The magneto-electric effect – A Neutron scattering perspective

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From rechargeable batteries to Magneto-electric effect

Ionic conductors

Polycrystalline samples

Rojo – Bilbau, Spain

Barberis – Campinas, Brazil

Magnetolectric materials

Single crystals

Schmid, Rivera– Geneva

Jiying Li – Ames Lab - ISU

$(Li_xFe_y)NiPO_4$ $x << y$

$Li_3Fe_2(PO4)_3$

↓

$LiNiPO_4$

Single crystals →

$LiNiPO_4$

$LiCoPO_4$

↑

$(Li_xFe_y)MPO_4$

M = Ni, Co Fe, Cu

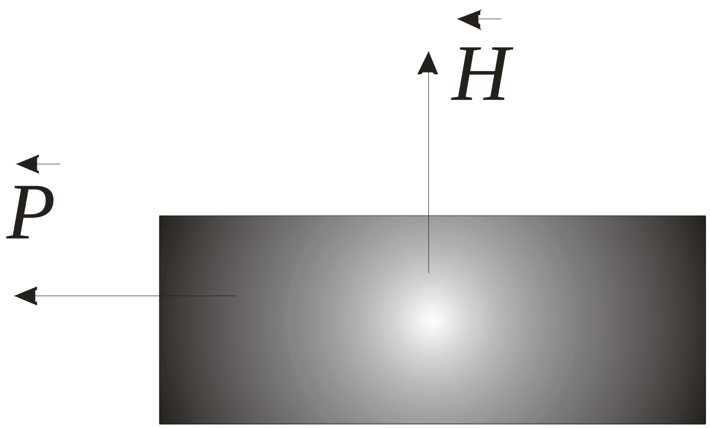
Magneto-Electric Effect

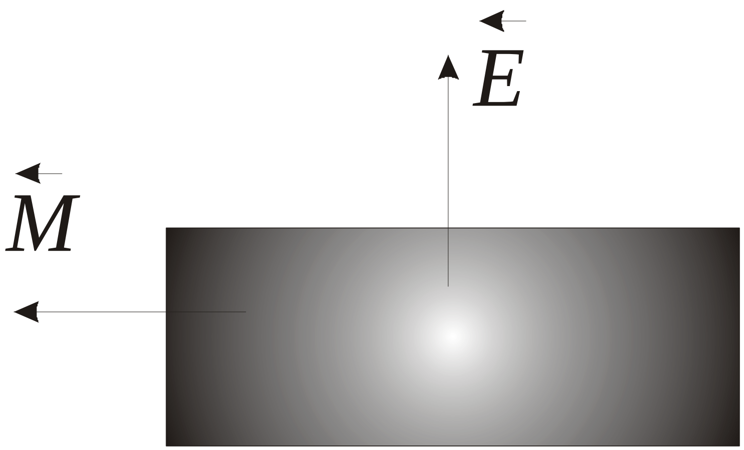
ME_H

Polarization induced by applied magnetic field

ME_E

Magnetization induced by applied electric field





Time reversal symmetry is broken i.e, Antiferromagnets, ferromagnets

History of ME effect

- **1894** **Pierre Curie** – on symmetry grounds
- **1922-1926** **Debye** - effect impossible - a series failed experiments
- **1932** **van-Vleck** – No ME effect
- **1937** **Condon** - QM arguments in favor.
- **1957** **Landau and Lifshitz** – effect should exist in magnetically ordered materials
- **1959** **Dzyaloshinskii** – effect predicted on symmetry grounds in Cr_2O_3
- **1960** **Astrov** – discovery of ME_H effect in Cr_2O_3
- **1961** **Rado** – discovery the ME_E effect in Cr_2O_3

More:

- *The Electrodynamics of Magneto-electric Media* – T. H. O'Dell (1970).
- *Magnetoelectric Interaction Phenomena in Crystals* – A. J. Freeman and H. Schmid (Edts.) (1973)

Landau *vs* Néel on Antiferromagnetism

Louis Néel (1904–2000)

"… Once asked by Anatole Abragam why he had persisted with his theory of antiferromagnetism in the light of Lev Landau's prediction that only ferromagnetism was possible in nature, Néel thanked heaven he was not that smart."

M. Coey *Nature* **409**, 302 (18 January 2001)

Neutron scattering from MnO

Shull and Smart (1949)

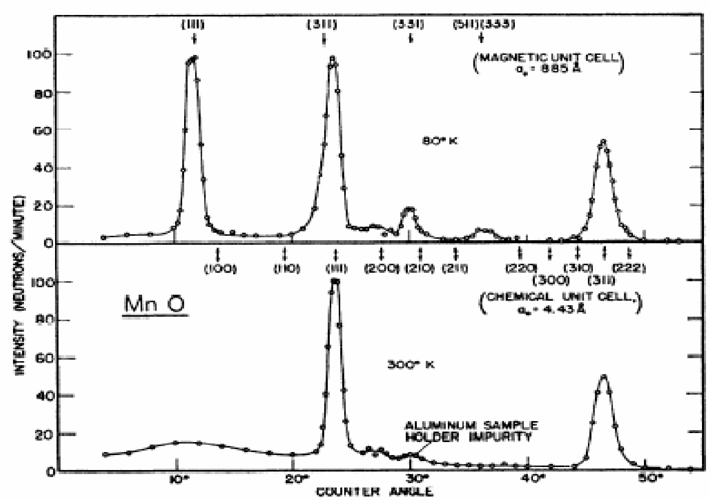


FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

Phenomenology

The enthalpy can be expanded in terms of electric and magnetic fields as follows,

$$-u(H,E;T) = ... + \kappa_i E^i + \mu_i H^i + \frac{1}{2}\varepsilon_0 \kappa_{ik} E^i E^k + \alpha_{ik} E^i H^k + \frac{1}{2}\mu_0 \mu_{ik} H^i H^k ....$$

$$P_k = -\frac{\partial u}{\partial E_k} = \kappa_k + \varepsilon_0 \kappa_{ik} E^i + \alpha_{ik} H^i ....$$

$$M_k = -\frac{\partial u}{\partial H_k} = \mu_k + \mu_0 \mu_{ik} H^i + \alpha_{ik} E^i ....$$

Dimensions [coefficient of ME_H effect]

P = αH

[α] = [P]/[H] = [Q/L2]/[Q/TL] = [Time/Length]

The polarization includes:

spontaneous polarization, electric susceptibility, linear ME_H effect to an applied magnetic field and higher terms.

The magnetization includes:

spontaneous magnetization, magnetic susceptibility, and the linear ME_E effect response to an applied electric field.

Origin of the ME effect

- **Electro-dynamic effect**

  Toroidal moment is it a real entity or a ghost

Toroidal moment

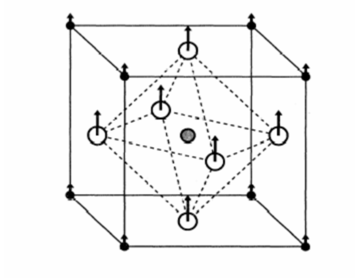
$$\boldsymbol{T} \sim \frac{1}{V}\int\left[\left(\boldsymbol{j}\cdot\boldsymbol{r}\right)\boldsymbol{r} - 2r^2\boldsymbol{j}\right]\mathrm{d}^3r$$

$$\boldsymbol{T} = \frac{1}{2}\mu_B\sum_i \boldsymbol{r}_i \times \boldsymbol{S}_i$$

- I.S. Zel'dovich
- V. L. Ginzburg
- D. Sannikov*

•Spin-orbit coupling (*L·S*)

Does the magnetic field induce ionic displacements as in ferroelectric materials?



