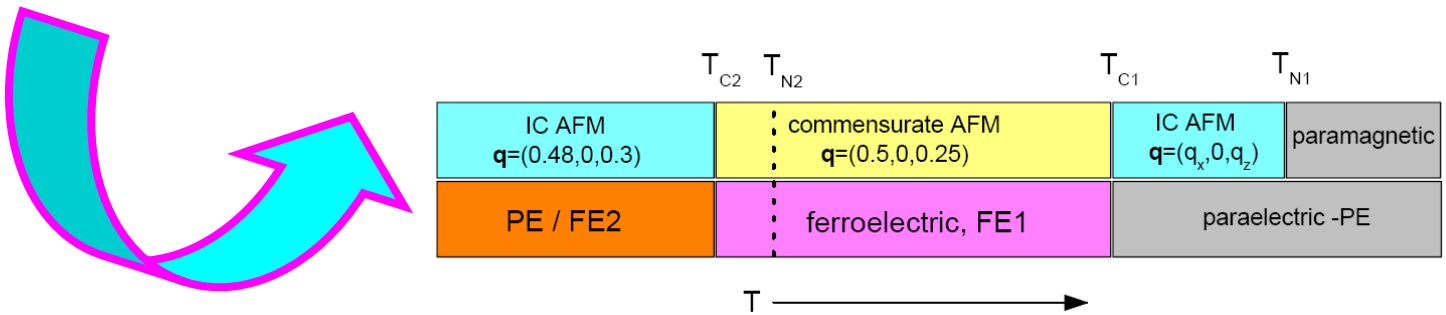
Mainly AFM superexchange coupling between Mn moments

Ferroelectricity arises just below the A ordering temperature, $T_N \approx 40$ K

Additional phase transitions at lower T

Magnetic frustration among the Mn spins !





B. Lorenz Talk

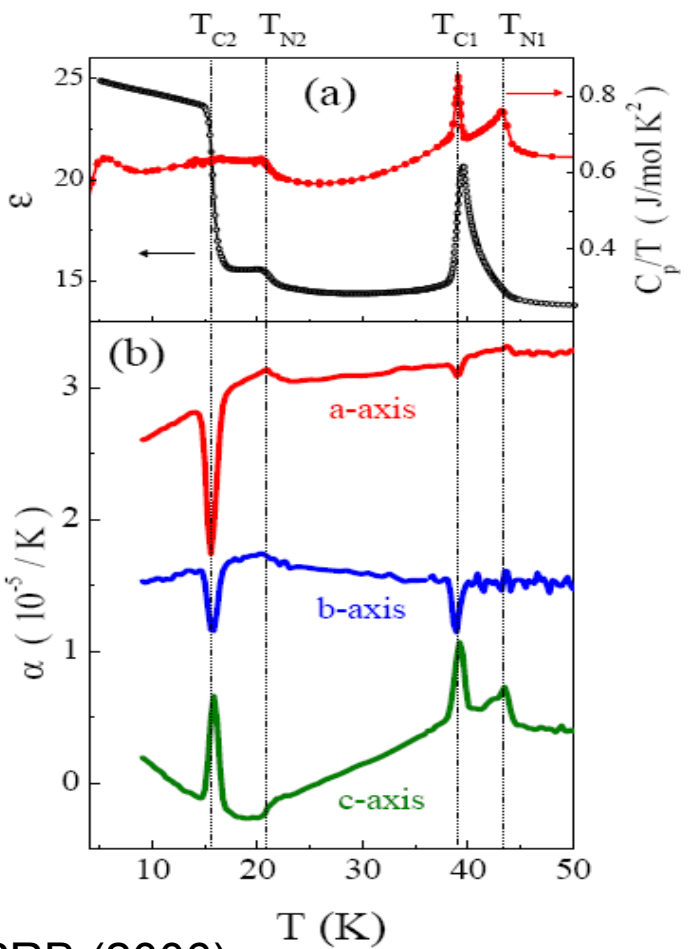
But they don’t tell you what the lattice is doing.

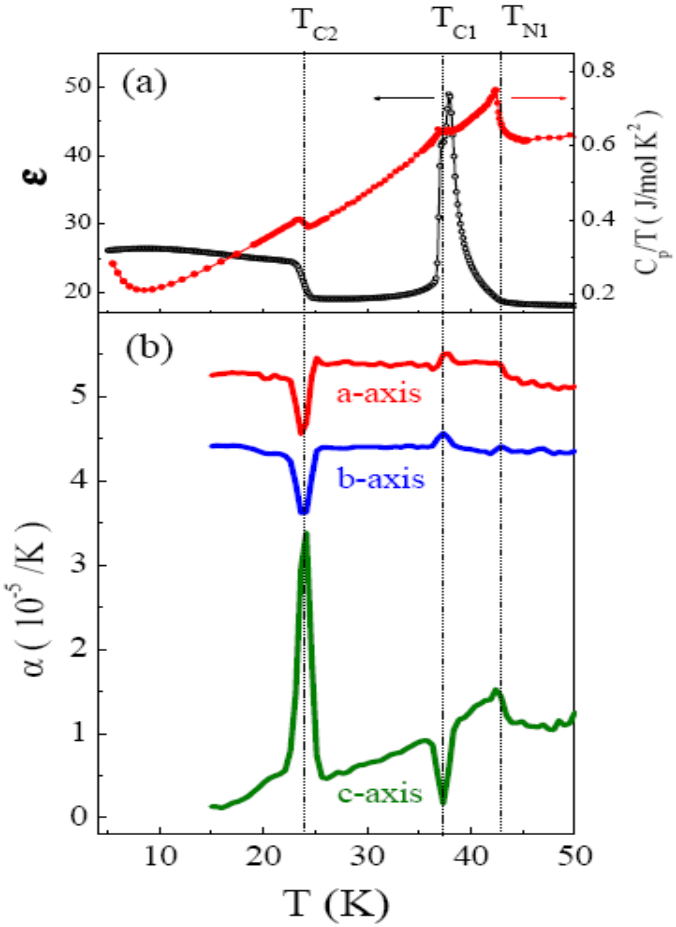
Search for structural anomalies at the FE and AFM transitions

The lattice strain associated with the ferroelectric transitions in RMn_2O_5 clearly revealed

Largest lattice anomalies at the low-temperature FE transitions – this is the phase that is most susceptible to perturbations (magnetic field, pressure)

$HoMn_2O_5$



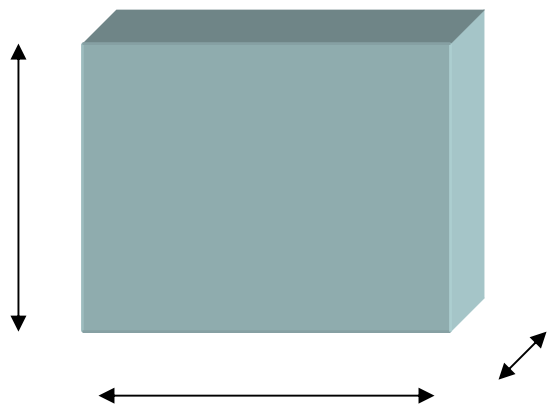


$TbMn_2O_5$

dela Cruz, PRB (2006)

