Studies of Charge Order in Single Crystals of $LuFe_2O_4$ and Fe_2OBO_3

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Work supported by BES Division of Materials Sciences and Engineering

Collaborators

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N.C. State – H. J. Xiang, M.-H. Whangbo

Ames -- J. W. Kim

UK – V. Varadarajan, J. W. Brill

Special thanks to Art Sleight

Andy Christianson

Manuel Angst

Motivation

- Search for model charge order systems in which electrostatics play an important role

- Charge ordering is an intriguing route to ferroelectricity, and there may be strong coupling between magnetic & ferroelectric order parameters

- ORNL has good tools for these studies – i.e., neutron scattering, electron microscopy, piezoelectric force microscopy

Outline

$LuFe_2O_4$ – snapshot of work in progress

- Magnetization & thermal properties
- Neutron scattering
- Resonant Ultrasound Spectroscopy
- IR spectroscopy

Fe_2OBO_3 – summarize results presented in 2 papers*

- first growth of single crystals
- first observation of C.O. superstructure
- BVS analysis showing integer iron valence
- discovery of incommensurate phase

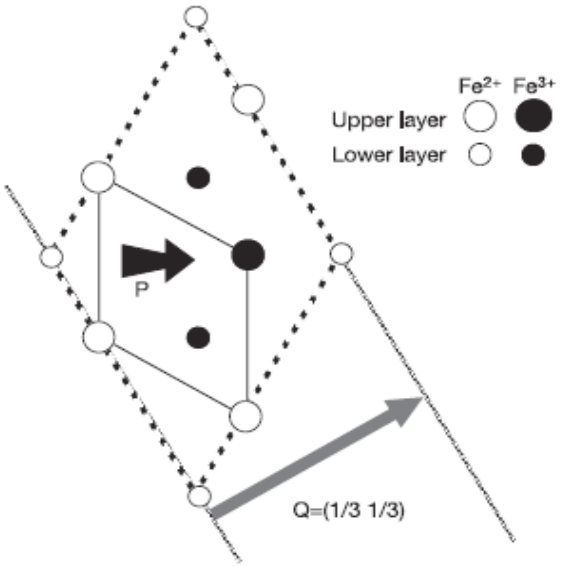
*M. Angst, et al. PRL **99**, 086403 (2007)
M. Angst, et al. cond-mat: 0707.3127

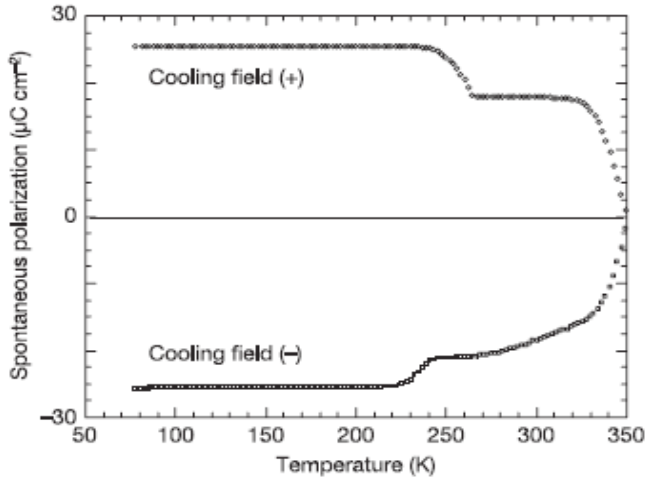
nature Vol 436|25 August 2005|doi:10.1038/nature04039

LETTERS

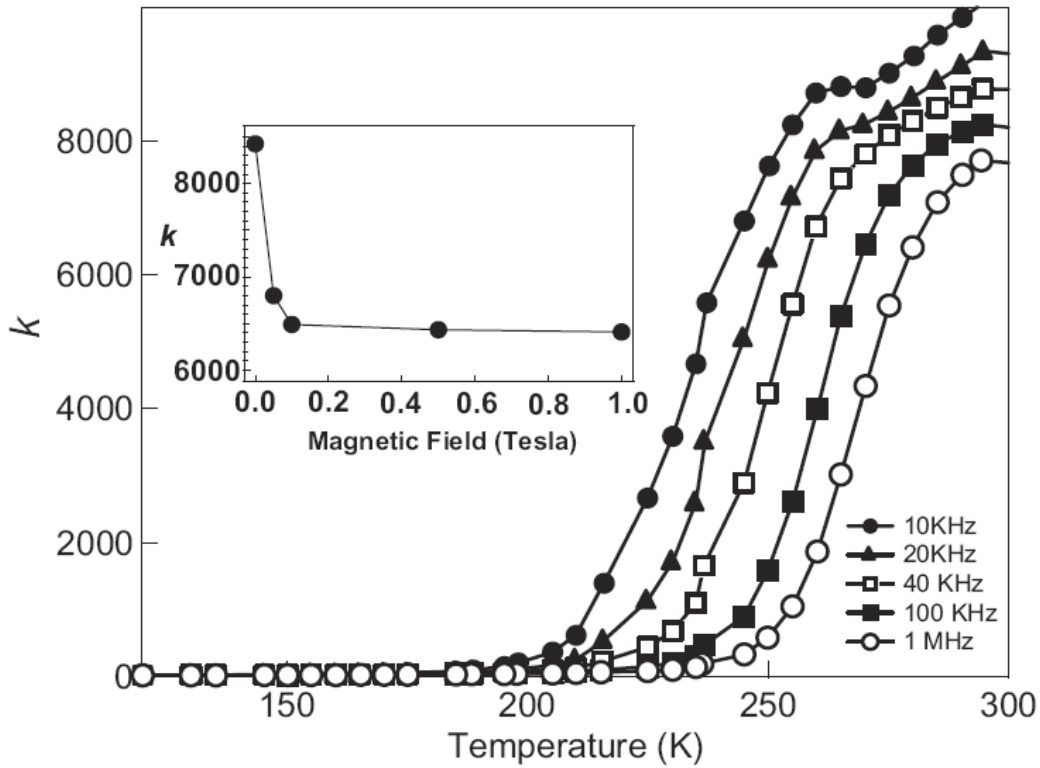
Ferroelectricity from iron valence ordering in the charge-frustrated system $LuFe_2O_4$

Naoshi Ikeda[1], Hiroyuki Ohsumi[1], Kenji Ohwada[2], Kenji Ishii[2], Toshiya Inami[2], Kazuhisa Kakurai[3], Youichi Murakami[4], Kenji Yoshii[2], Shigeo Mori[5], Yoichi Horibe[5] & Hijiri Kitô[6]





Large Magneto-Dielectric Effect in $LuFe_2O_4$



M. Subramanian et al., Adv. Mater. **18**, 1737 (2006)

Structure of $LuFe_2O_4$

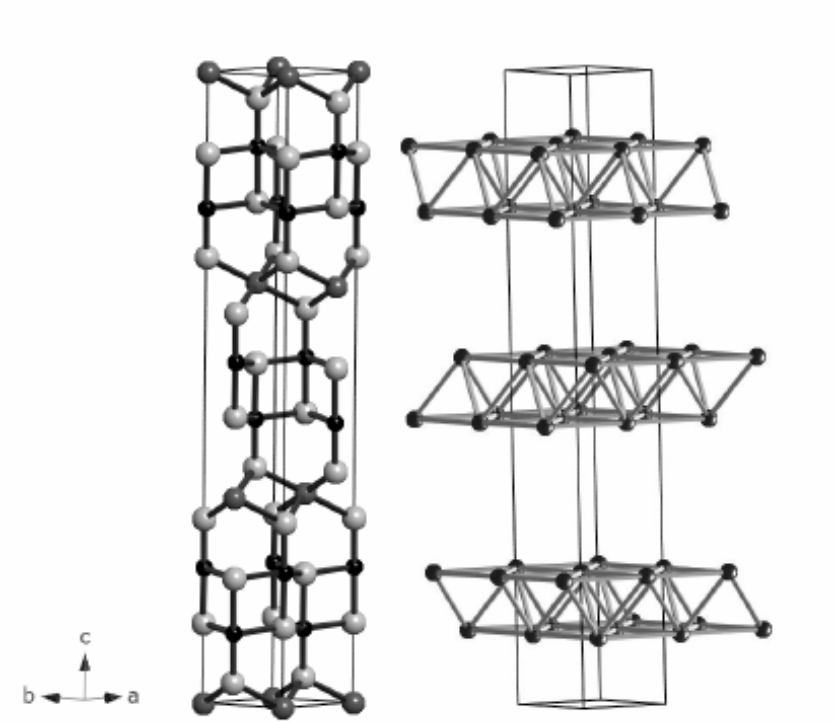
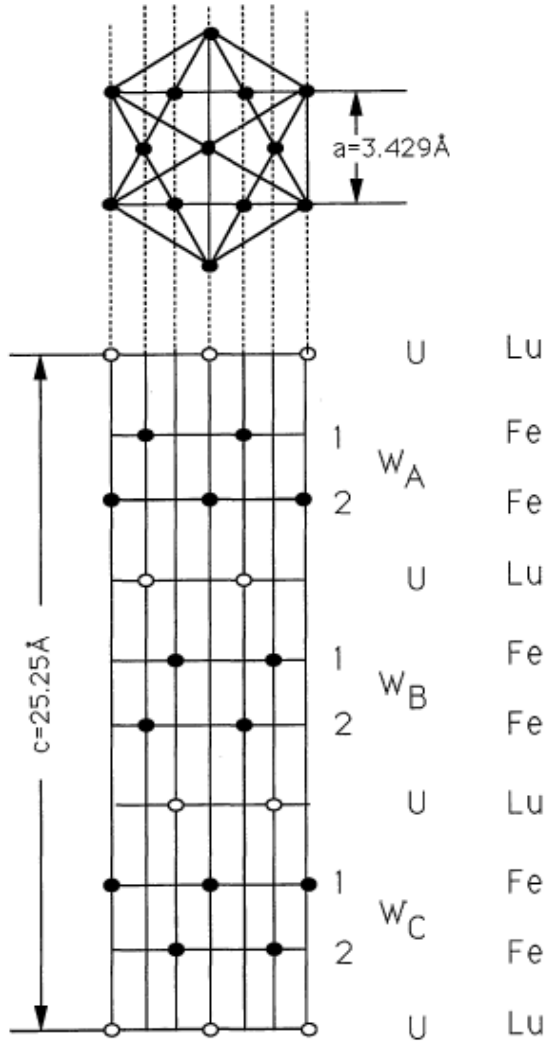