- **Other ?**

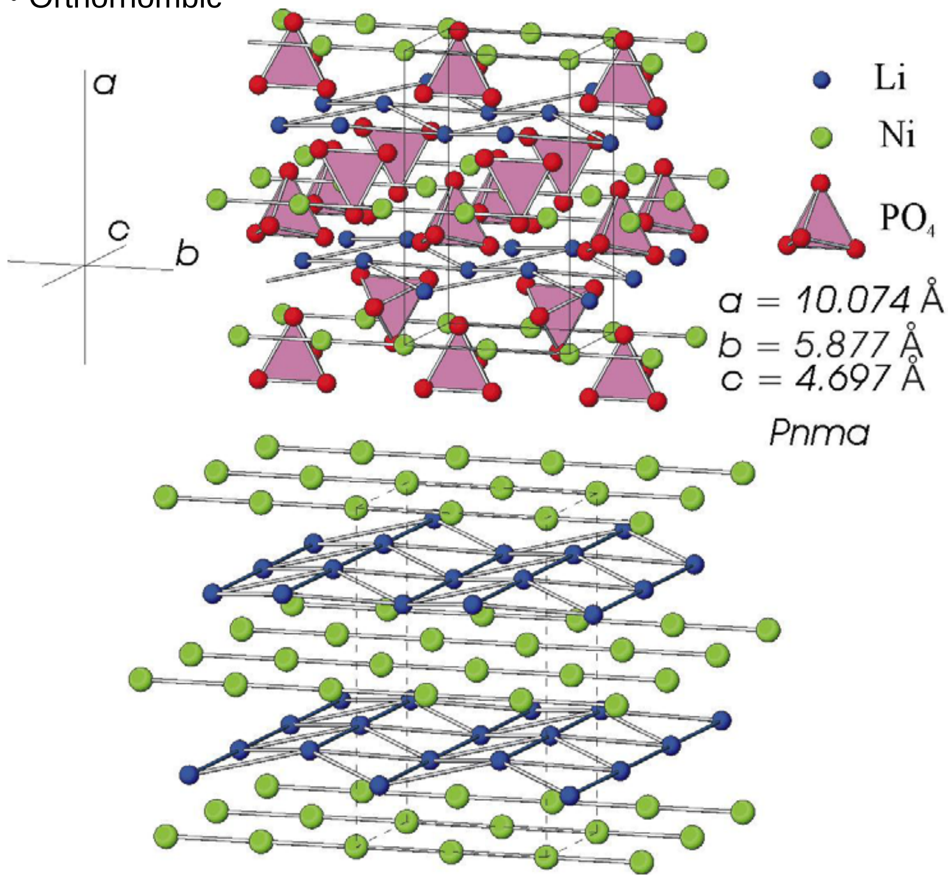
Materials-Physics Phenomena:

- Subtleties in magnetic symmetry
- To what extent the measured coefficients represent the staggered magnetization?
  - Are the coefficients proportional to the staggered magnetization?
- Domain structure

* Dubovik & Tosuyan *Physics of Elementary Particles and Atomic Nucleus* (EPAN) **14**, 1193 (1983).

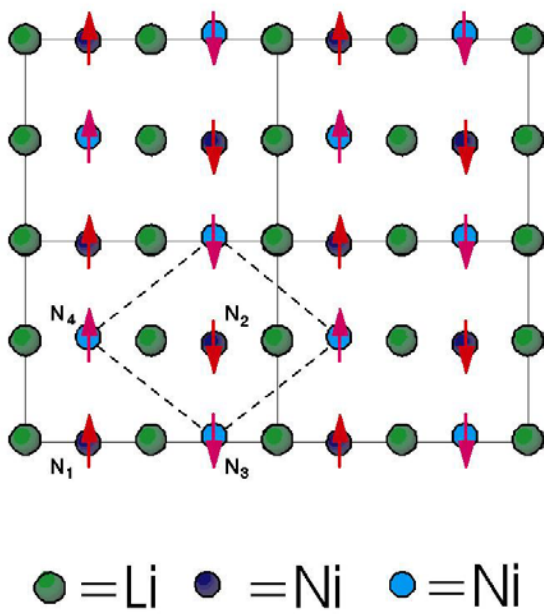
$LiMPO_4$ – (*M* = Ni, Co, Mn, Fe, ?Cu?)

- Insulators
- Orthorhombic

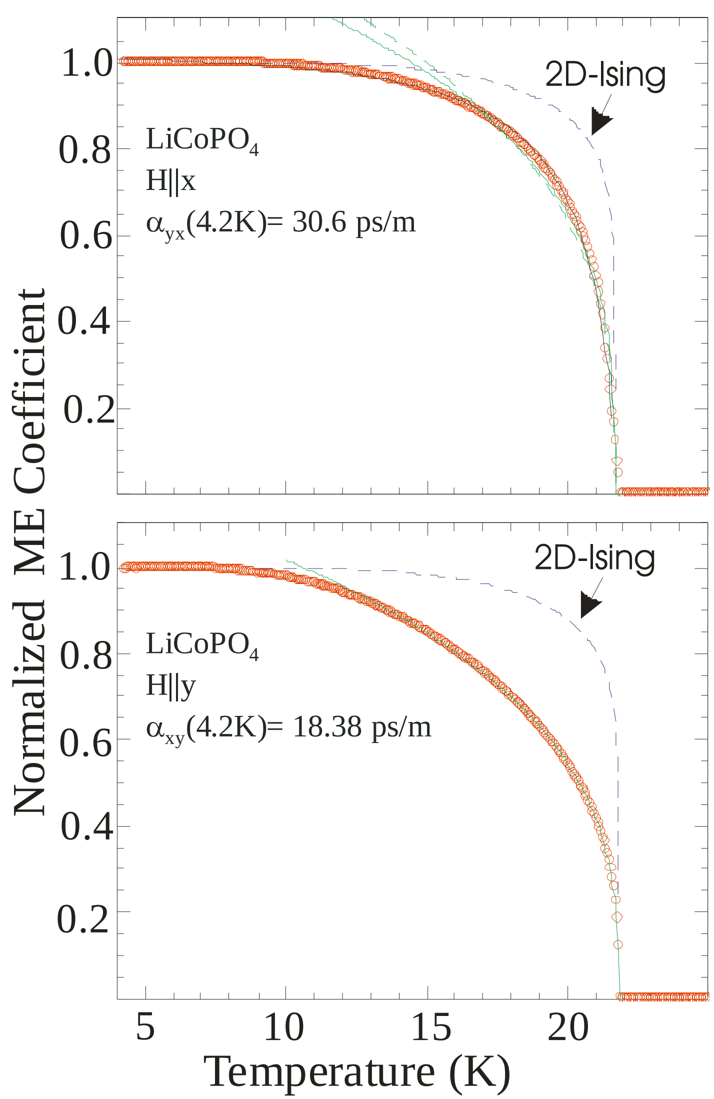


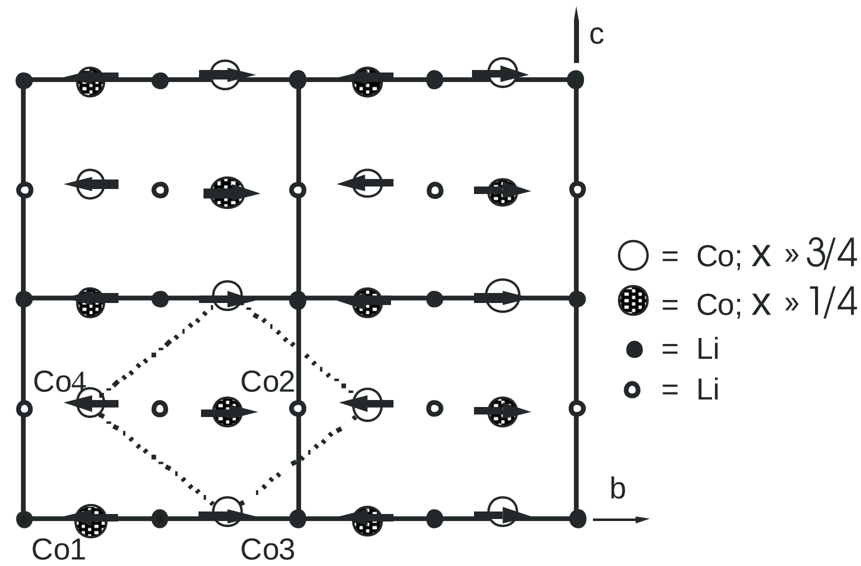
Antiferromagnets

Spin M^{2+} : S=1, 3/2,



T-dependence of coefficients for $LiCoPO_4$



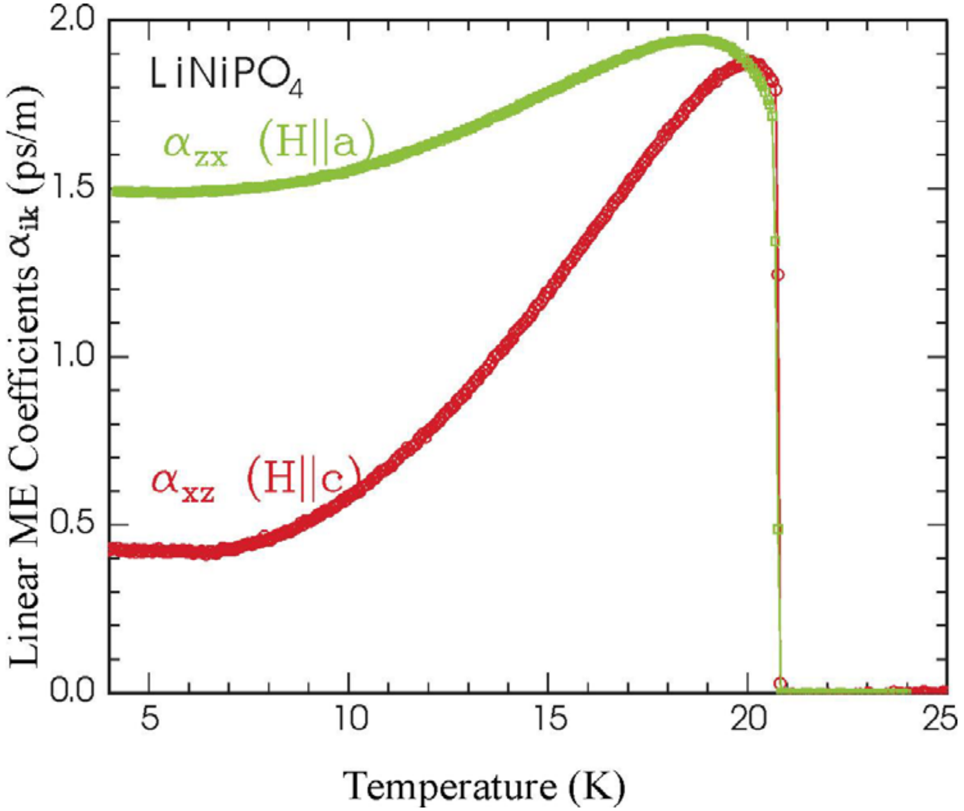


- **The effect is measurable below T_N – the antiferromagentic transition**
- **Reproducible from sample to sample – most likely domains do not play a role**
- **Different elements of the tensor α are different.**