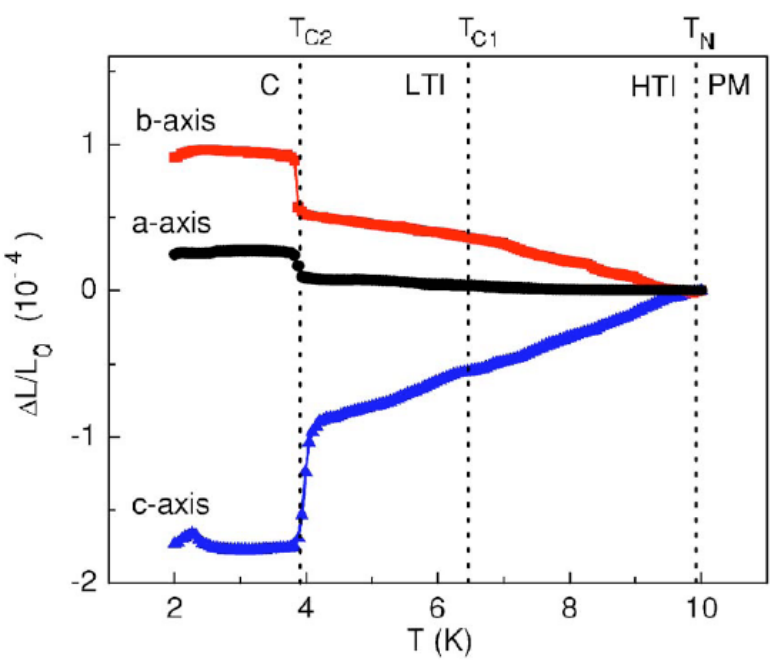
The Lattice is Important

Dilatometry is Very Sensitive to the Lattice Parameters

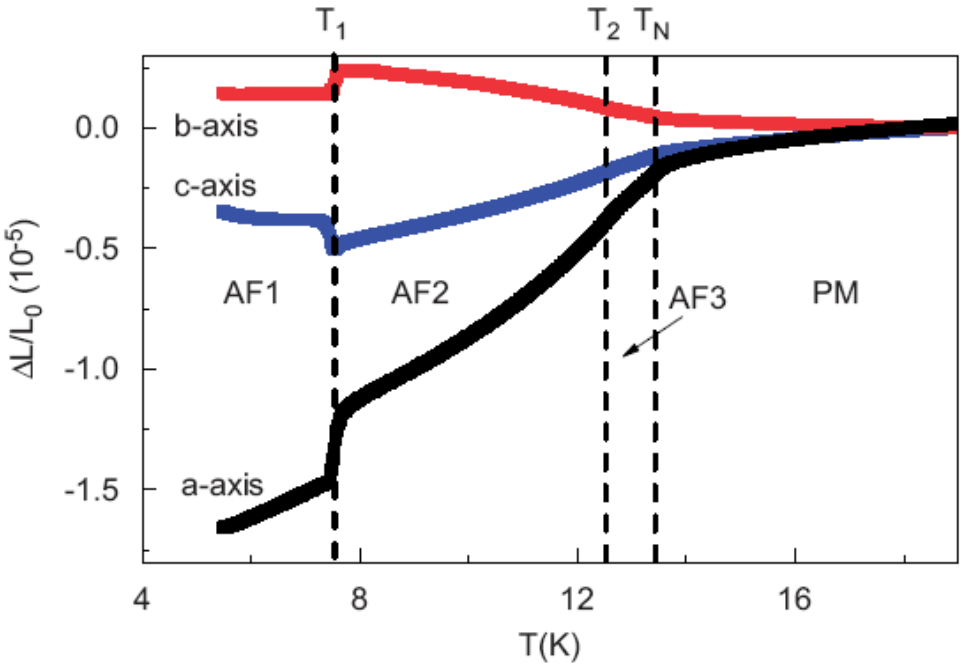


Other multiferroic compounds

$Ni_3V_2O_8$



$MnWO_4$



As with the RMn_2O_5 compounds – the strongest lattice anomalies are at the low-T transition from the ferroelectric to the reentrant paraelectric phase

→ Effects of lattice strain and external pressure are significant at low T's

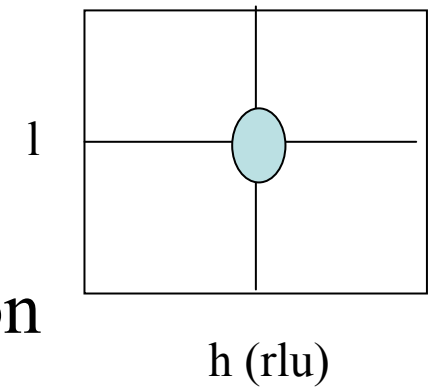
B. Lorenz Talk

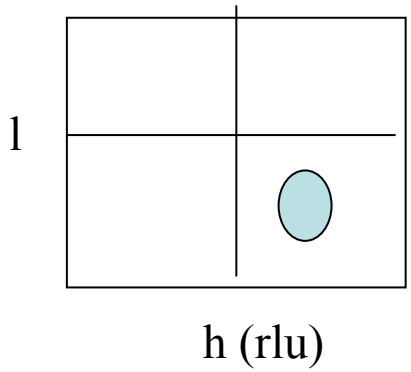
The Lattice is Important

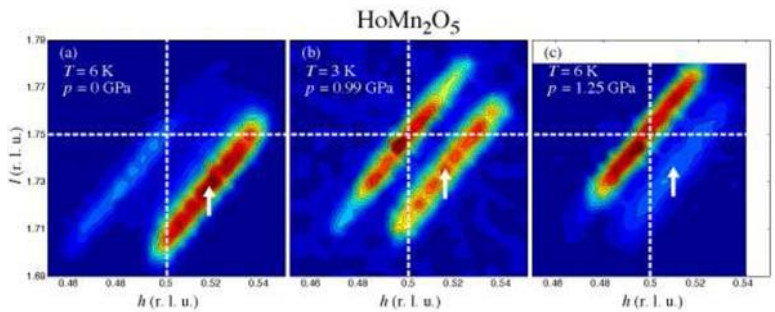
And it's Critical to Measure Very Small Changes Properly

X-Ray and Neutron Diffraction

- "Regular" x-ray scattering measures bulk or average structure
- Y. Noda says displacements on $Mn^{4+}(z) = 74$ fm and $O2(x) = 99$ fm in RMn_2O_5
- Displacements are small and can only be measured by specialized techniques
- Location of magnetic Bragg peaks (for instance), can distinguish commensurate and incommensurate structures







Y. Noda.

Perturbation Theory

Expand Hamiltonian as function of atomic distortion (normal coordinate), Q:

$$H = H^{(0)} + H^{(1)}Q + \frac{1}{2}H^{(2)}Q^2$$

where $H^{(1)}Q = (\delta H/\delta Q)_0 Q$

$H^{(2)}Q^2 = (\delta^2 H/\delta Q^2)_0 Q^2$

|0>, |n> are ground, nth excited electronic state at Q=0

then

$$E(Q) = E(0) + <0|(\delta H/\delta Q)_0|0> Q + \frac{1}{2}\left(<0|(\delta^2 H/\delta Q^2)_0|0> - 2\Sigma'_n \frac{|<0|(\delta H/\delta Q)_0|n>|^2}{E_n - E(0)}\right) Q^2 + \ldots$$

1st-order JT
Non-zero for orbitally degenerate states
want this to be zero
NOT d1, d2, d4, etc.!

always positive (moving nuclei with fixed electrons);
want this to be small

always negative (relaxation of electron distribution);
want this to be large
need a non-zero matrix element for E_n close to E(0)

Second-order Jahn-Teller effect

The Lattice is Important

But What is Q?

(1 or More Important Distortions?)

Lattice Distortion at Magnetic Ordering Temperature in $TbMn_2O_5$: Lattice Symmetry Broken

TABLE II: Comparison of the calculated and measured atom positions of $TbMn_2O_5$. L and H are the ground state structure and the high-symmetry structure respectively. $|\delta a|$, $|\delta b|$, and $|\delta c|$ denote the atomic displacements from H to L. The experimental values are taken from Ref. 13.

	L $(Pb2_1m)$			H $(Pbam)$			$H \rightarrow L(10^{-4})$			Exp. $(Pbam)$		
atom	a	b	c	a	b	c	$\|\delta a\|$	$\|\delta b\|$	$\|\delta c\|$	a	b	c
Tb_1^{3+}	0.1410	0.1733	0	0.1407	0.1732	0	3.0	1.5	0	0.1399	0.1726	0
Tb_2^{3+}	0.6404	0.3270	0				3.0	1.5	0			
Mn^{4+}	0.0001	0.5003	0.2558	0	0.5	0.2558	0.8	2.9	0	0	0.5	0.2618
Mn_1^{3+}	0.4012	0.3558	0.5	0.4014	0.3551	0.5	2.2	6.6	0	0.4120	0.3510	0.5
Mn_2^{3+}	0.9016	0.1456	0.5				2.2	6.6	0			
O1	0.0008	0.0002	0.2709	0	0	0.2709	8.2	2.3	0	0	0	0.2710
$O2_1$	0.1646	0.4480	0	0.1647	0.4481	0	1.2	1.2	0	0.1617	0.4463	0
$O2_2$	0.6648	0.0517	0				1.2	1.2	0			
$O3_1$	0.1560	0.4329	0.5	0.1565	0.4337	0.5	5.3	7.8	0	0.1528	0.4324	0.5
$O3_2$	0.6571	0.0655	0.5				5.3	7.8	0			
$O4_1$	0.3977	0.2077	0.2438	0.3968	0.2079	0.2430	8.8	2.2	8.5	0.3973	0.2062	0.2483
$O4_2$	0.8959	0.2919	0.7579				8.8	2.2	8.5			

Predicted Distortions are Small… How to Find Them?