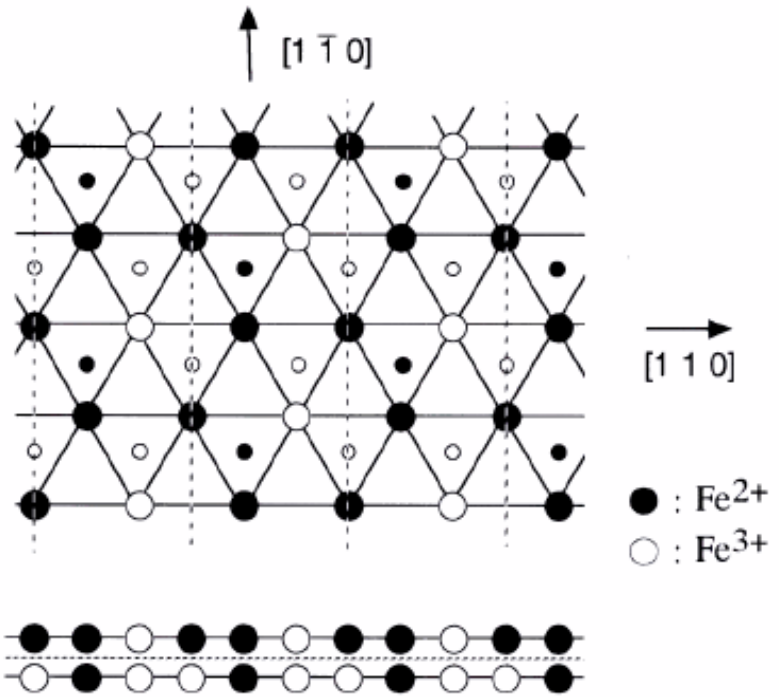
Figure 1. Crystal structure of $LuFe_2O_4$ showing the layered arrangement of Lu (large dark–grey spheres), Fe (small black spheres), and oxygen (large white spheres) along the *c*–axis (left). The Fe double layers are shown with a triangular interconnectivity (right). The Fe—Fe distances within a layer (3.44 Å) are longer than the Fe—Fe distances between the layers (3.156 Å).

M. Subramanian et al., Adv. Mater. (2006)

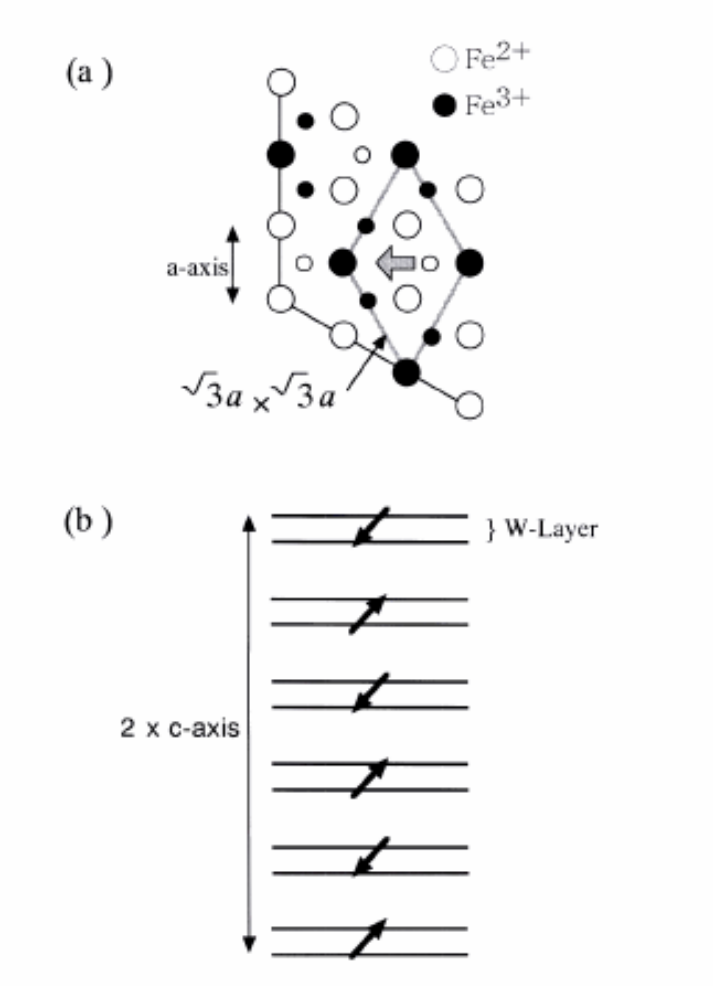


Iida, et al. JPSJ (1993)

Proposed Charge Ordering Pattern (Ikeda)