problem - correlating with the spontaneous staggered magnetization

J.-P. Rivera, *Ferroelectrics* **161**, 147 (1994).

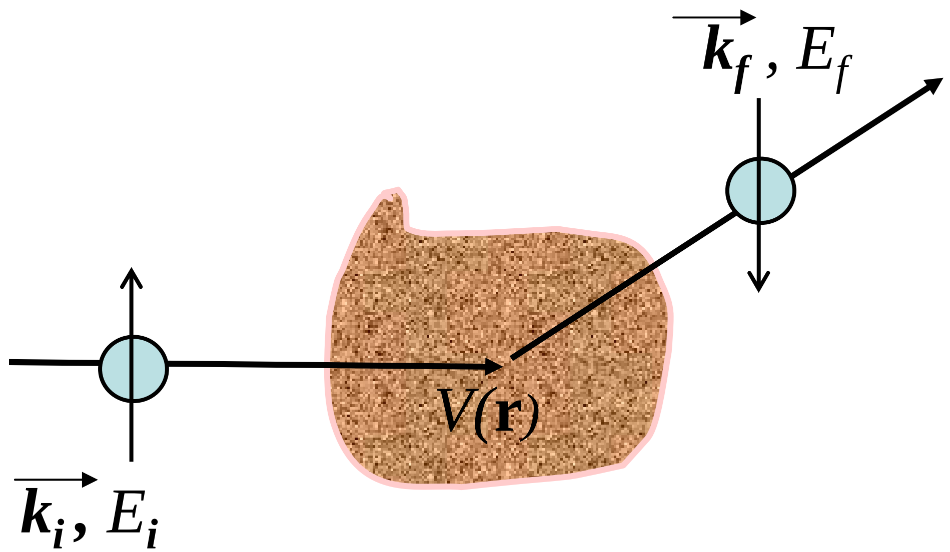
Anomalies in the ME coefficients of $LiNiPO_4$



1. An abrupt increase in ME coefficients T = 20.8 K - characteristic of a first-order phase-transition

2. A anomalous decrease in the coefficients below the transition.

Neutron Scattering



$p = \hbar k$

$E = \hbar^2 k^2/2m$

$\mu_n = -1.91\mu_N\sigma$

$(\mu_N = \hbar e/2m_p)$

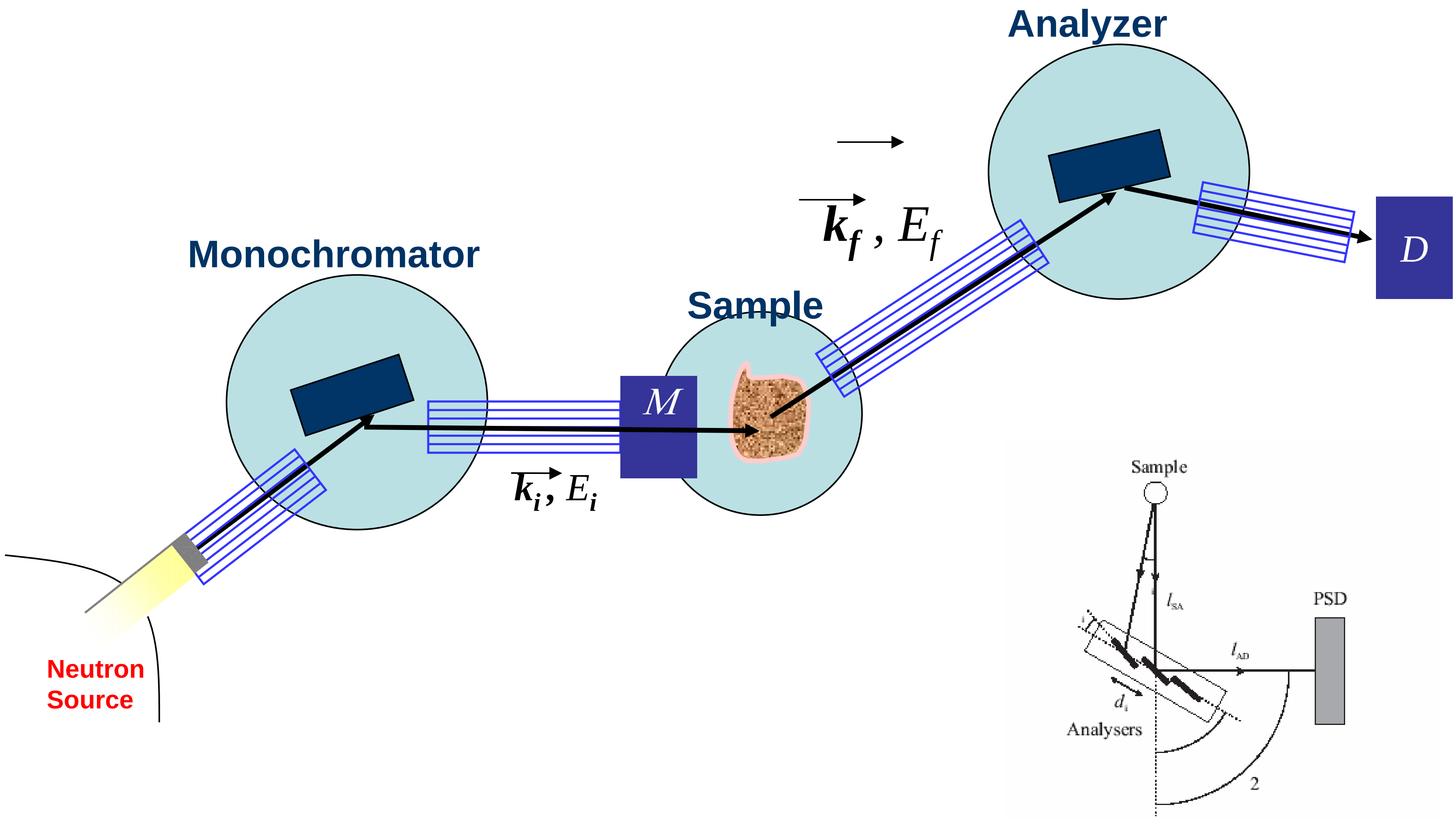
Momentum Transfer: $Q = k_i - k_f$

Energy transfer: $\omega = E_i - E_f$

$\omega = 0$ *elastic scattering (diffraction - structure)*

$\omega \neq 0$ *inelastic scattering (phonons, spin-waves, magnetic excitations, diffusion etc.)*