L. He, PRB (2008)

Can calculate Born Effective charges

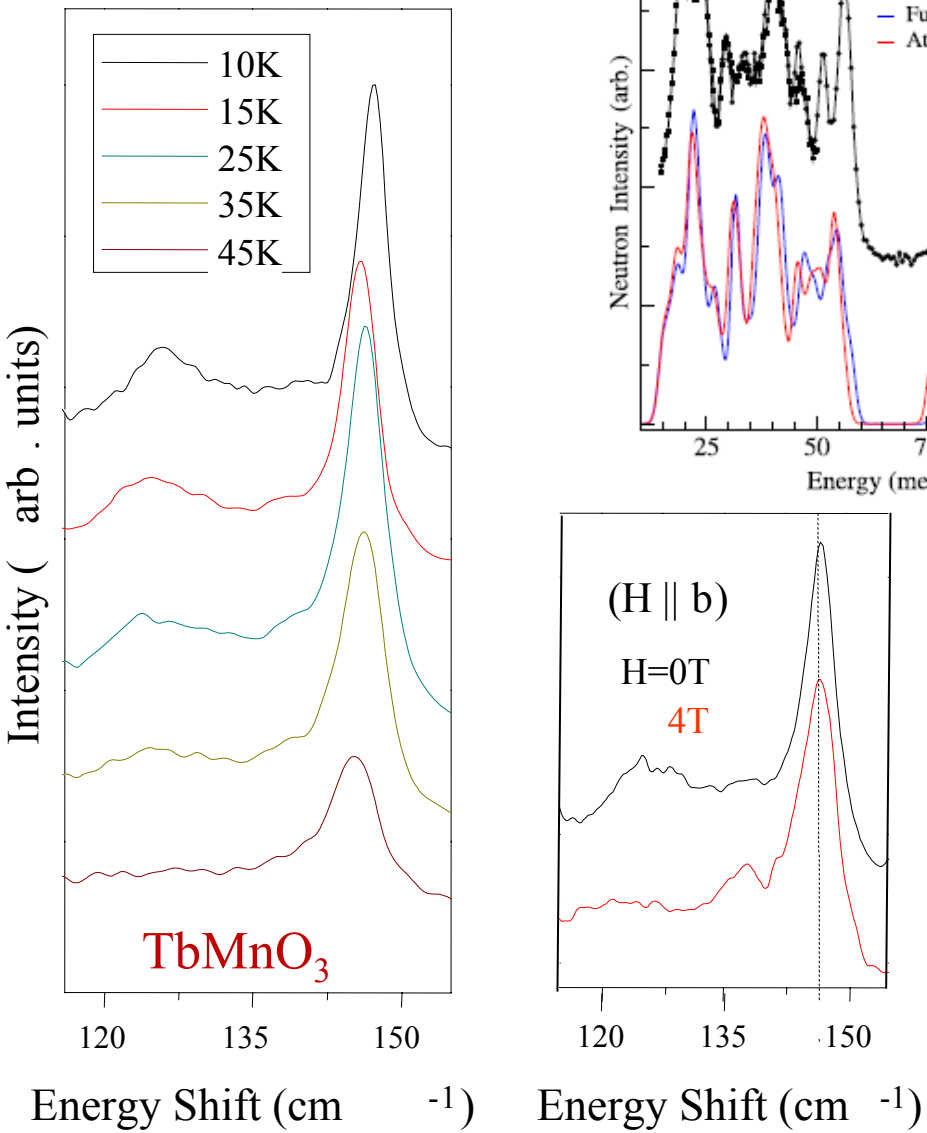
$$Z^* = \frac{\Omega(\Delta P)}{|e|u}$$

Certain P coming from certain displacements… But displacements are small.

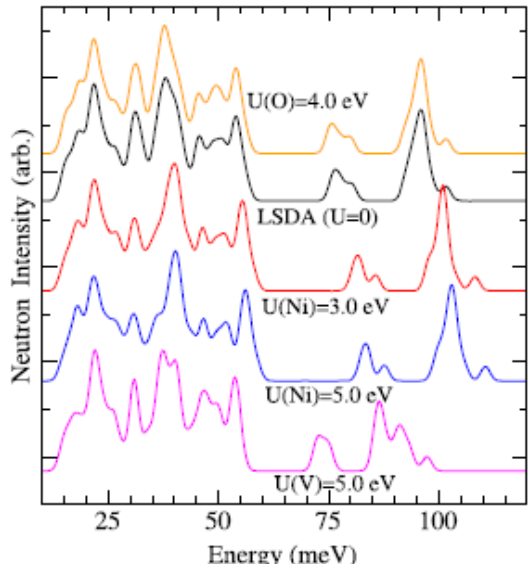
Bulk vs Microscopic Techniques

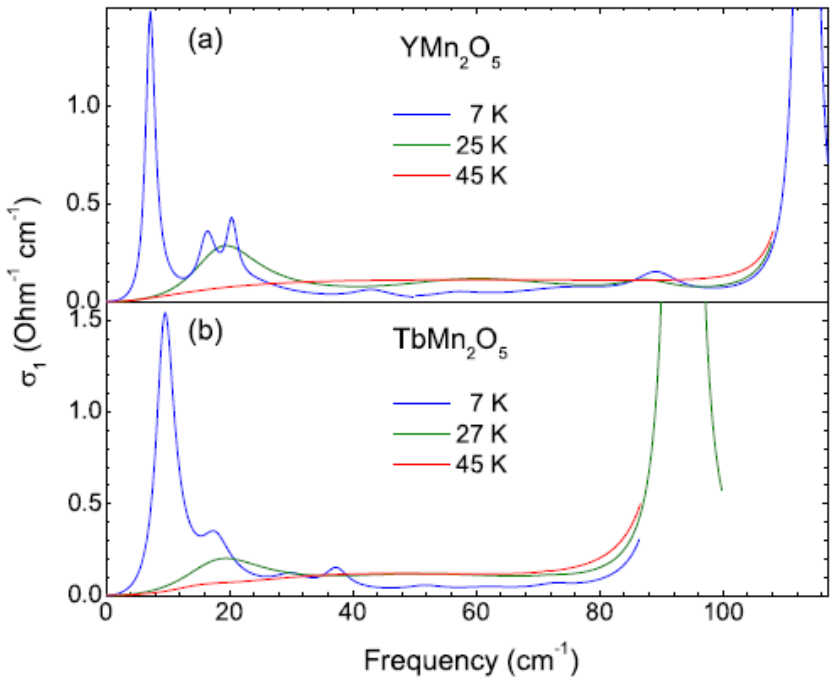
- Bulk probes measure average properties
- Sometimes magnetostriction, average structure, bulk phonon contribution not enough
- Microscopic probes measure local properties
  - neutron scattering
  - Raman scattering
  - optical spectroscopies
  - second harmonic generation
- Symmetry and selection rules, Other issues

$TbMnO_3$



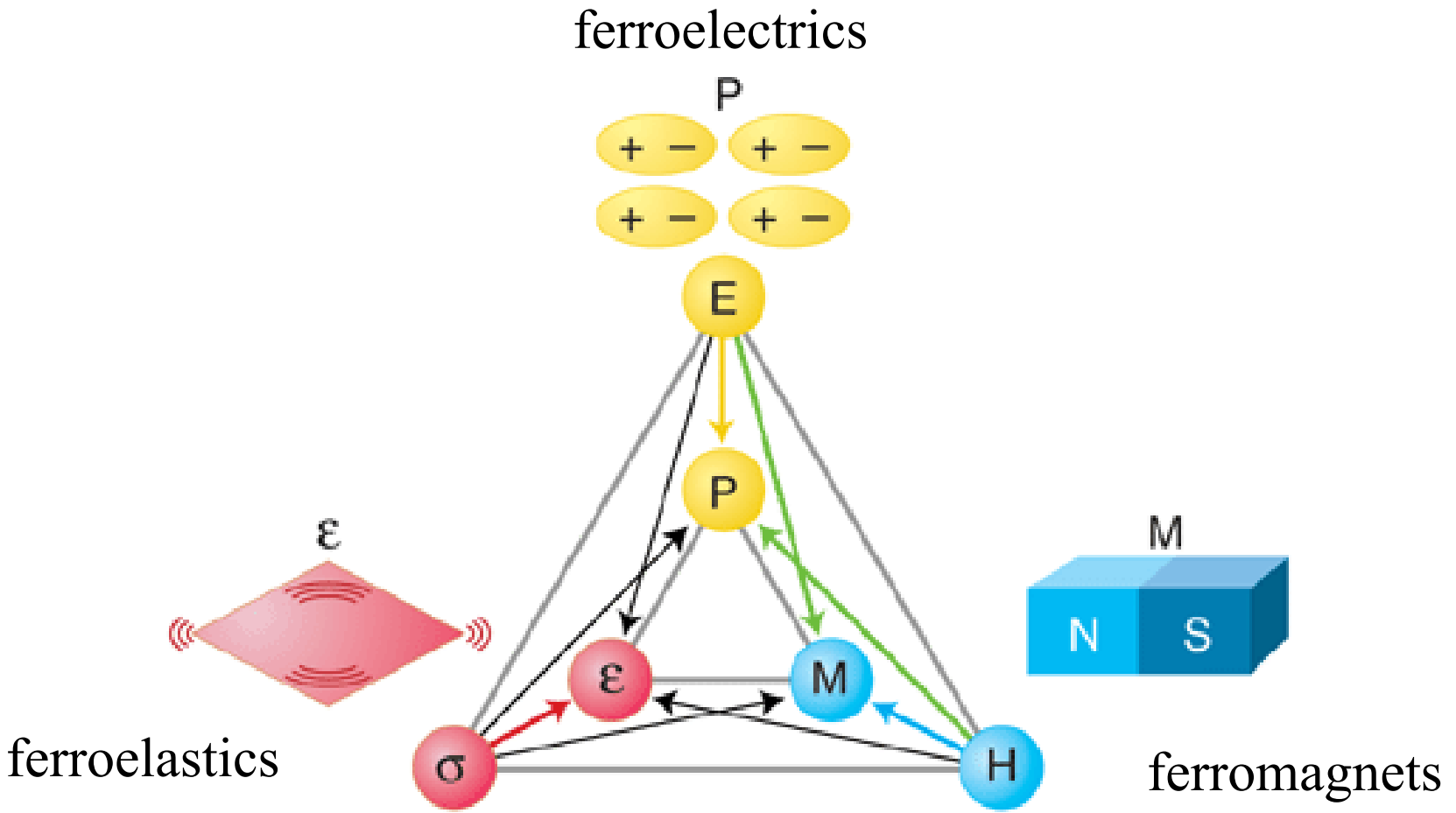
$Ni_3V_2O_8$





L. Cooper, unpublished, Yildirim, J. Cond. Mat. (2008), Sushkov, PRL, 2006

Cross Coupling Distinguishes Multiferroics from Other Correlated Oxides



The renaissance of magnetoelectric multiferroics, N. A. Spaldin and M. Fiebig, Science **15**, 5733 (2005)