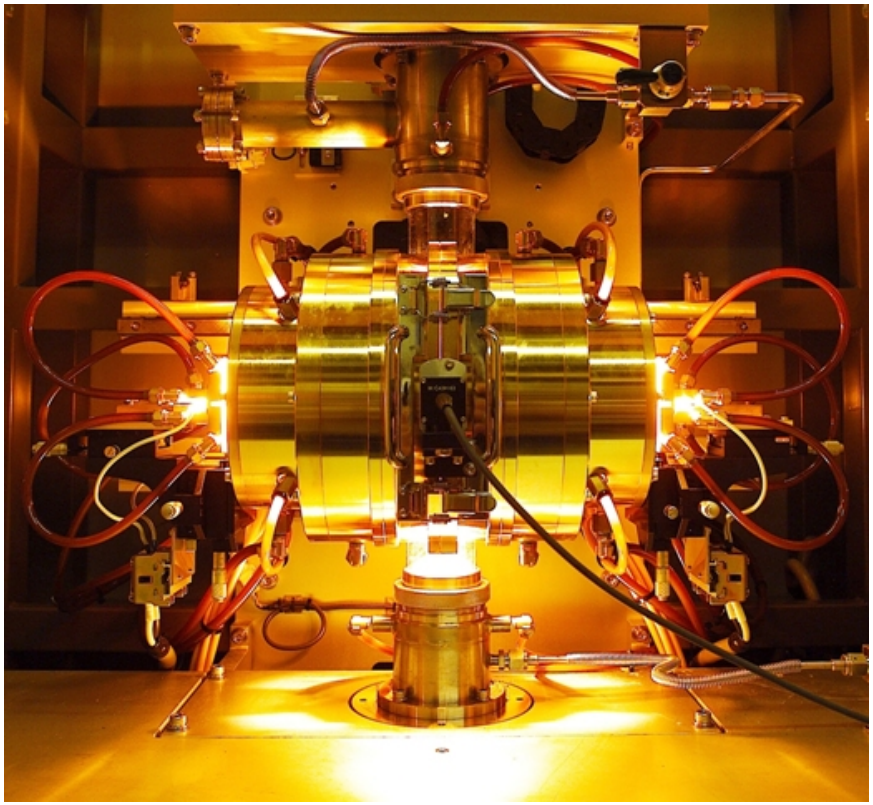


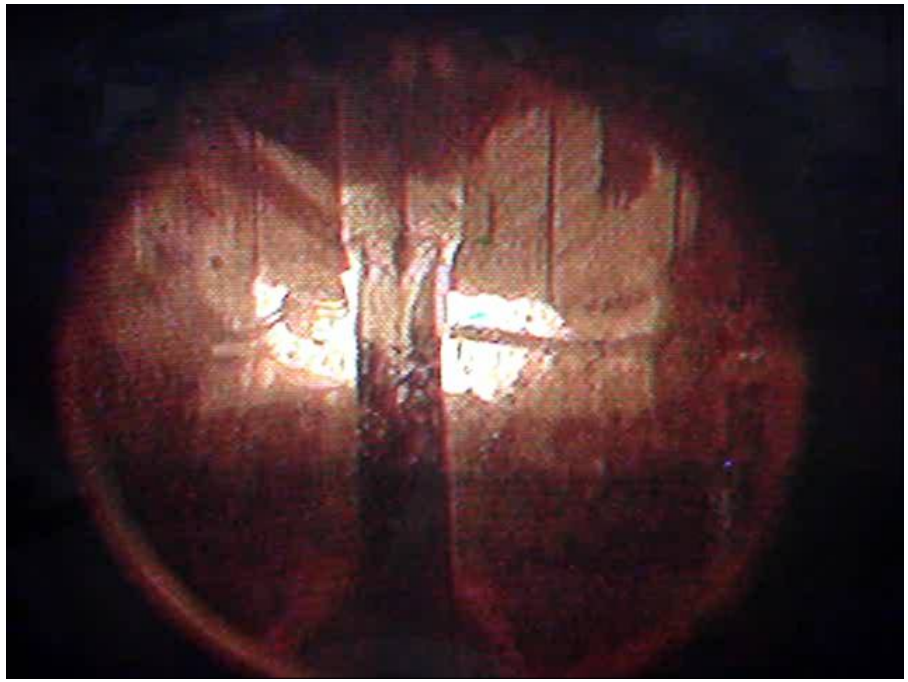
Yamada & Ikeda, JKPS (1998)



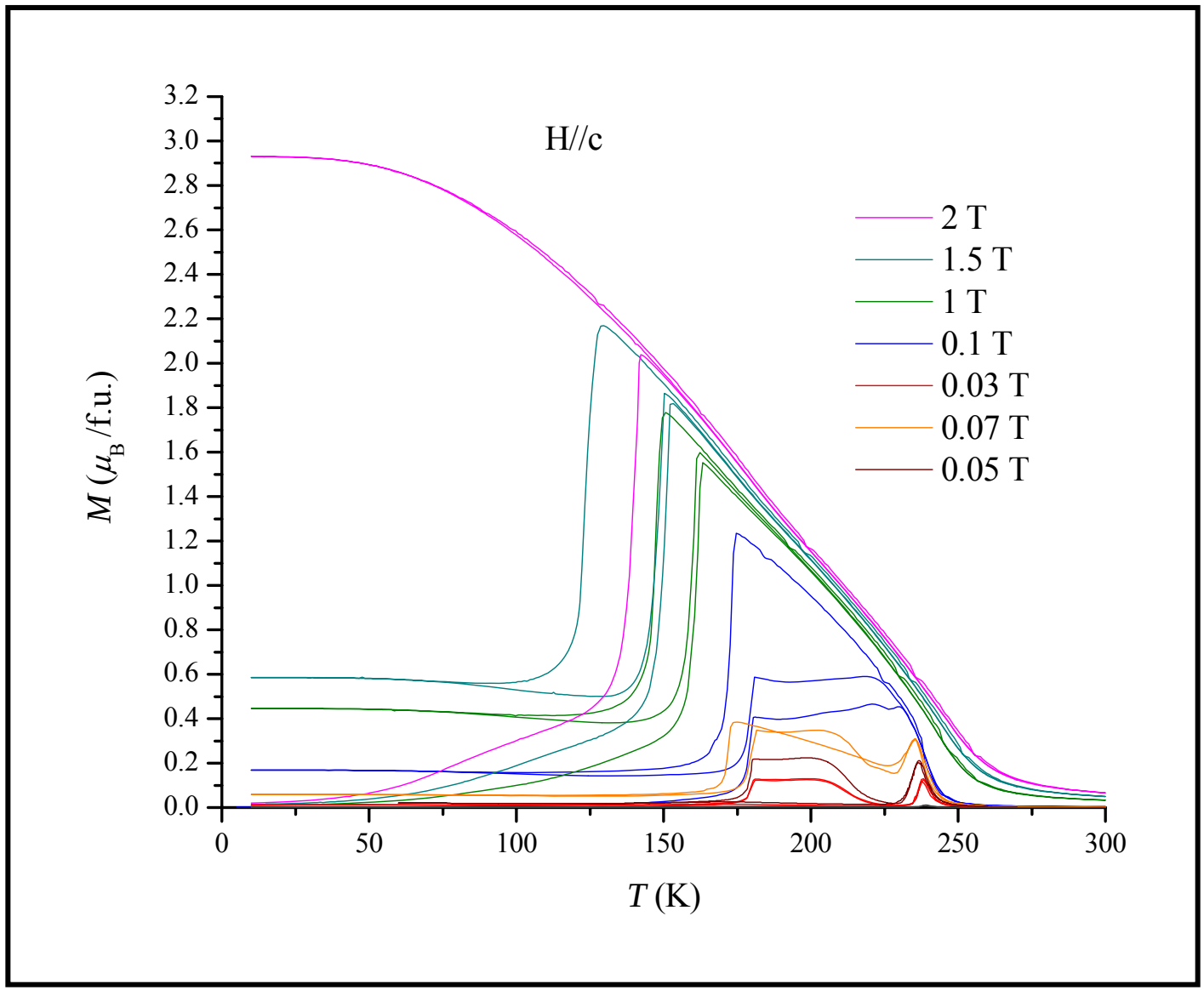
Ikeda, Nohdo, Yamada
JKPS (1998)

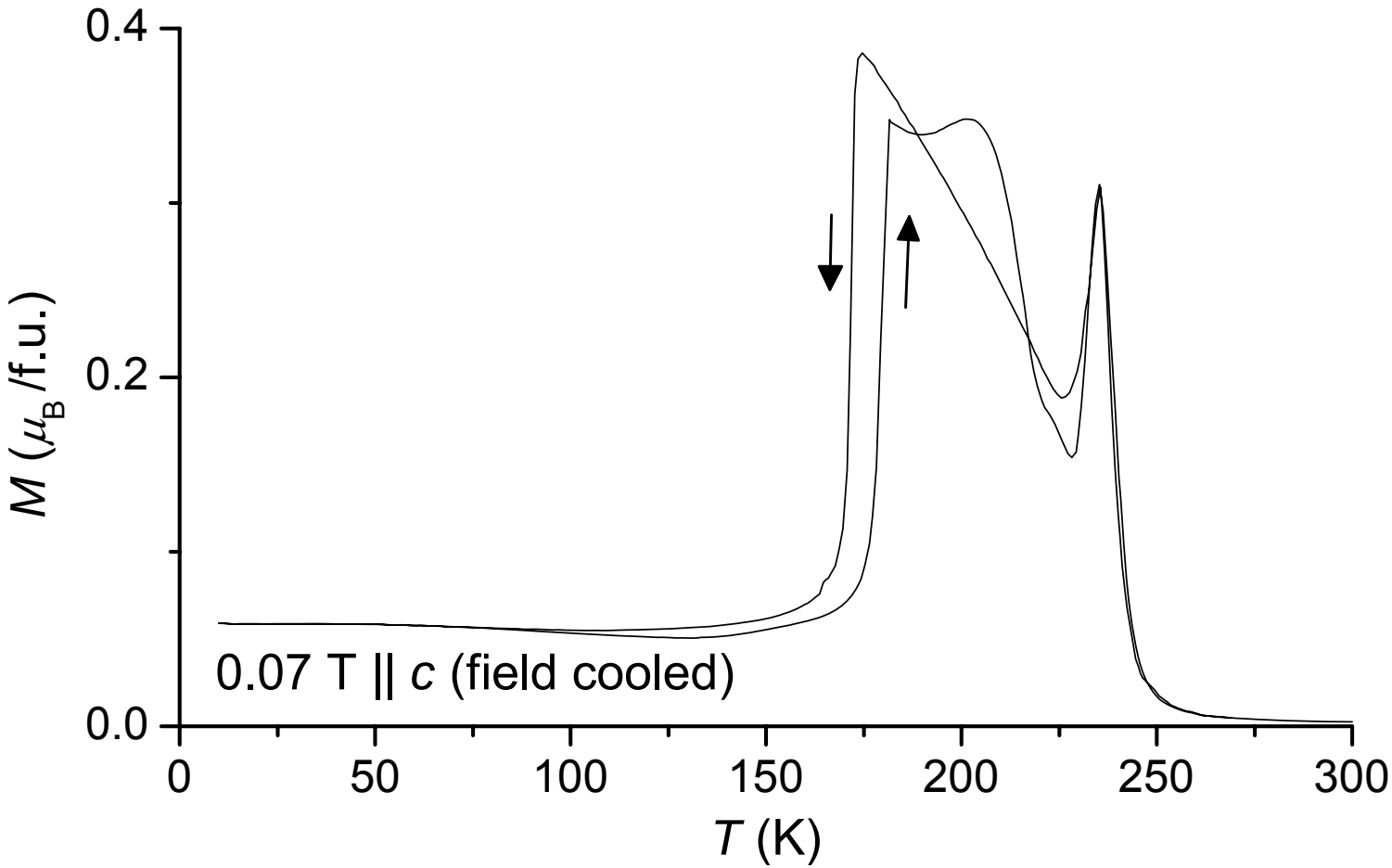
$LuFe_2O_4$ Optical Floating Zone Growth