Triple-axis Spectrometer



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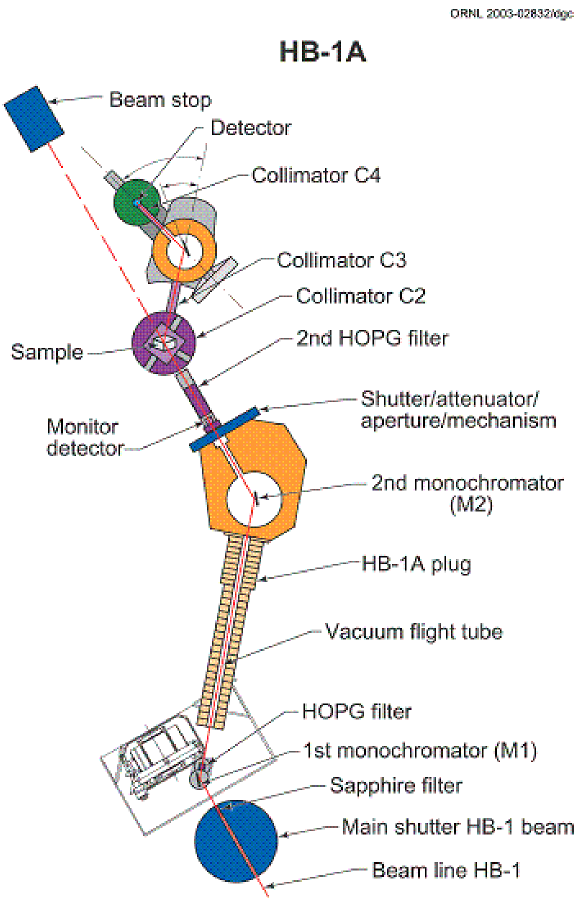
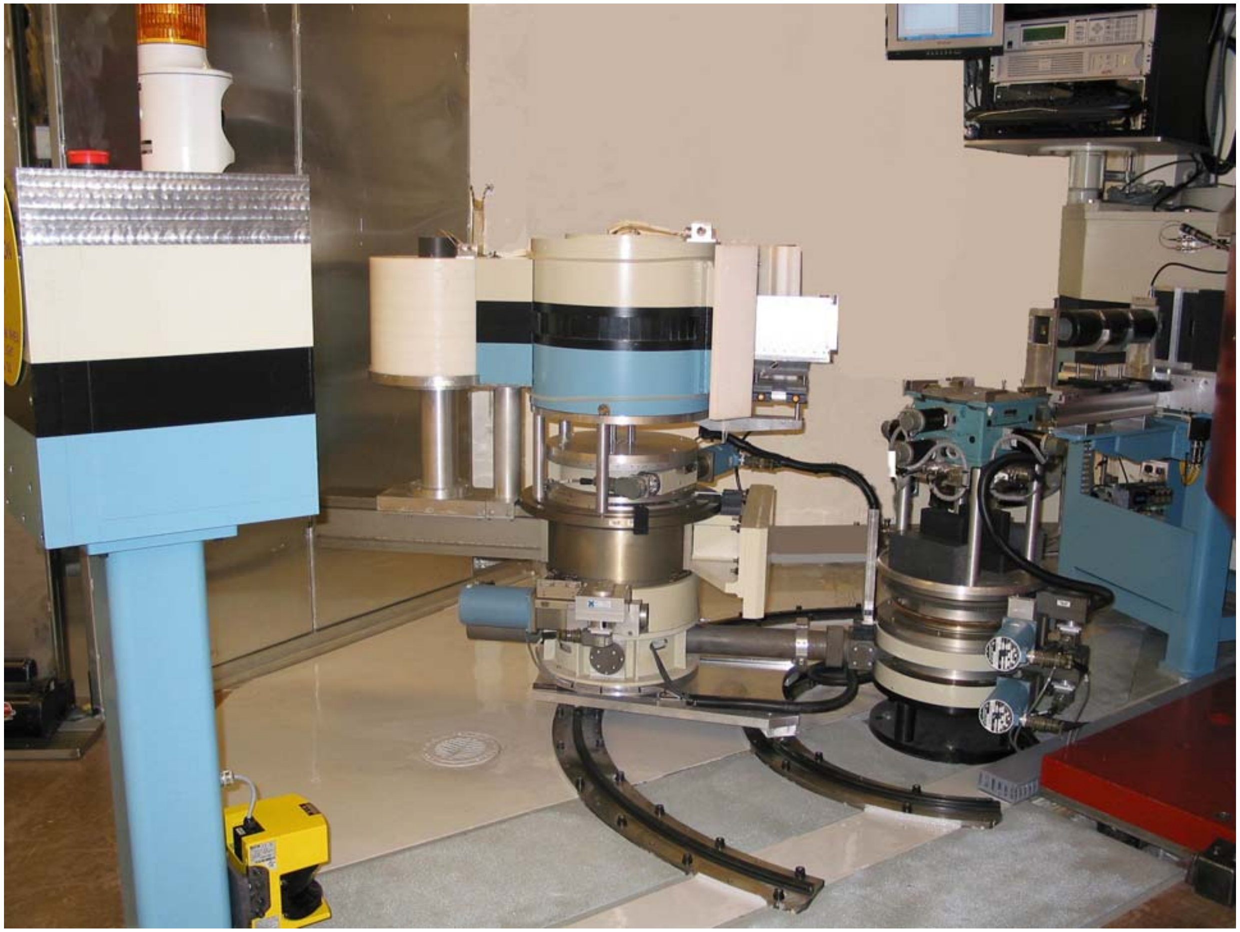
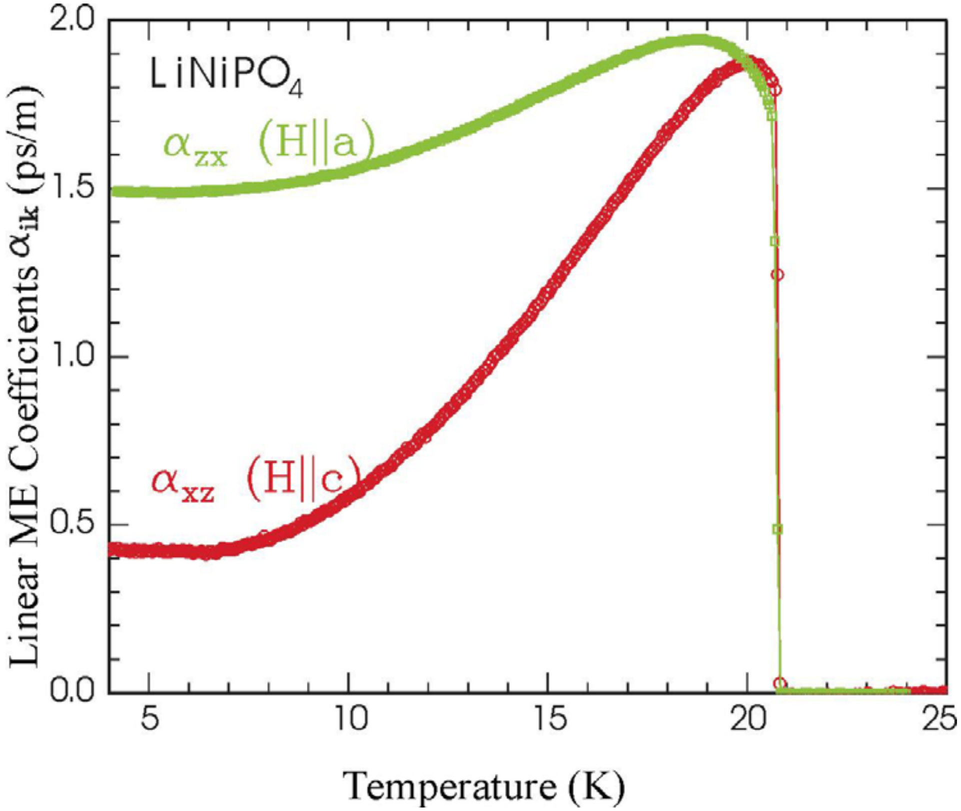
HB1A at High Flux Isotope Reactor (HFIR)





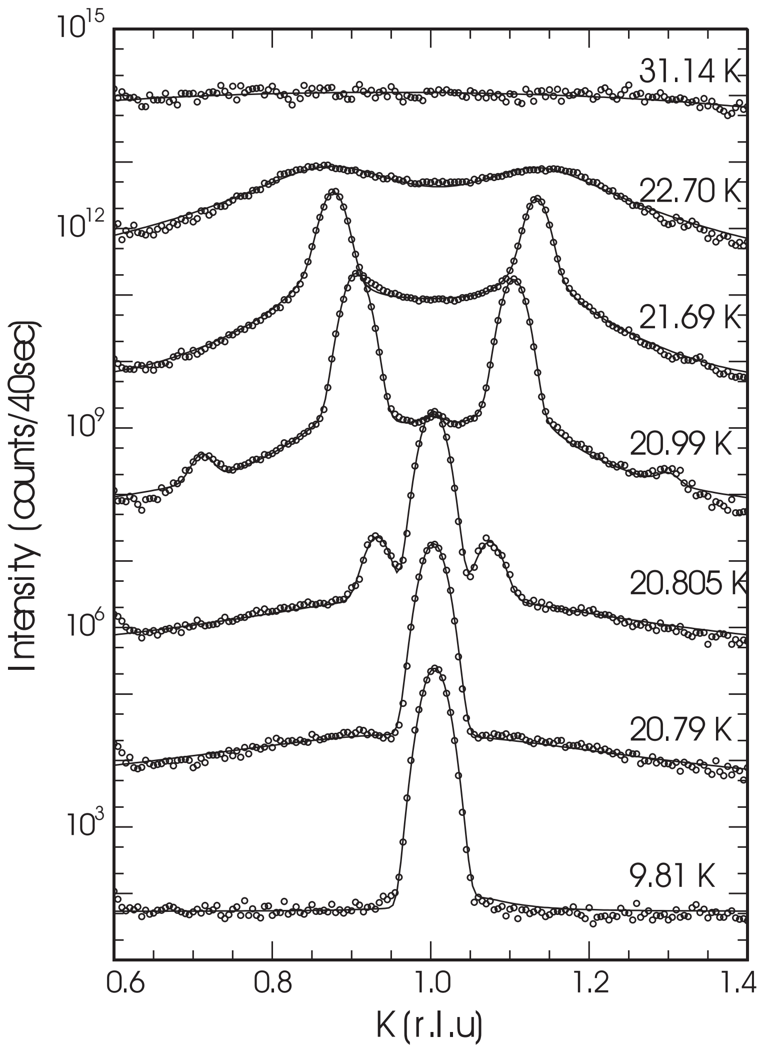
Anomalies in the ME coefficients of $LiNiPO_4$