Magnetoelectric coupling by Landau theory...

$$-F(E,H) = \frac{1}{2}\varepsilon_0\varepsilon_{ij}E_iE_j + \frac{1}{2}\mu_o\mu_{ij}H_iH_j + \frac{\alpha}{2}E_iH_j + \frac{\beta_{ijk}}{2}E_iH_jH_k + \frac{\gamma}{2}H_iE_jE_k + \ldots$$

Free energy

Magnetic equivalent of first term

β_{ijk}(T) and γ_{ijk}(T): higher order magnetoelectric coefficients

Contribution from electrical response to electric field

Linear magnetoelectric coupling via α_{ij}(T)

Differentiating F wrt E (or H) and setting E_i (or H_i) = 0

$$P_i = \varepsilon_{ij}E_j + \alpha_{ij}H_j + \frac{\beta_{ijk}}{2}H_jH_k + \ldots$$

$$M_i = \mu_{ij}H_j + \alpha_{ji}E_j + \frac{\gamma_{ijk}}{2}E_jE_k + \ldots$$

A multiferroic that is ferromagnetic and ferroelectric is liable to display large linear magnetoelectric effects.

The Big Rub

- Many different microscopic mechanisms to couple P and M
- Magnetostriction is controlling the whole problem but almost no one pays attention
- Want larger, but limits on the size of α

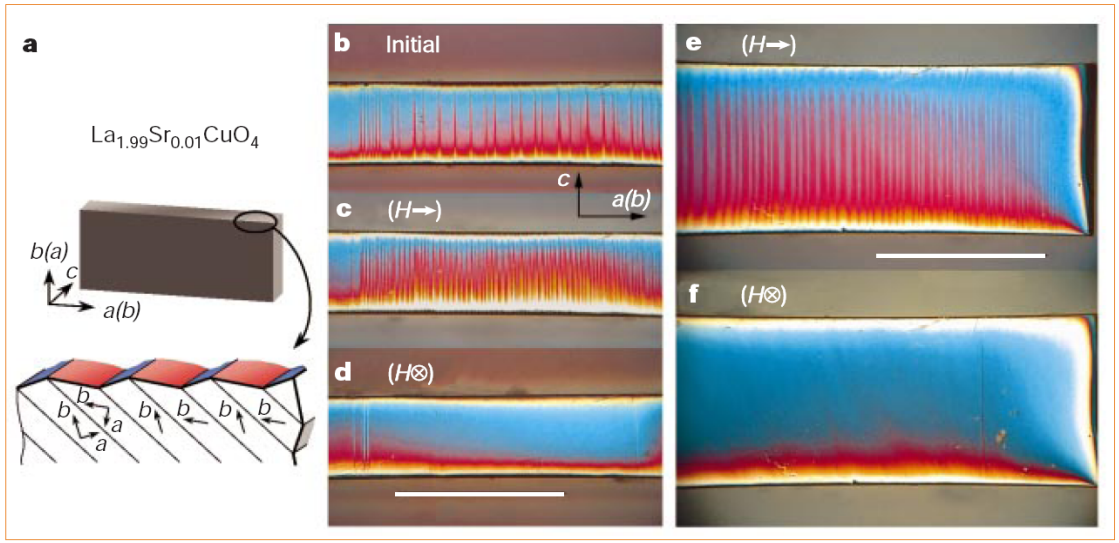
$$\alpha_{ij}^2 \leq \varepsilon_0 \mu_0 \varepsilon_{ii} \mu_{jj}$$

- Large α yields big, cross-coupled P and M. (Then can operate devices at 300 K.)
- Therefore, need significant magnetoelastic coupling.

$$\omega^2 \sim \omega_0^2 - \frac{\partial^2 J}{\partial u^2} \left\langle S_i \bullet S_j \right\rangle$$

MOTIVATION

Magnetic shape-memory effects



A.N. Lavrov et al., Nature, 2002

Using magnetostriction to measure magnetoelastic coupling…

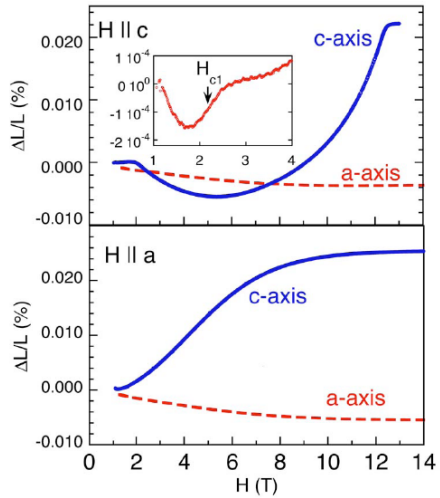


FIG. 4. (Color online) Normalized percentage length change $\%\Delta L/L$ as a function of magnetic field of $NiCl_2{-}4SC(NH_2)_2$ as a function of magnetic

V.S. Zapf et al., J. Appl. Phys, 2007

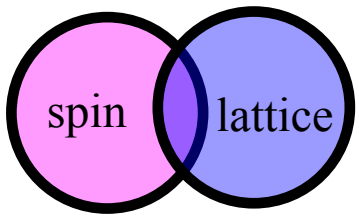
bulk

- magnetostriction
- thermal expansion
- heat capacity
- dielectric constant

✓ average structure

✓ lattice constants

✓ bulk phonon contributions



spin-lattice coupling

microscopic distortions still unknown for many materials

flexible crystalline lattice !!

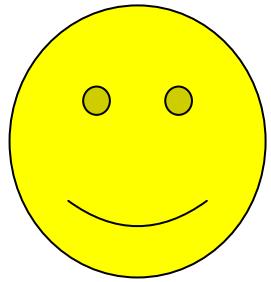
~~rigid lattice?~~

which phonons?

dependence with magnetic state?

My Plan

- $DyMn_2O_5$
- $Ni_3V_2O_8$



Then we will go to Golleta Beach for a picnic!

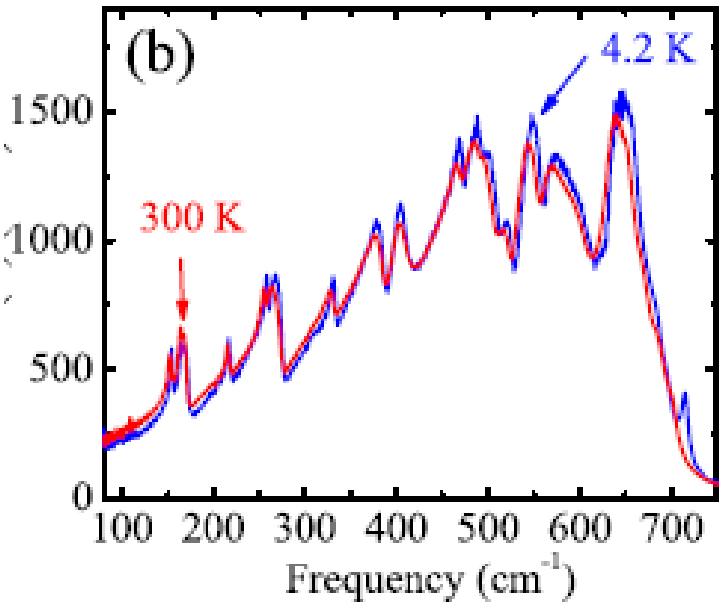
Why I like these systems

- Interplay between S, L, C and O degrees of freedom drives rich physics in complex oxides
- Interactions are strong, so materials on “knifes edge”, straddling unique areas of H, T, P space
- Delicacy of interplay makes materials susceptible to tuning
- Role of lattice is commonly acknowledged, little is known about magnetic ordering-induced lattice distortions or the effect of high magnetic field on local structure.
- Generally assumed that lattice is rigid, with coupling limited by different energy scales
- Recent experiments are starting to yield a different consensus…
- Materials with strong spin-phonon coupling (such as the multiferroics) offer the opportunity to investigate potentially larger effects

Focused search for magnetoelastic coupling on geometrically frustrated $DyMn_2O_5$

TABLE I: Comparison of calculated phonon modes and experimental peak frequencies for $DyMn_2O_5$. All frequencies are in cm^{-1}.