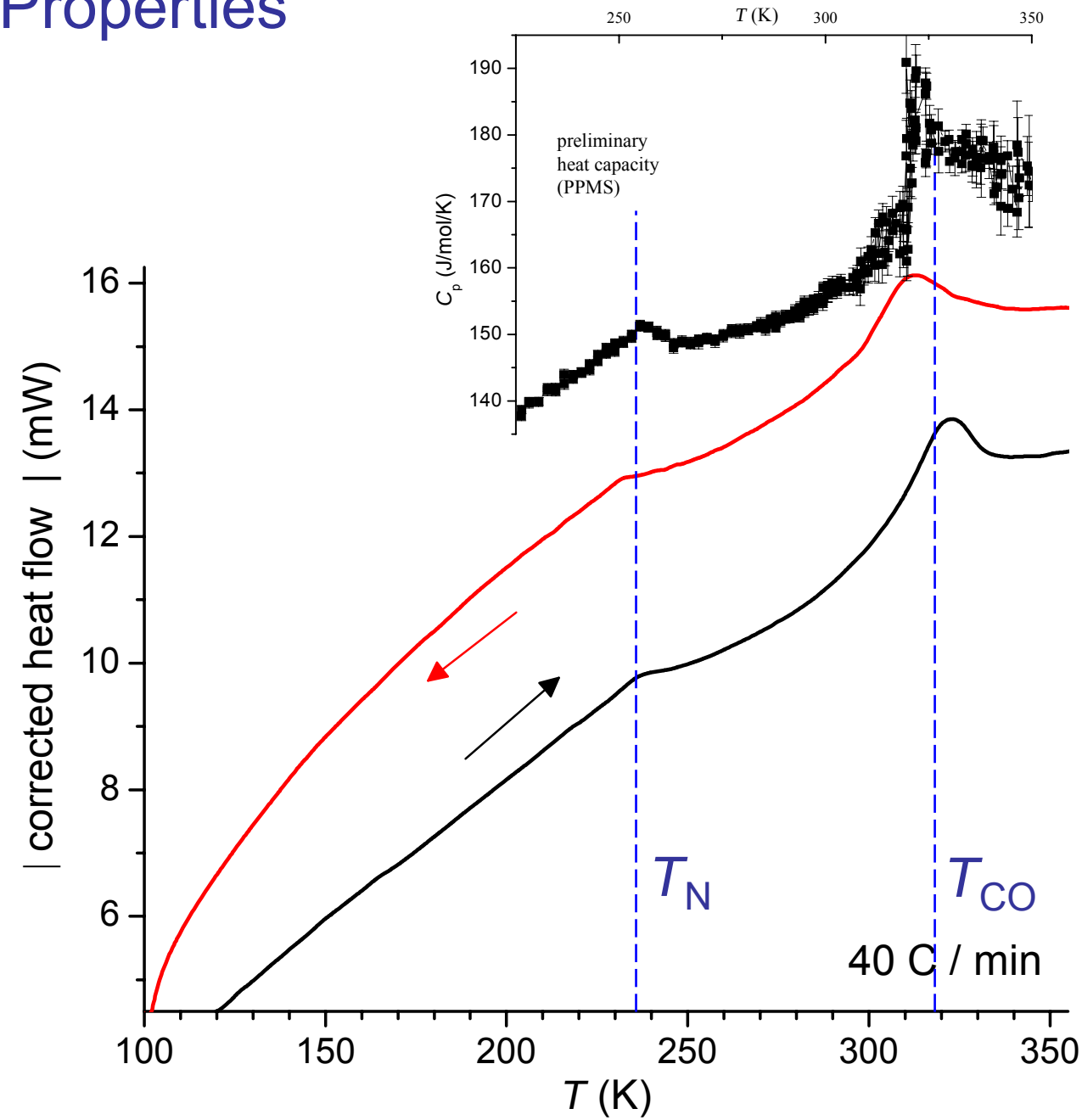


$LuFe_2O_4$ Magnetic Response



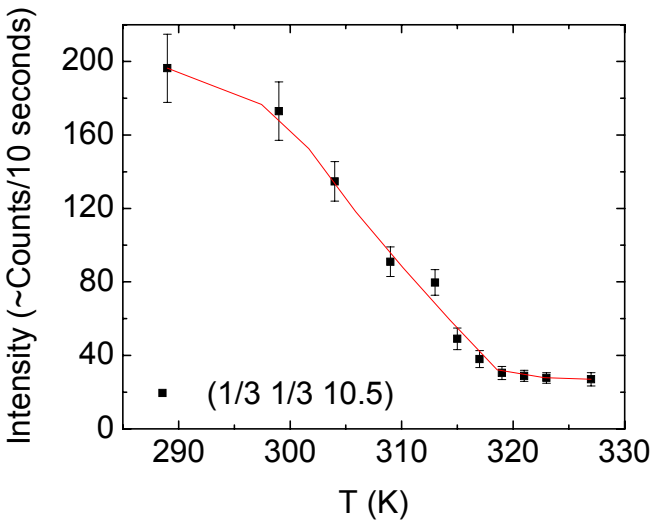

0.4
0.2
0.0
M (μB /f.u.)
0.07 T || c (field cooled)
0
50
100
150
200
250
300
T (K)

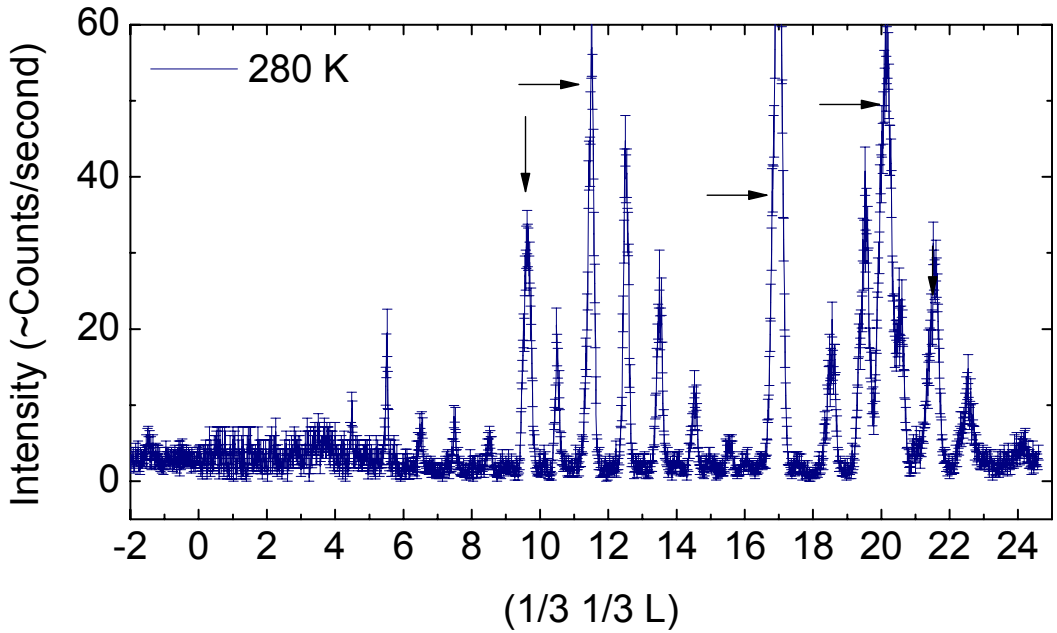
Thermal Properties



3D Charge Order below 320 K

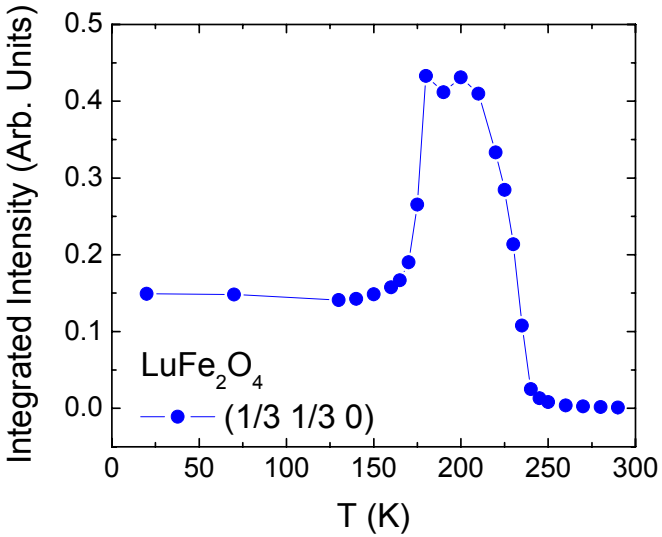
Neutron work by
Andy Christianson
Shull Fellow, ORNL