1. An abrupt increase in ME coefficients T = 20.8 K - characteristic of a first-order phase-transition

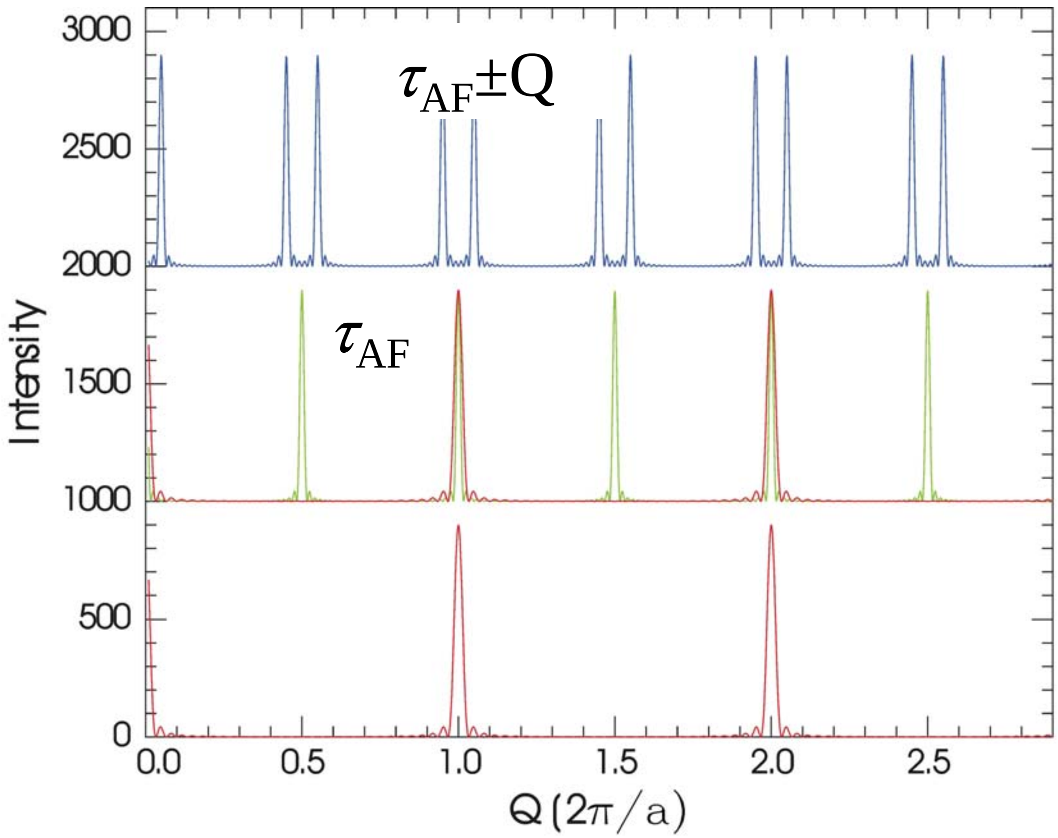
2. A anomalous decrease in the coefficients below the transition.

Longitudinal scans along (0K0) single crystal $LiNiPO_4$



D. Vaknin, et al., *Phys. Rev. Lett.* (2004).

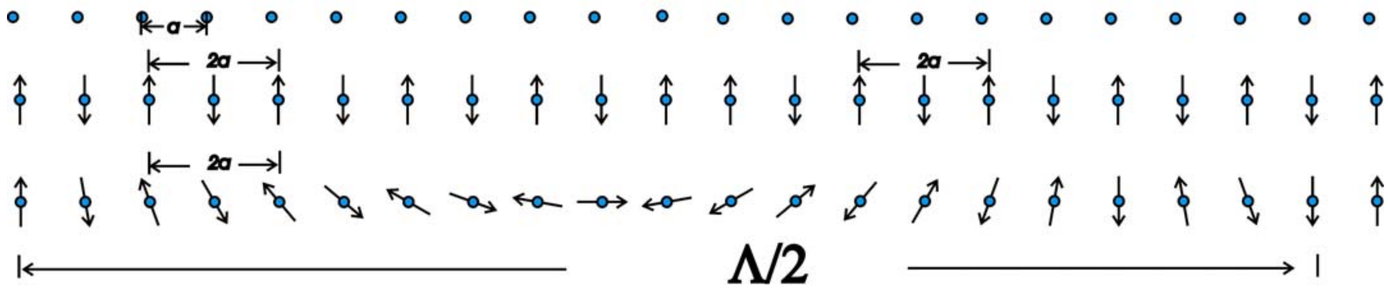
Antiferromagnetic and Incommensurate Patterns