B_{3u}(a)	B_{2u}(b)	B_{1u}(c)	Experimental Range
95	104	117	95-110
170	176		140-180
189	184		
208			217
	231	245	230-260
	283		267
310			290
336	339	325	310-350
382	387	368	350-385
403			403
	441	456	430-470
475	464	473	470-510
486	475		
		509	519
567	576		530-555
585	589		555-600
617	626	655	610-670
	728		680
762			713



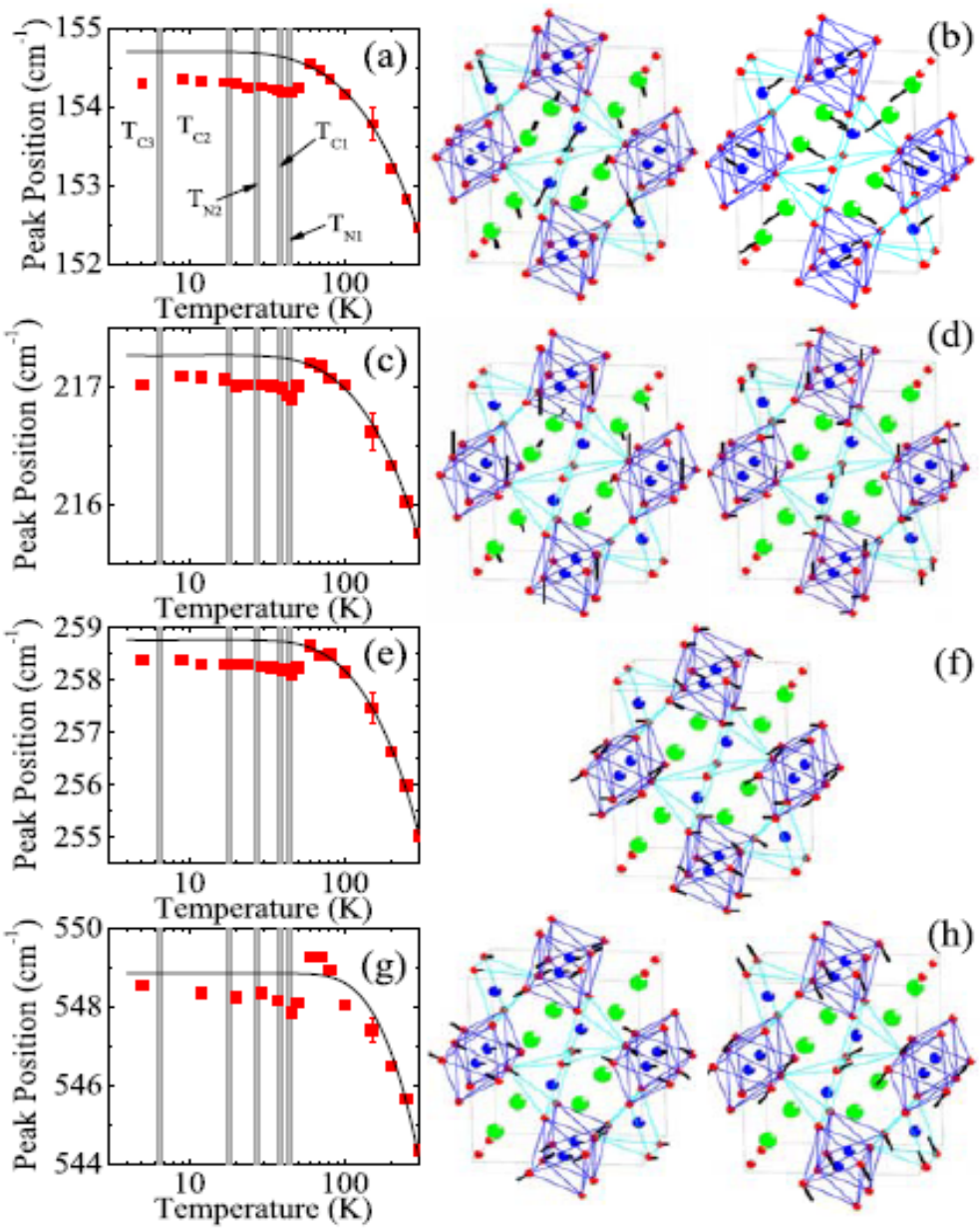
$\Gamma_{IR} = 14B_{3u}$ (a) + $14B_{2u}$ (b) + $8B_{1u}$(c)

36 IR active modes in PE phase

No symmetry breaking… Displacements that lower symmetry to non-centrosymm point group very small.

Cao et al, PRB (2008).

Phonon modes through the magnetic ordering transitions



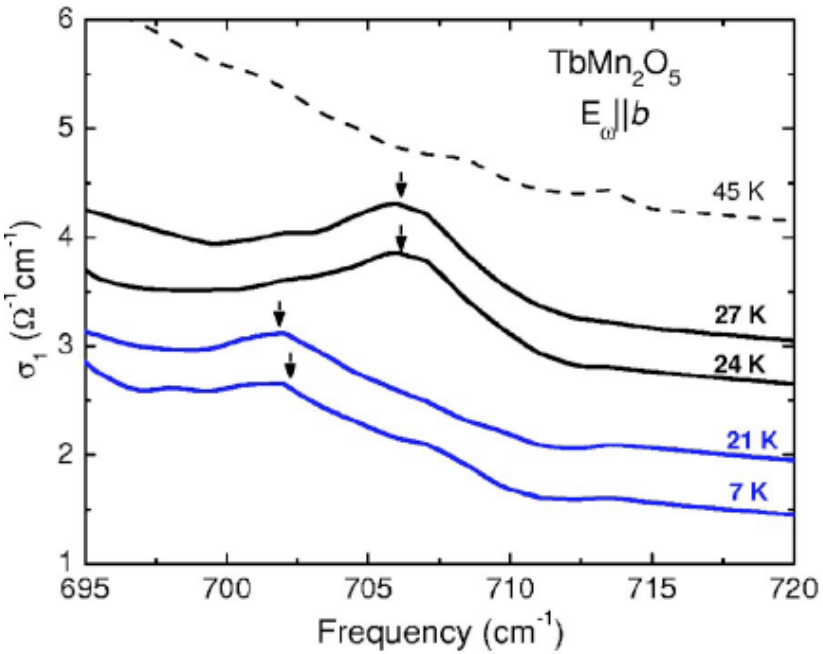
- FE1 to FE2: modest change in Mn-O streching modesof octahedra and square pyramids + relative motion of polyhedra and Dy^{3+} centers

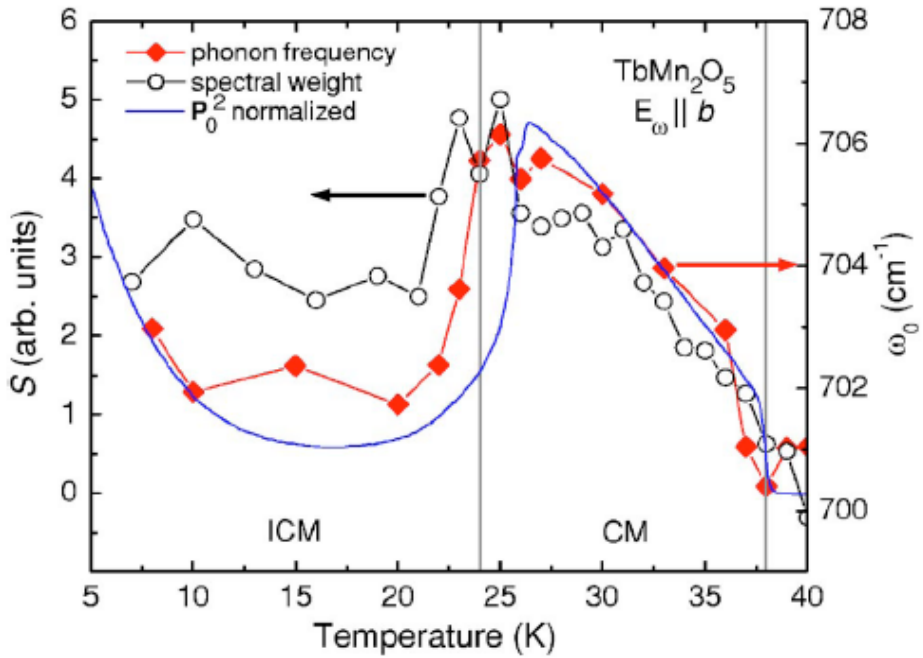
- FE2 to FE3: Same distortions + changes in Mn-O bending modes and relative motion of Dy^{3+} and O centers

No mode splitting at low temperature transitions…Different than $TbMn_2O_5$.

Cao et al, PRB (2008).