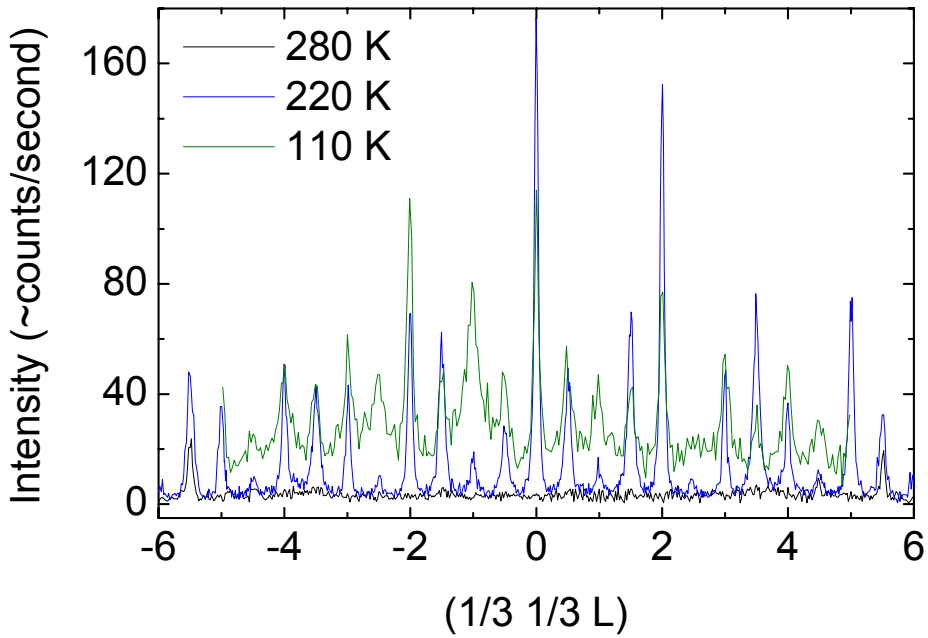




- 3D charge order develops below 320 K and is observed with propagation vector (1/3 1/3 1/2)

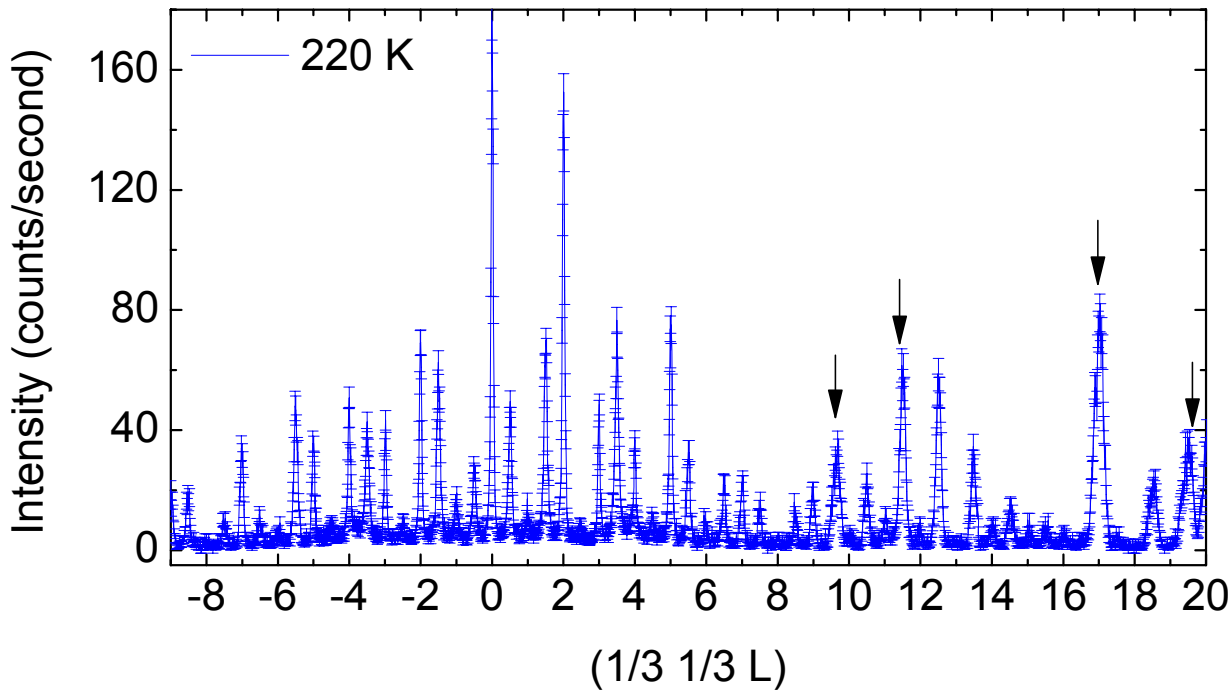
Magnetic Ordering In $LuFe_2O_4$





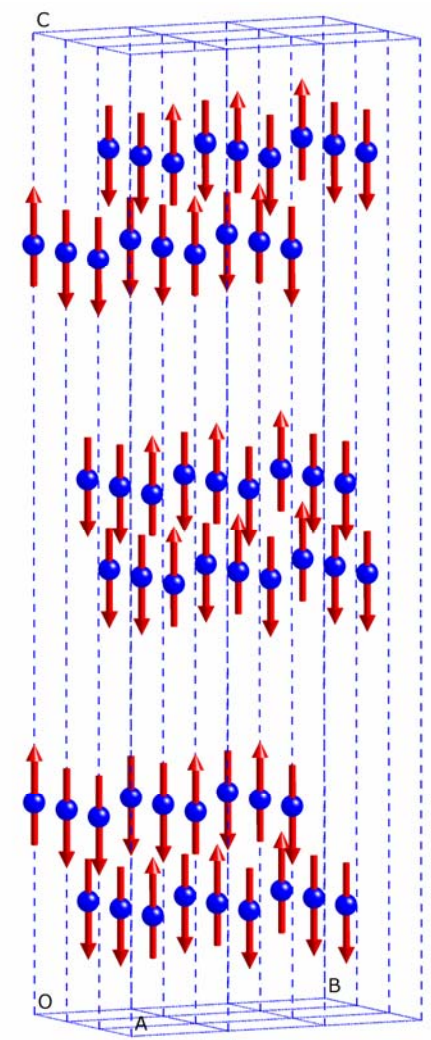
- Two Magnetic transitions-240 K (previously observed) and 180 K (new).
- Both transitions are 3D, however the peaks are not resolution limited (indicating a finite correlation length).
- Intensity occurs on peaks indexed as (1/3 1/3 L) where L is either an integer or half integer. The L integer peaks are the fundamental magnetic peaks and the half integer peaks are a consequence of the charge order at 320 K.