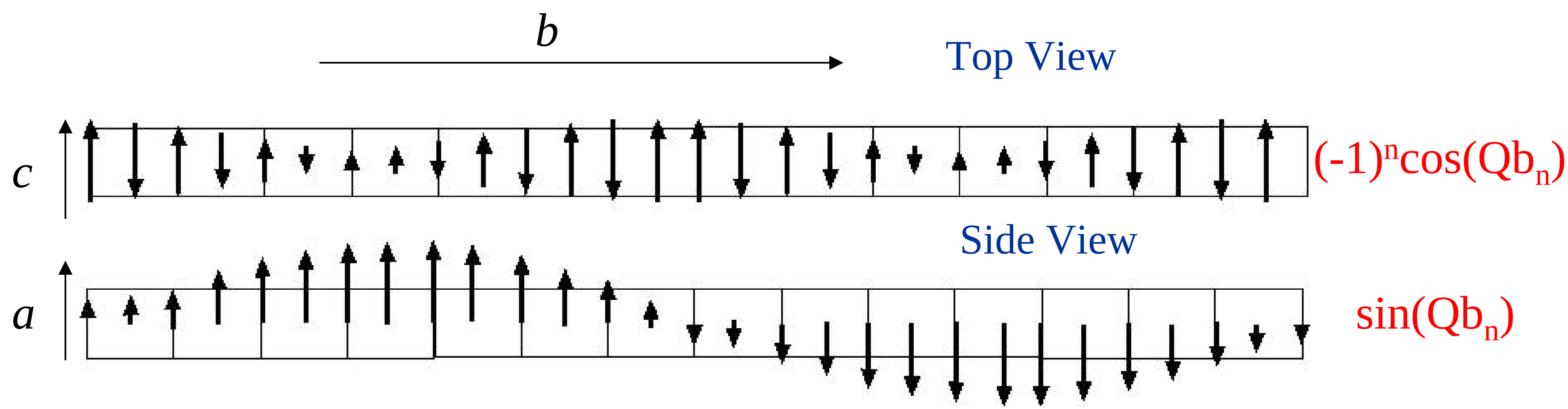
Incommensurate State

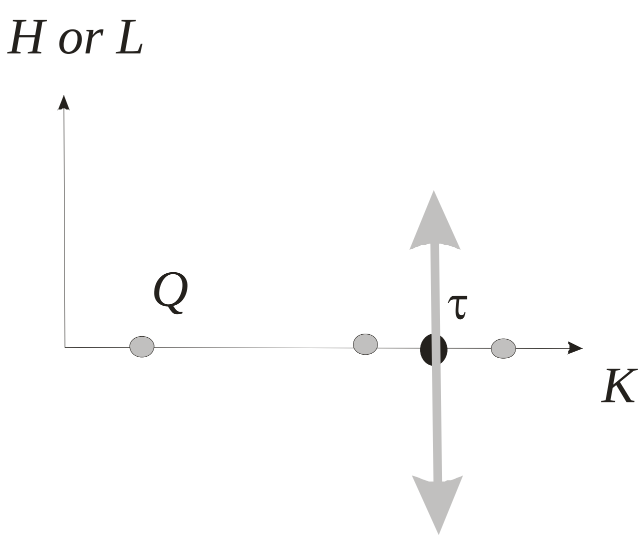
Antiferromagentic state

Chemical Structure
Paramagnetic State

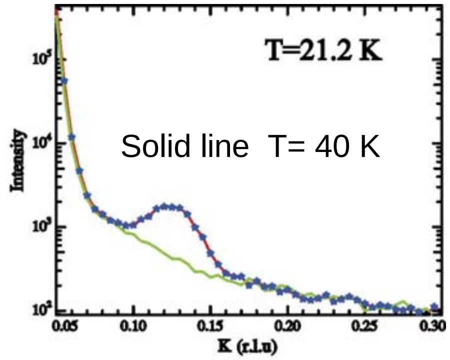


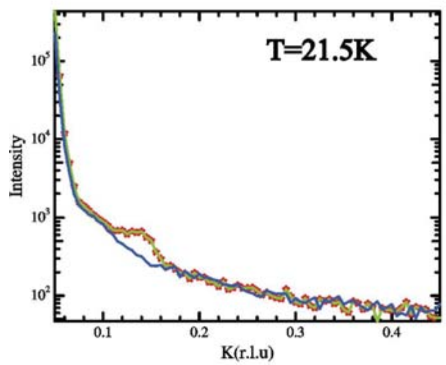
Components Magnetic Modulations

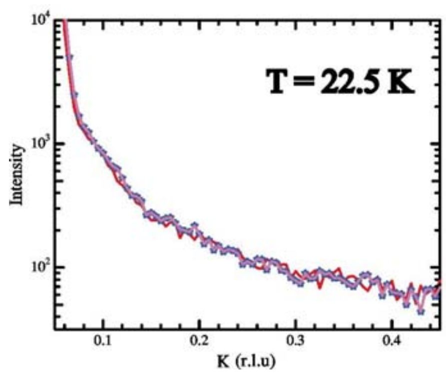




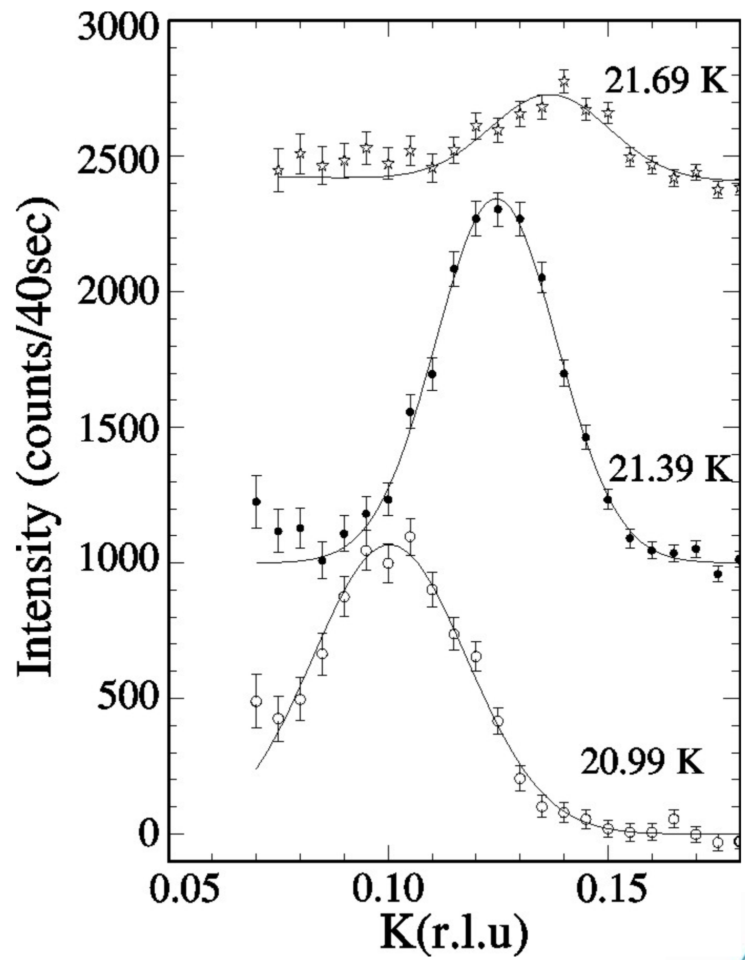
Ferromagnetic Modulations – small Q's



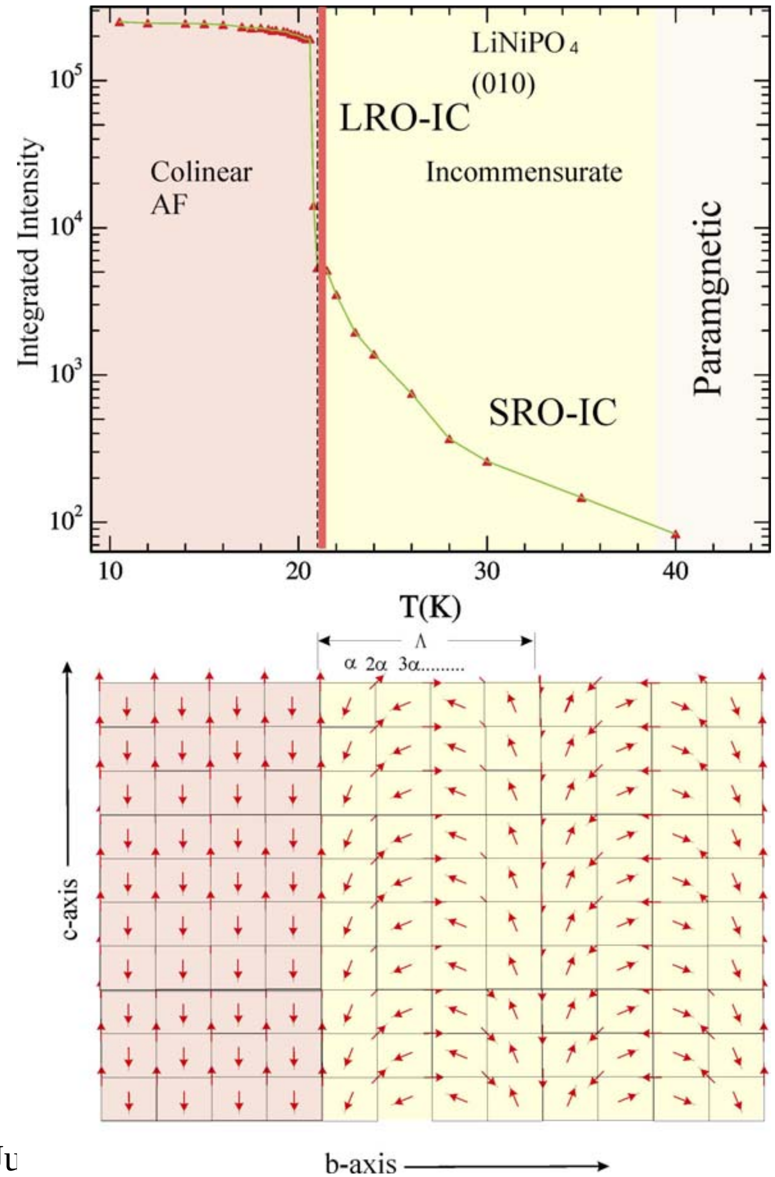




The Intensity of the AF-IC peak compared to the FM modulation peak ($\tau \pm Q$) goes like $1/Q^2$.



New phases



The occurrence of the incommensurate structures – short and long range IC is between two high symmetry phases AF and paramagnetic.