Symmetry Breaking in $TbMn_2O_5$

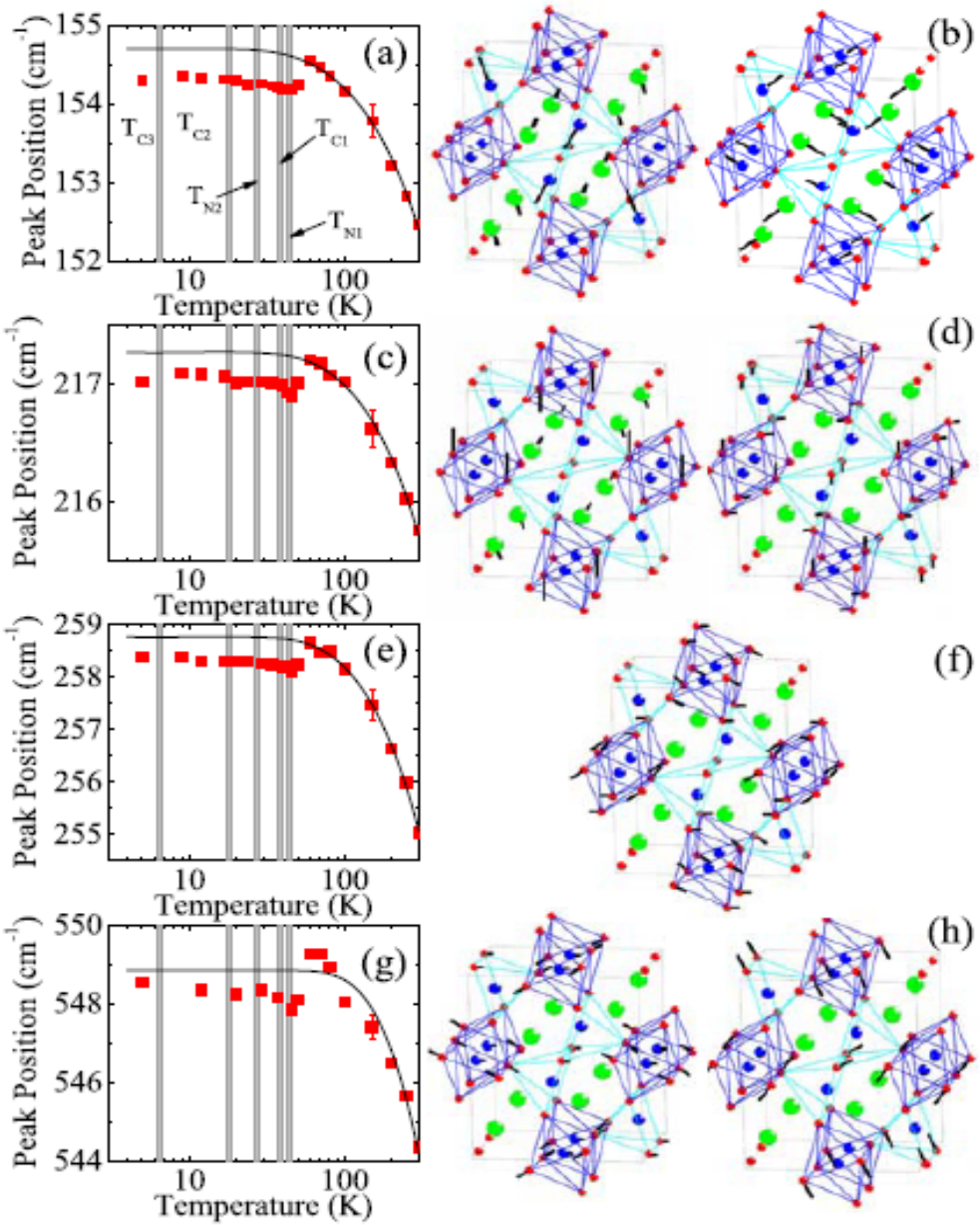




- b-polarized mode activated in low temperature ferroelectric phase
- normally, mode is Raman-active
- spectral weight and frequency tracks polarization
- good order parameter

Valdes-Aguilar, PRB (2006).

Phonon modes through the magnetic ordering transitions



Fitting the temperature dependence:

$$\omega_m(T) = \omega_{0m} - C_m[1 + \frac{2}{exp(\hbar\omega_{0m}/2k_BT) - 1}]$$

Evaluating the coupling:

$$\omega_m = \omega_m^0 + \lambda_m <\mathbf{S}_i \cdot \mathbf{S}_j>$$

Weak dips at T_{N1} (43 K), T_{N2} (27 K), and T_{c2} (18 K)

3 different FE phases associated w/ slightly different phonon characteristics, although magnetic ordering-induced lattice distortion small.

Cao et al, PRB (2008).

Several coupling constants are large

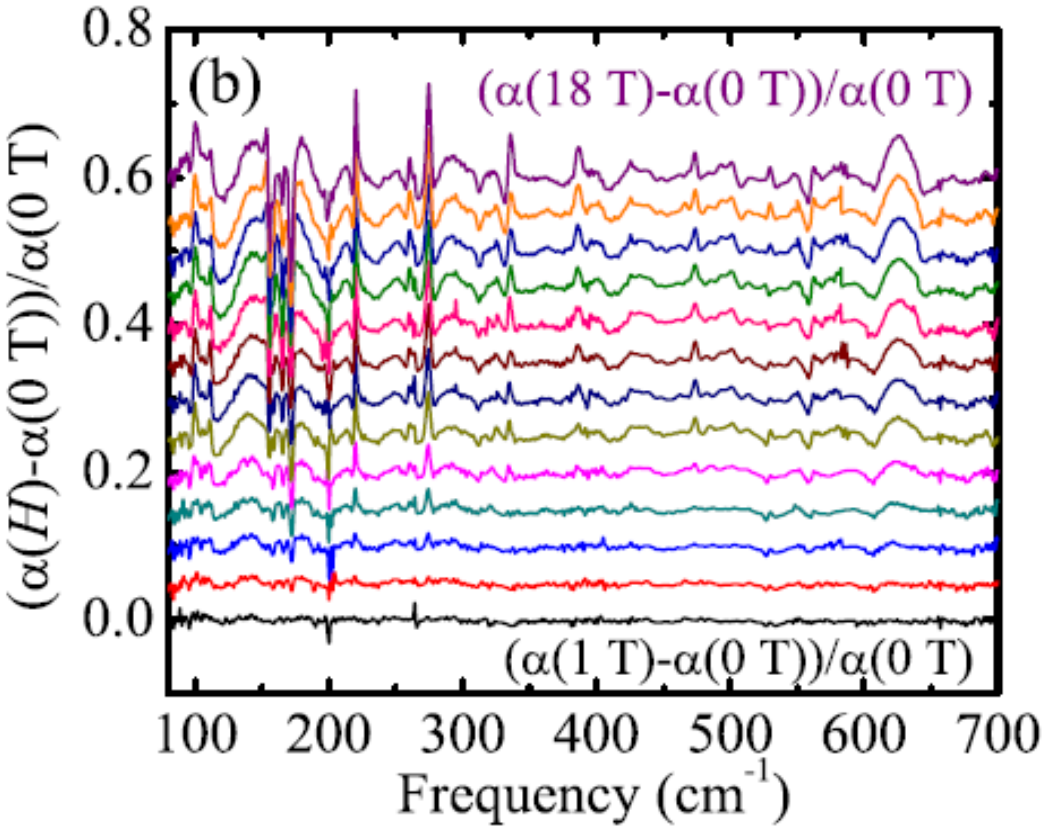
TABLE II: Spin-phonon coupling constants, λ_m, for selected modes of $DyMn_2O_5$ estimated from the observed softening $\Delta\omega_m$ assuming $<\mathbf{S}_i \cdot \mathbf{S}_j> \sim$ -0.5. The last column gives the mode description. All frequencies, frequency differences, and coupling constants are in cm^{-1}. The large coupling constants demonstrate that the lattice is not rigid.

Mode position at 60 K (Experiment)	$\Delta\omega_m$	λ_m	Mode description
154.5	0.3	0.6	
165.4	0.2	0.3	Relative motions of Mn polyhedra and Dy^{3+} ions
168.7	0.3	0.5	
217.2	0.3	0.6	Relative motions of Dy^{3+} ions and oxygens
258.7	0.5	1.0	Mn-O bending motions in MnO_6 octahedra
331.9	1.0	2.0	Mn-O twisting motions in Mn polyhedra
468.3	0.3	0.6	Mn-O bending motions within equatorial MnO_2 planes in MnO_6 octahedra
549.3	0.8	1.6	Mn-O stretching motions in MnO_6 octahedra and MnO_5 square pyramids

This suggests that some modes may be sensitive to applied magnetic field.

Cao et al, PRB (2008).