Magnetic Structure at 220 K

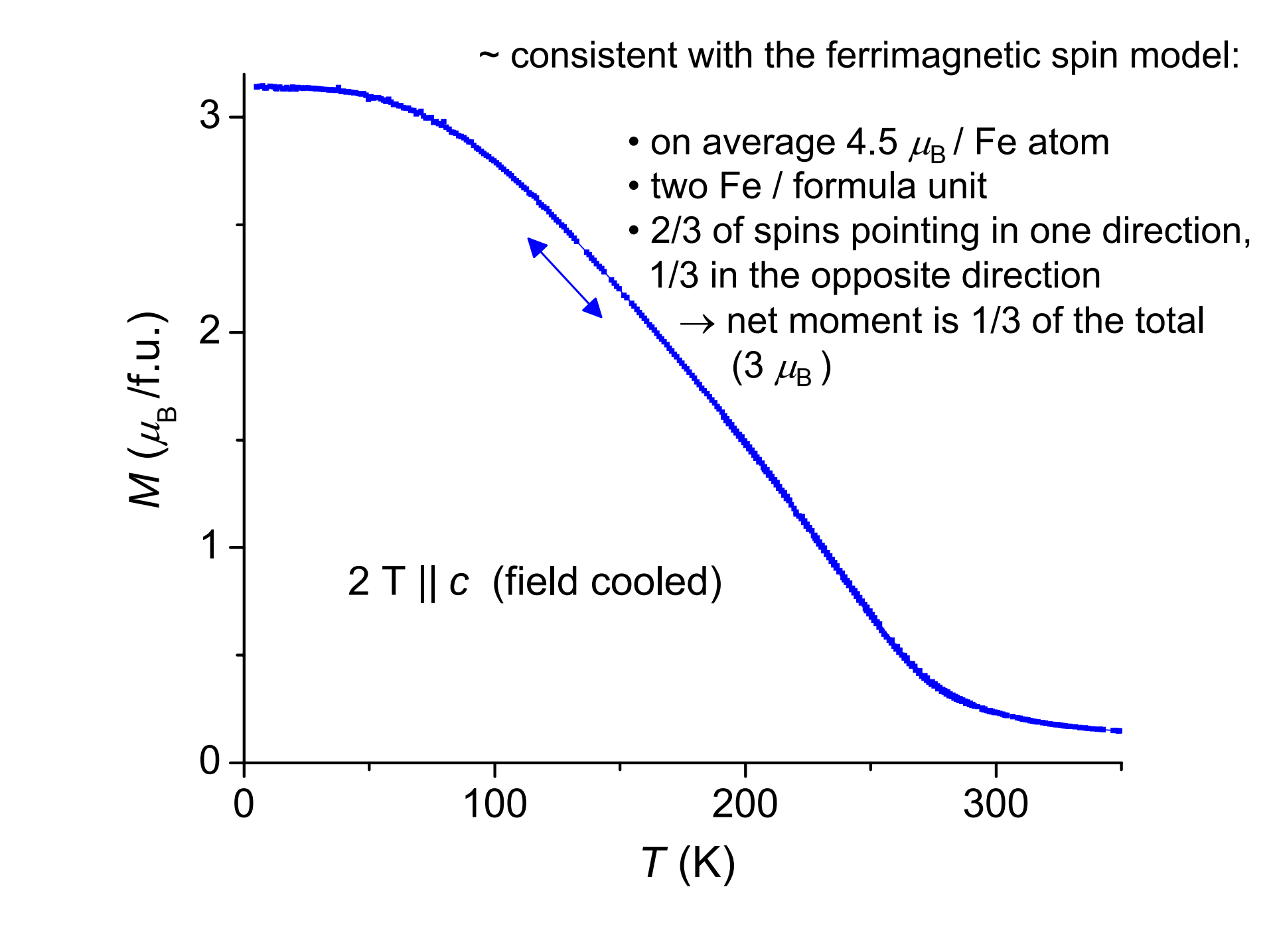


- Peaks at Integer L are purely magnetic while peaks at ½ integer L are related to both the charge order and magnetic order.
- The magnetic contribution to the L=1/2 integer peaks arises solely due to the charge order.

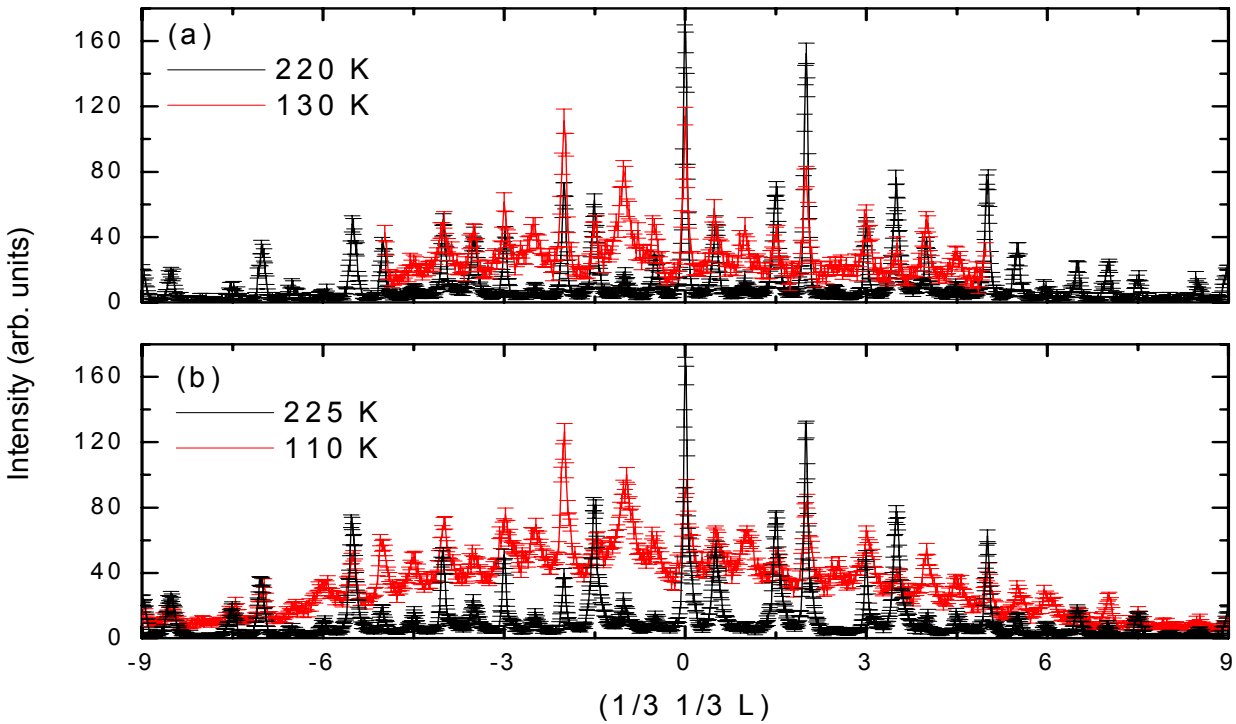
Magnetic Structure of $LuFe_2O_4$ at T = 220 K



- Spins point along c-axis
- Ordering wavevector (1/3, 1/3, 0)
- 3 symmetry equivalent mag. structures
- 2/3 moments point up, 1/3 down
- Consistent with magnetization

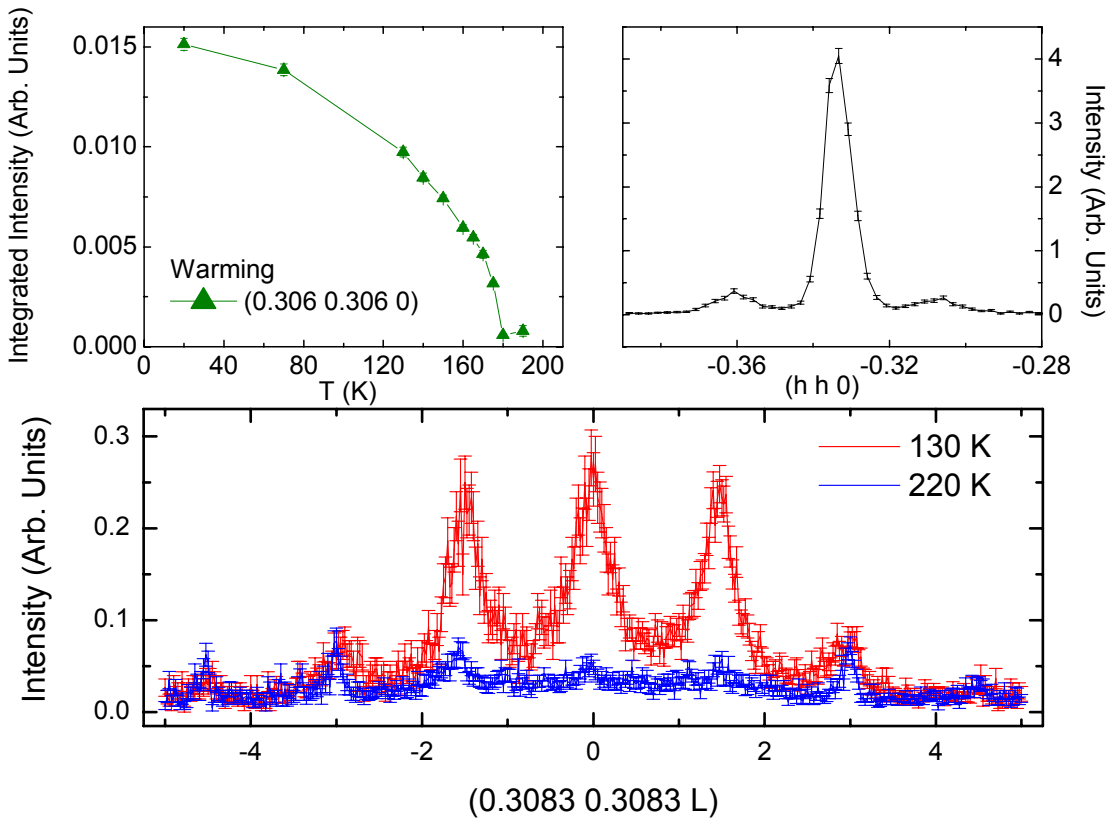

~ consistent with the ferrimagnetic spin model:
• on average 4.5 μ_B / Fe atom
• two Fe / formula unit
• 2/3 of spins pointing in one direction, 1/3 in the opposite direction
→ net moment is 1/3 of the total (3 μ_B)
2 T || c (field cooled)
M (μ_B/f.u.)
T (K)
0
1
2
3
0
100
200
300

180 K Transition



- Significant broadening occurs in magnetic peaks below 180 K.
- A 2D component to the scattering becomes easily observable below 180 K, however, this appears to be the remnants of unordered parts of the sample as this 2D diffuse scattering is stronger in samples with worse oxygen stoichiometry (comparison above). This is consistent with the old work which shows only 2D scattering.