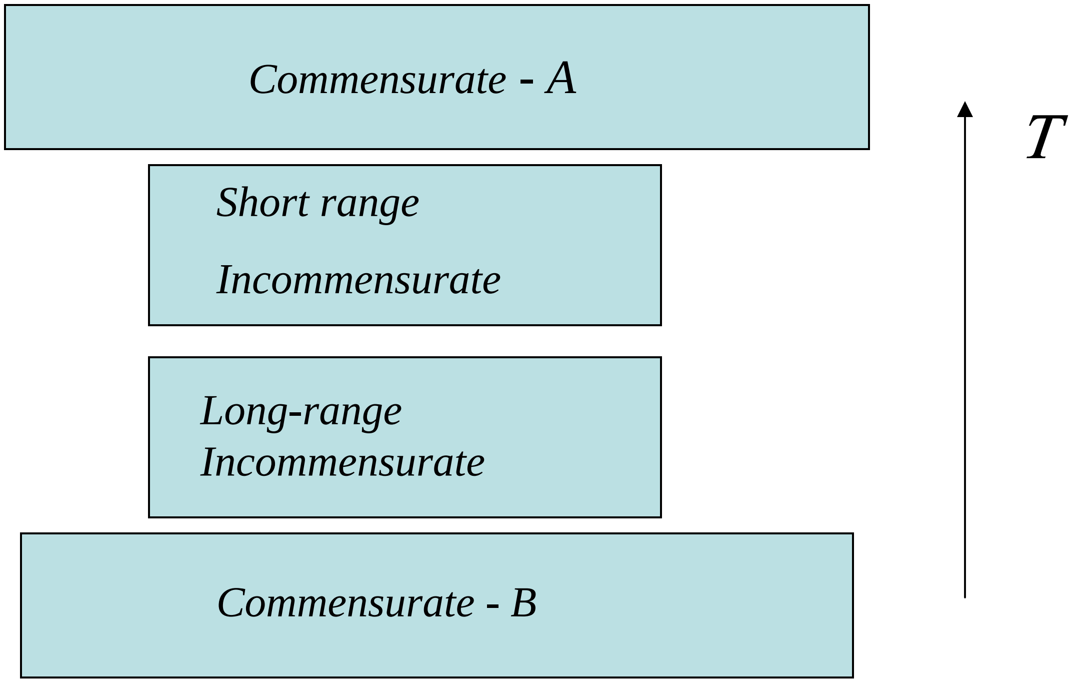
Two simple IC models

I -- FM sine component either in the b-axis as shown

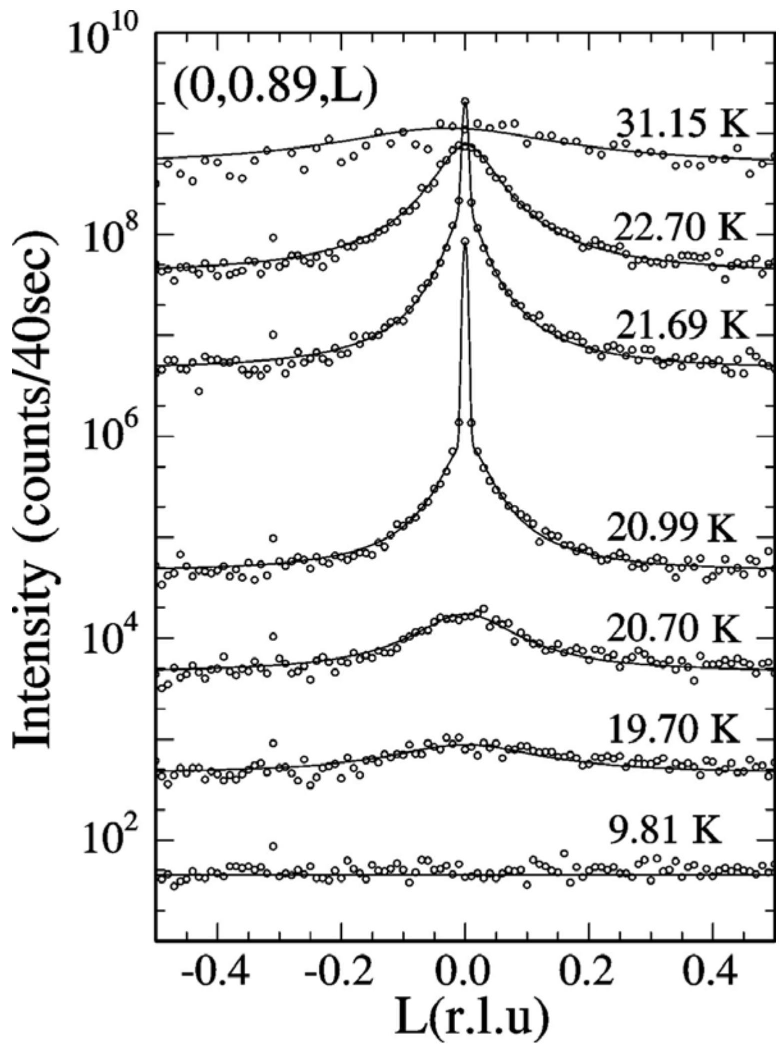
II -- same propagation vector with sine component in the a-axis (normal to the plane of the picture).

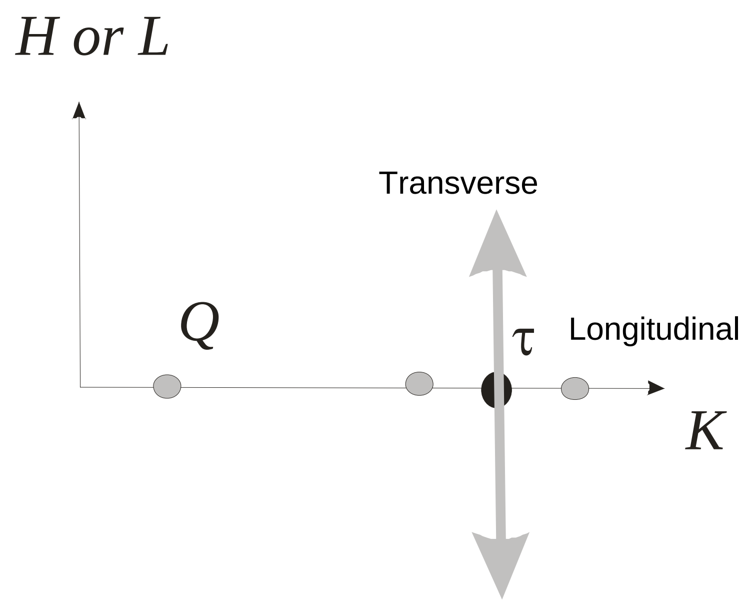
The second predicts FM scattering at small Q's - FM modulations.

Universal Properties of C-IC transitions



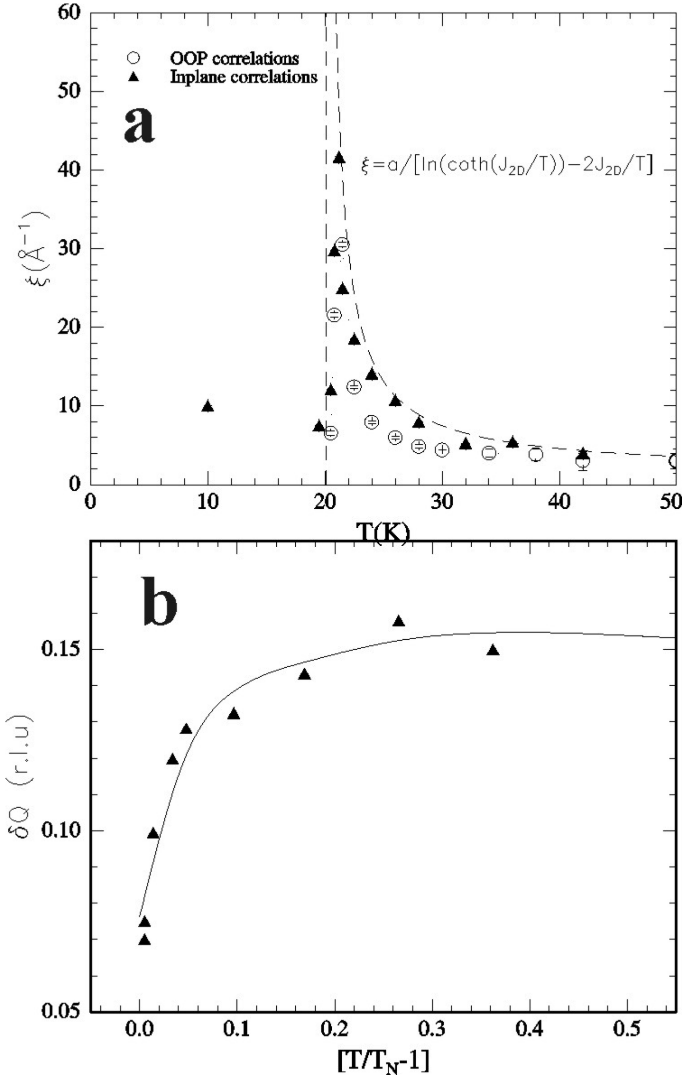
- *Strong diffuse Scattering*
- *Anomalies in phonon dispersions*
- *First order transition*





- Diffuse scattering below and above T_N
- IC phase is long-range order within 0.8 K above T_N