$DyMn_2O_5$ in Magnetic Field

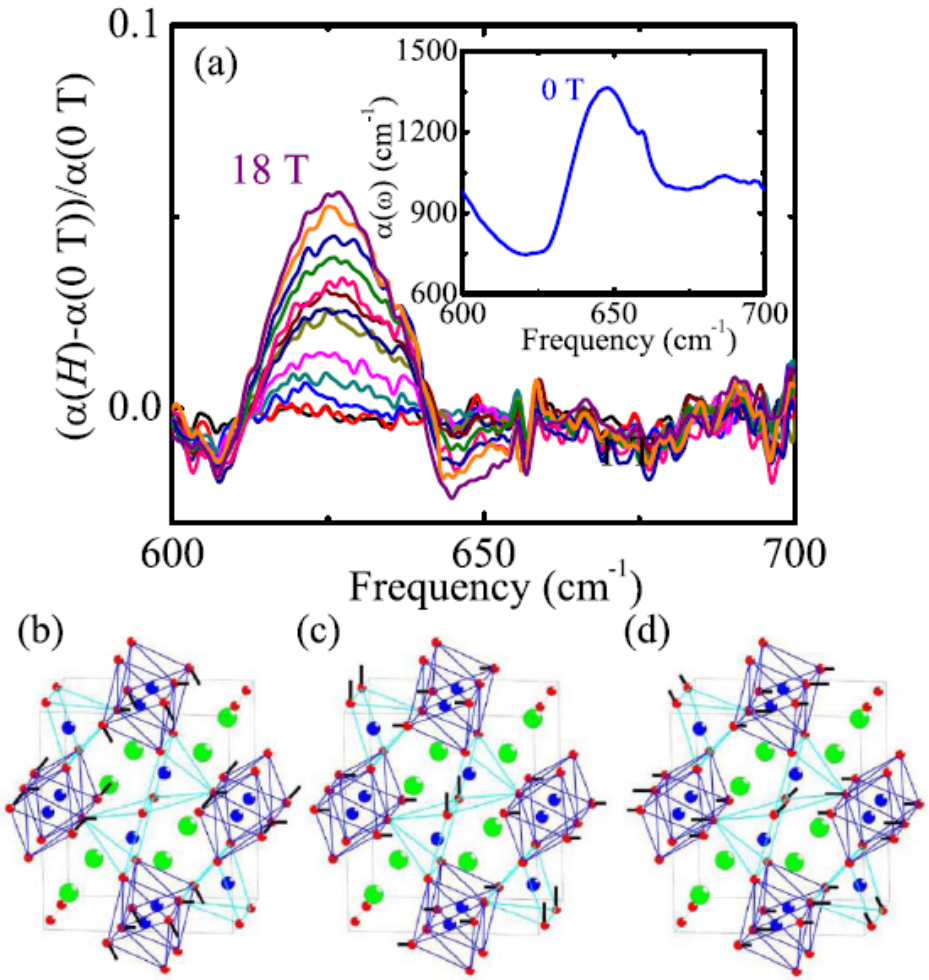


- **majority of modes display rich and surprisingly strong field dependence**
- **suggests that applied field modifies local MnO_6 and MnO_5 structure and, as consequence, affects Mn-O-Mn superexchange interactions**
- **many changes ~10% at 18 T and appear w/ complex derivative-like structures, indicative of frequency shifts**
- **let's look closely at 4 different mode clusters… good opportunity to elucidate magnetoelastic coupling effects**

J. Cao, PRL (2008).

Modes between 600 – 700 cm^{-1}

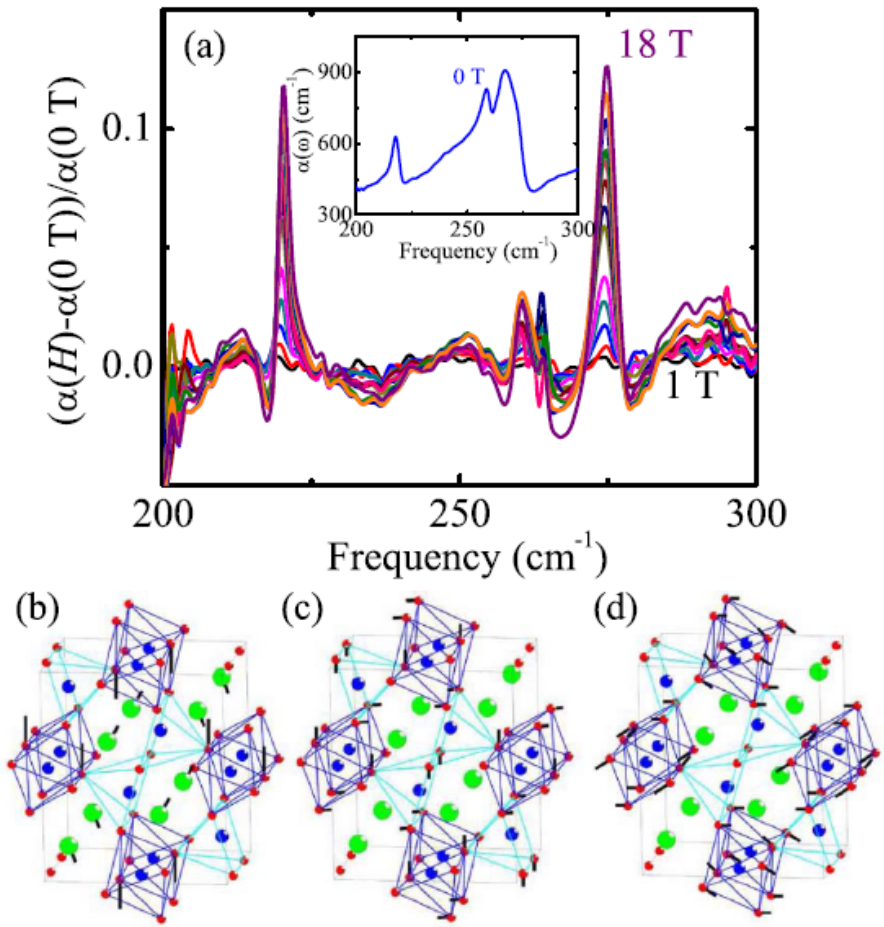
- **stretching of Mn-O octahedra**
- **broad spectral changes with H; gradual redistribution of spectral weight**
- **connection to longitudinal magnetostriction studies; changes on order of 10^{-4}**
- **find Δa/a increases with H**
- **a is "soft" direction, perpendicular to axial bonds of MnO_6 octahedra**
- **consistent with field-induced "squashing" of octahedra**
- **local structure changes effect orbital overlap, which modifies exchange interactions as $J \sim t^2/U$**



J. Cao, PRL (2008).

Large λ's observed for bending modes too

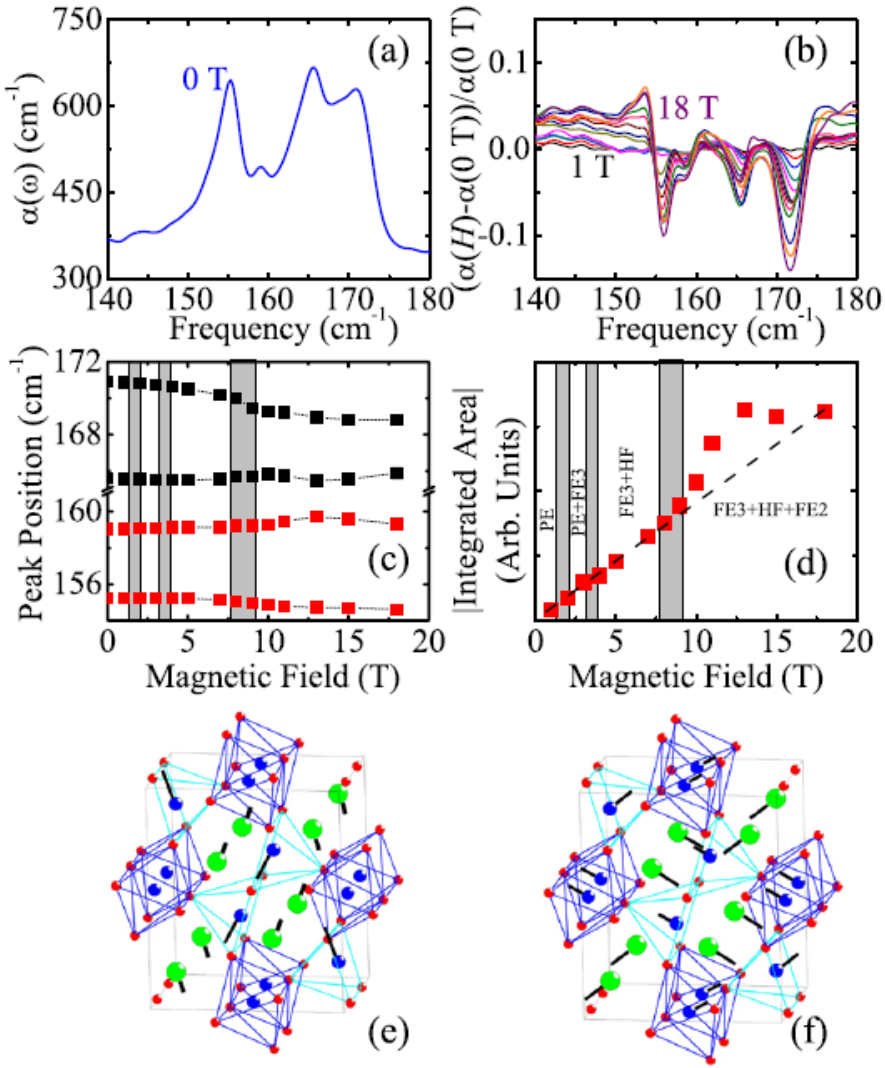
- **mode displacement patterns more complicated: relative motion between Dy^{3+} and equitorial O, relative motion of O centers, torsion and twisting motion of octahedra**
- **10% deviation at 18 T and lineshapes consistent with small frequency shifts**
- **Sensitivity of 217 cm^{-1} to H and T (across T_{N1} and T_{c2}) consistent with magnetoelastic coupling mechanism involving displacement of Dy centers wrt equitorial O plane in octahedra along b direction + local twisting and squashing of MnO_6 octahedra in soft a direction**
- **Both distortions modify Mn-O-Mn superexchange interactions**