Low Temperature Satellites

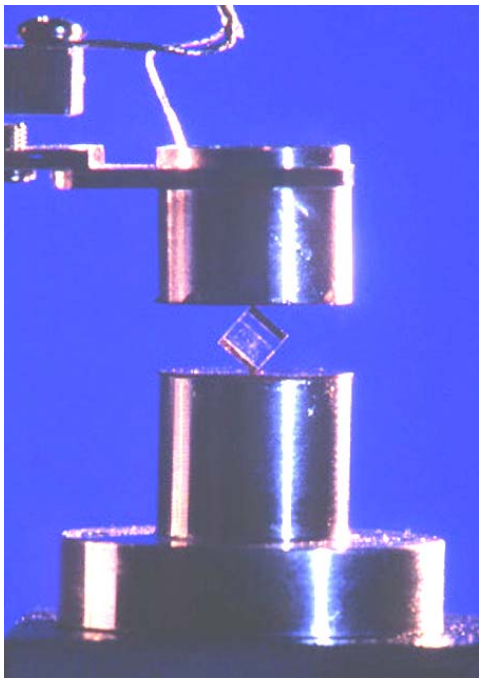


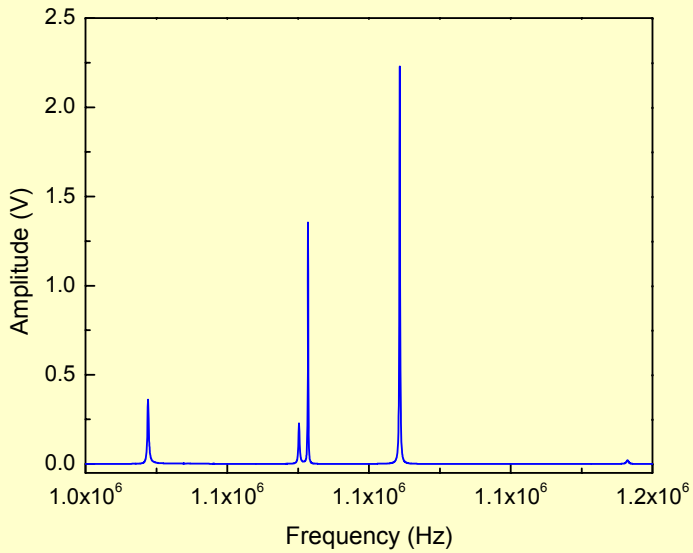
- New satellites appear below 180 K. At present the origin is unknown, however they appear to not be magnetic in origin.

Veerle Keppens

advantages of RUS: all elastic constants can be obtained in one measurement

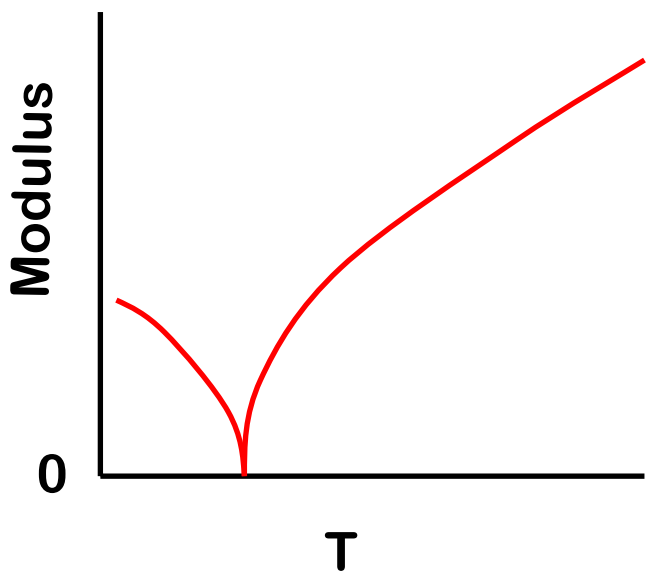
small samples (mm^3)





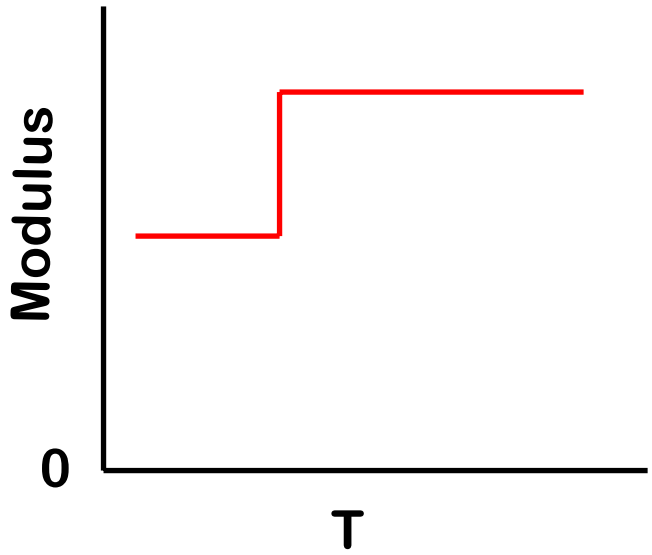
Strain-Order Parameter Coupling at Phase Transitions

Bi-Linear coupling:
$F_c = \beta Q \varepsilon$



$$c = c^0 - \frac{a}{T - \theta}$$

Quadratic coupling:
$F_c = \beta Q^2 \varepsilon$



$$c = c^0 \qquad T > T_c$$

$$c = c^0 - \frac{2h^2}{\beta} \qquad T < T_c$$

Magnetite Displays Bi-Linear Coupling at Verwey Transition

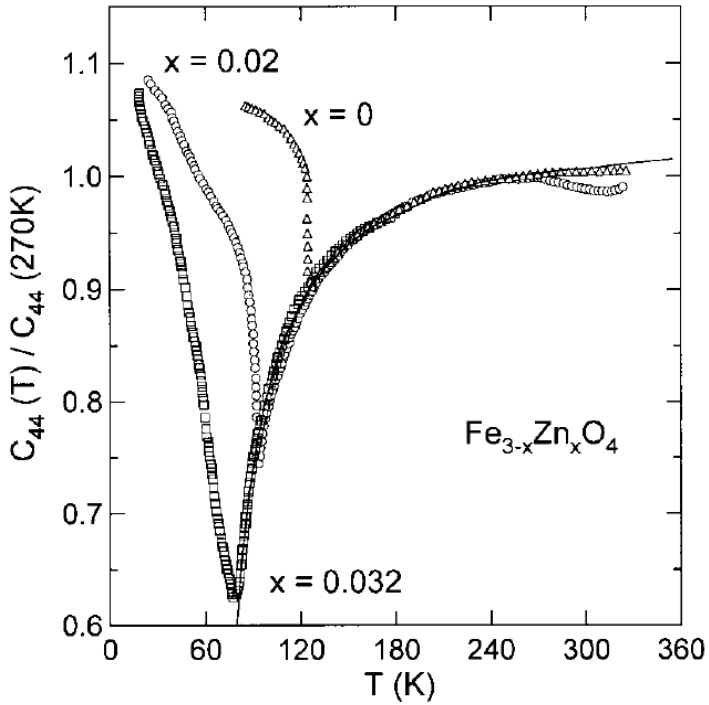
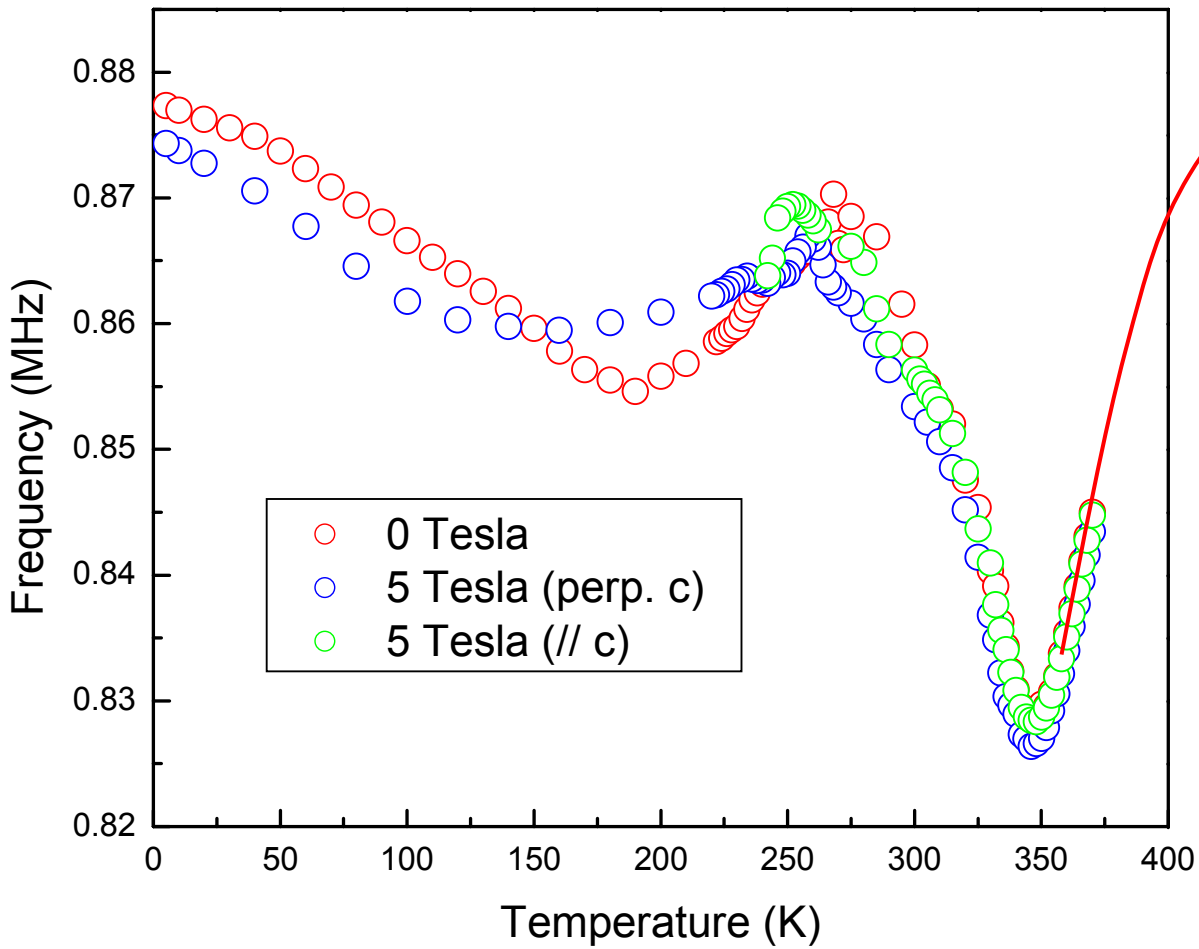


Figure 10. Normalized soft modes $c_{44}(T)/c_{44}(270\,\mathrm{K})$ for the $Fe_{3-x}Zn_xO_4$ ($x = 0$, 0.02 and 0.032) crystals together with a fit (———) discussed in the text.