Anisotropic Correlations Lengths



Spin Waves – magnons

$$-J\sum_{i,j} \boldsymbol{S}_i \bullet \boldsymbol{S}_j + \dots$$

Ferromagnets

$$\omega \approx Dq^2$$

$$D_{1D} = 2JSa^2$$

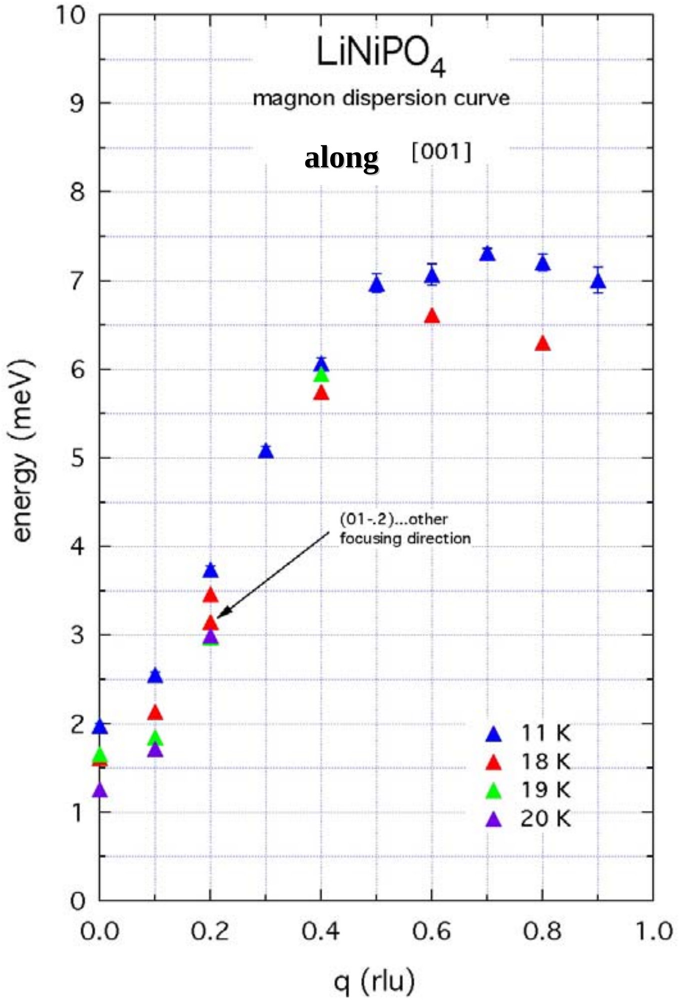
Antiferromagnets

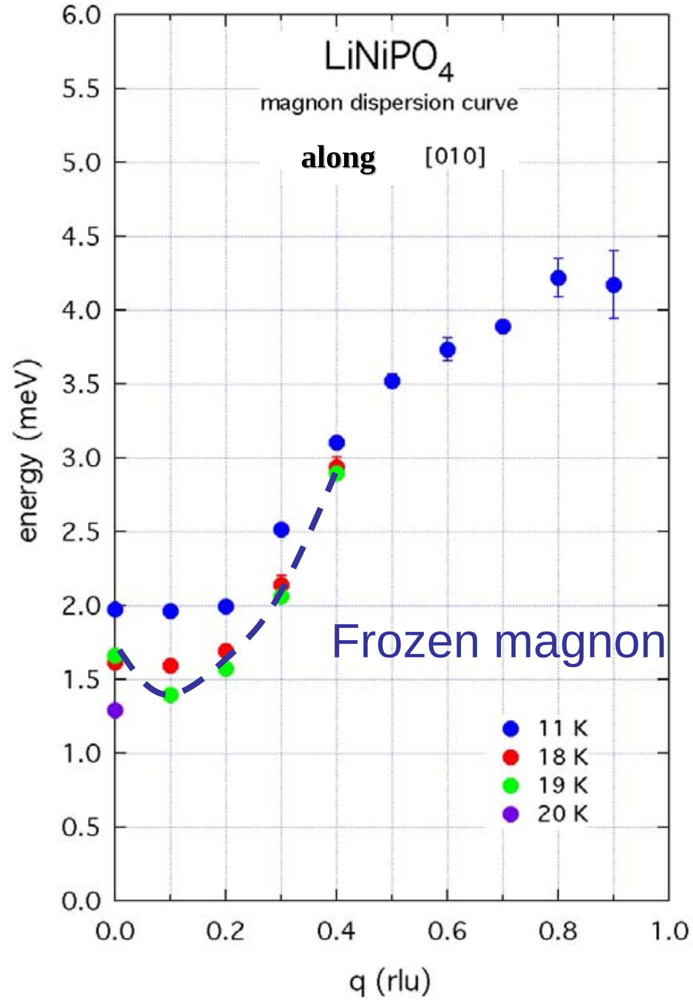
$$\omega \approx Dq + \omega_A$$

$$D_{1D} = 4JSa$$

Spin Waves in $LiNiPO_4$

Soft-magnon as a precursor to the IC phase





Observations:

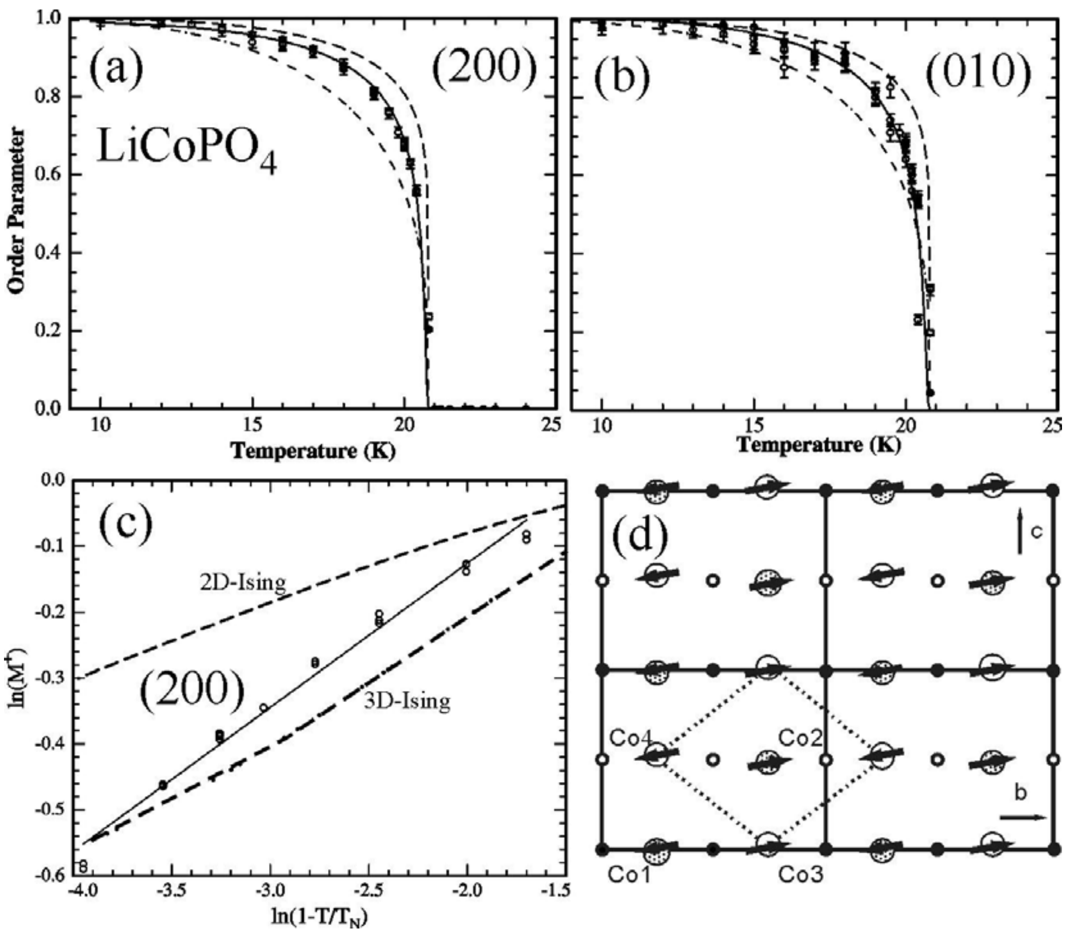
• Temperature dependent gap

• No spin waves observed above ~(T_N-1K) – might be related to the maximum observed in the ME-effect coefficient.

• Anomalous dispersion along the propagation vector of AFM order an of IC structure.

•Minimum in the dispersion along (010) as T approaches T_N – soft magnon – an analog to a soft phonon.

$LiCoPO_4$ – No IC structure



- Temperature dependence of order parameter is different than that measured with ME effect.
- Spins are slightly rotated from b direction.

Vaknin et al. Phys. Rev. B. (2002).

Conclusions

- A magnetic system that belongs to a universality class of incommensurate phase transitions
- Incommensurate to commensurate transition is first order and explains the sharp transition in the ME-effect
- Spin wave behavior – temperature dependent anisotropy-gap and a minimum in the dispersion.

Future Work

- Atomic displacements under magnetic field - X-ray and neutron (15 T magnet)
- Perturb the systems
  - $LiCuPO_4$ S = 1/2
  - Li(Fe)NiPO4 and others

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Acknowledgements

Ames Laboratory and DOE for support

J. L. Zarestky –	**Ames Lab**
Jiying Li –	**Ames Lab**
L. L. Miller –	**Ames Lab**
H. Schmid –	**University of Geneva, Switzerland**
J-P. Rivera –	**University of Geneva, Switzerland**
T. B S. Jensen –	**Risø National Lab, Denmark**
K. Lefmann –	**Risø National Lab, Denmark**
N. H. Andersen –	**Risø National Lab, Denmark**
C. Niedemayer –	**Paul Scherrer Institute, Switzerland**