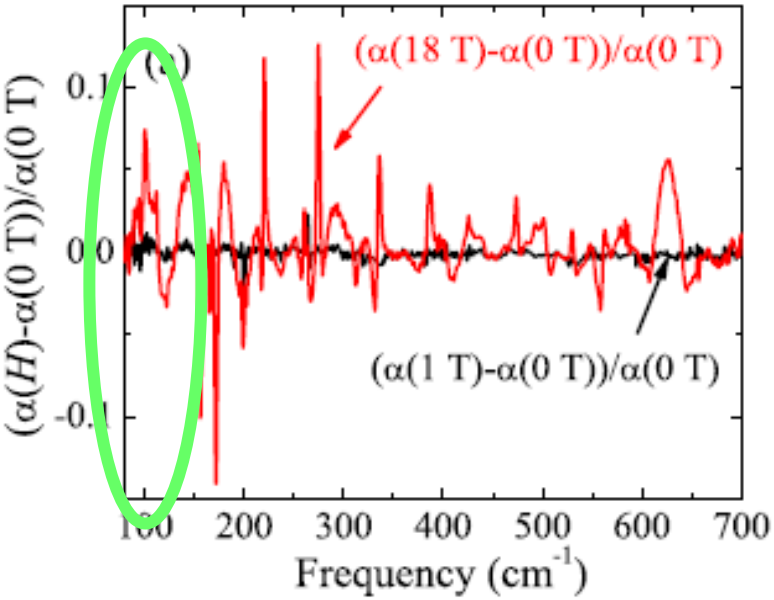
J. Cao, PRL (2008)

Applied Field Also Drives System Thru Series of Magnetic Ground States

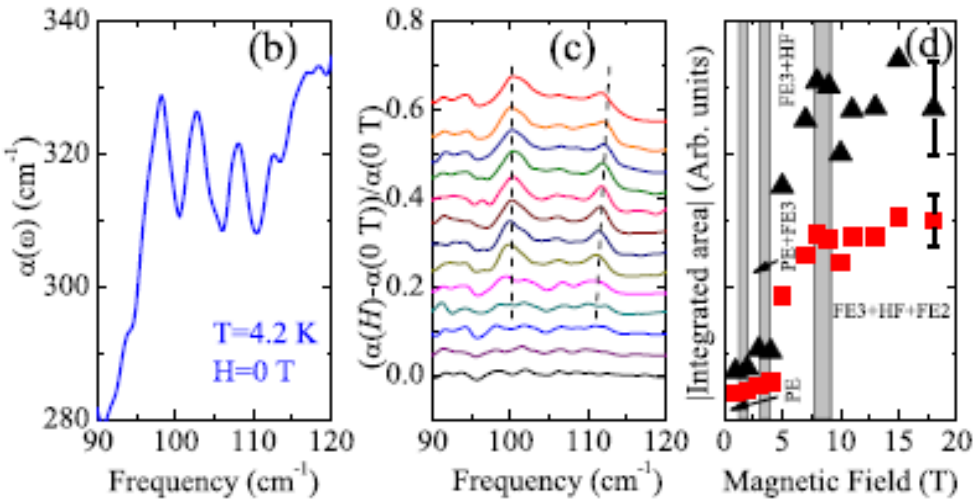
- this cascade of transitions has potential to be associate with changes in lattice
- lines in 140 – 180 cm^{-1} useful here
- peak positions and area sensitive to FE3 to FE2 transition (H||b) at 8.5 T
- additional evidence for strong S-L coupling + role of relative MnO_6 and MnO_5 motion wrt Dy^{3+} centers

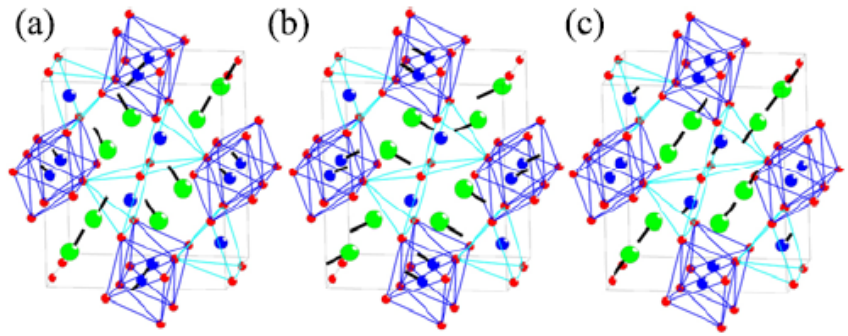


Low Frequency Displacement Modes



- **3 low frequency modes calculated to be at 95, 110, and 117 cm^{-1}, in good agreement with spectrum**
- **relative Mn polyhedra/Dy^{3+} displacements**
- **peaks develop in absorption difference spectra, signaling oscillator strength shifts**
- **integrating, spectral weight increases at 4 T, coincident with PE to HF transition.**

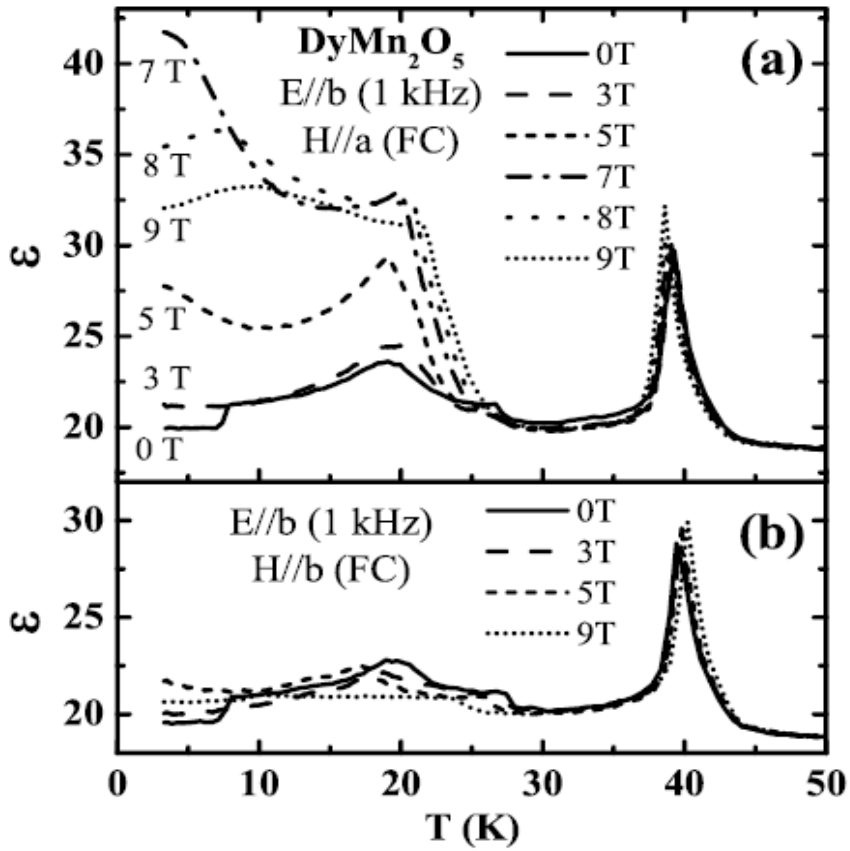




Cao et al, PRB (2008).

Static Magneto-Dielectric Effect: Prominent Example of Interplay Made Manifest in Bulk Properties

- **Dispersive contrast gains strength from nearby dipole allowed excitations**
- **Electromagnetons, crystal field excitations shown to contribute**
- **field-dependent phonons discussed here also have the right symmetry**
- **Relative importance depends on proximety**



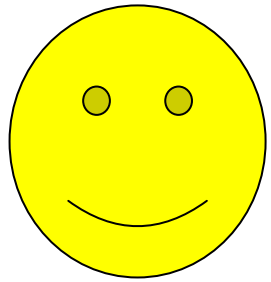
Hur *et al.*, PRL, 2004.

What We Learn: $DyMn_2O_5$

- Observation that local structure is sensitive to magnetic field in $DyMn_2O_5$ has important consequences for design of functional oxides
- Explains underlying phonon contribution to bulk property trends, detailing which phonons are involved and connecting important features to displacement patterns
- Such phenomena not only important for multiferoic oxides but for other correlated oxides, where many exotic properties derive from S-L-C coupling rather than a rigid lattice and separation of different degrees of freedom

My Plan

- $DyMn_2O_5$
- $Ni_3V_2O_8$



Then we will go to Laguna Beach for a picnic!

Musfeldt Group