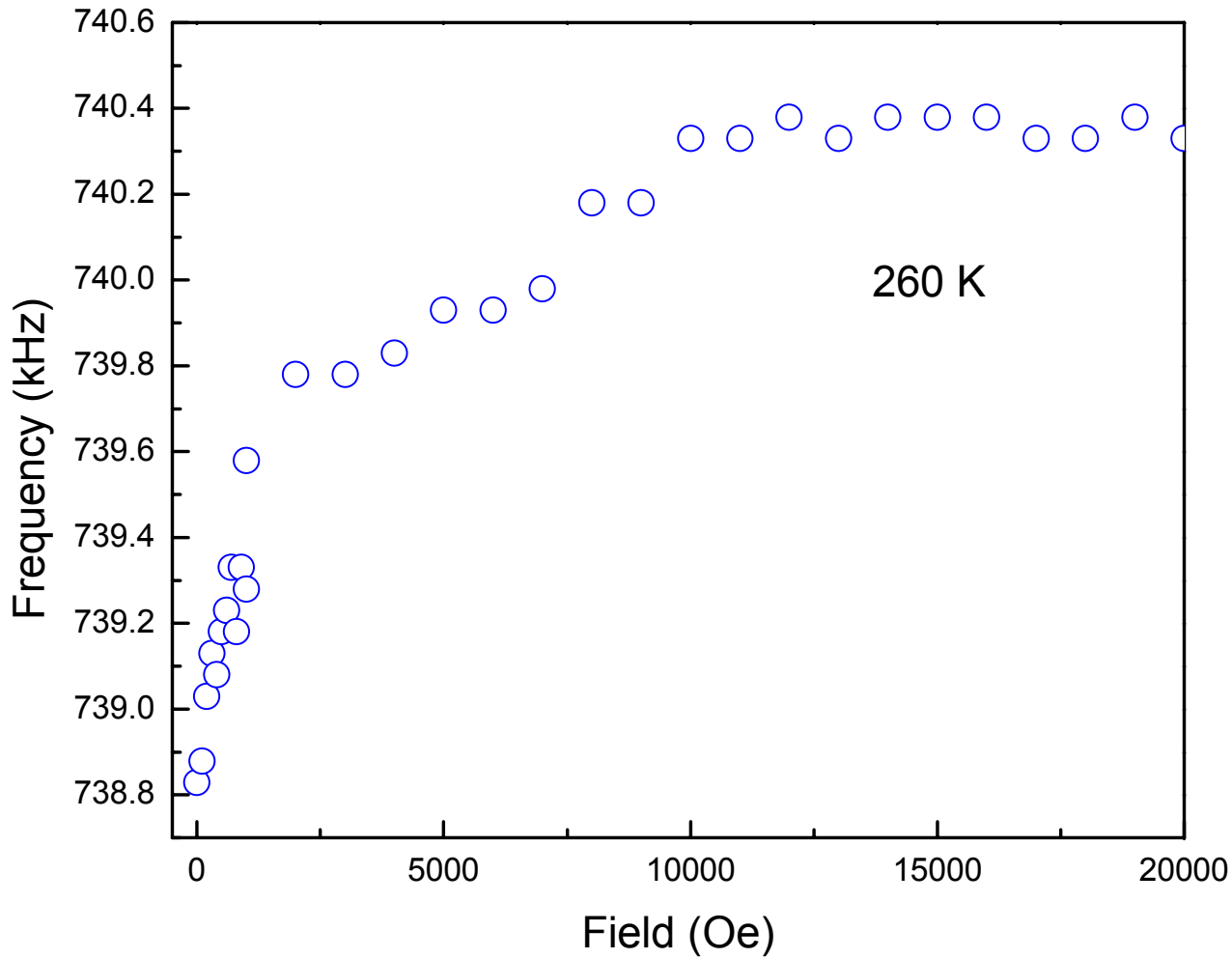
Schwenk et al., Eur. Phys. J. B **13**, 491 (2000)

Elastic strain induced by the ultrasonic wave couples to the charge fluctuation modes

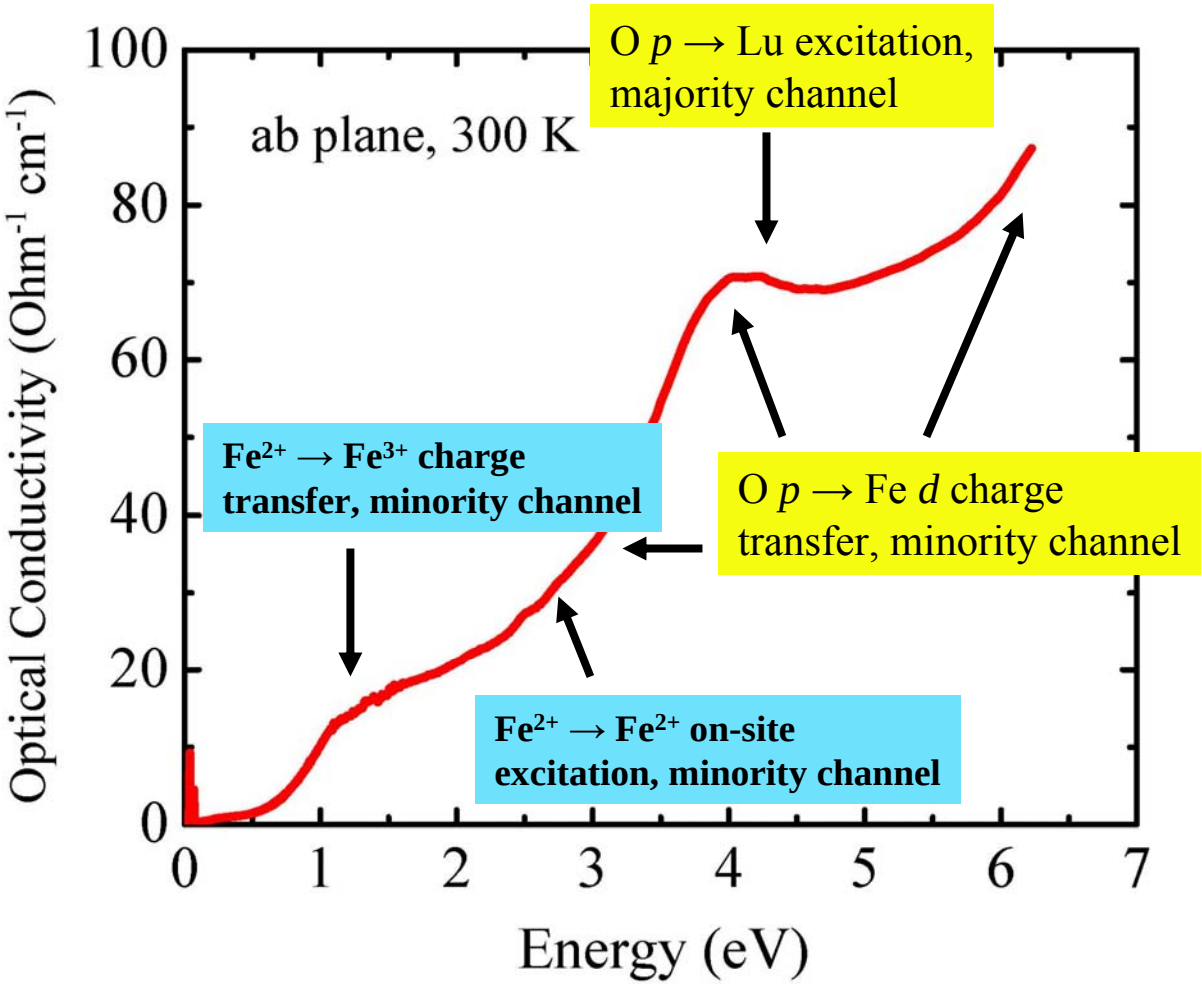
$LuFe_2O_4$ RUS Measurements in Magnetic Field

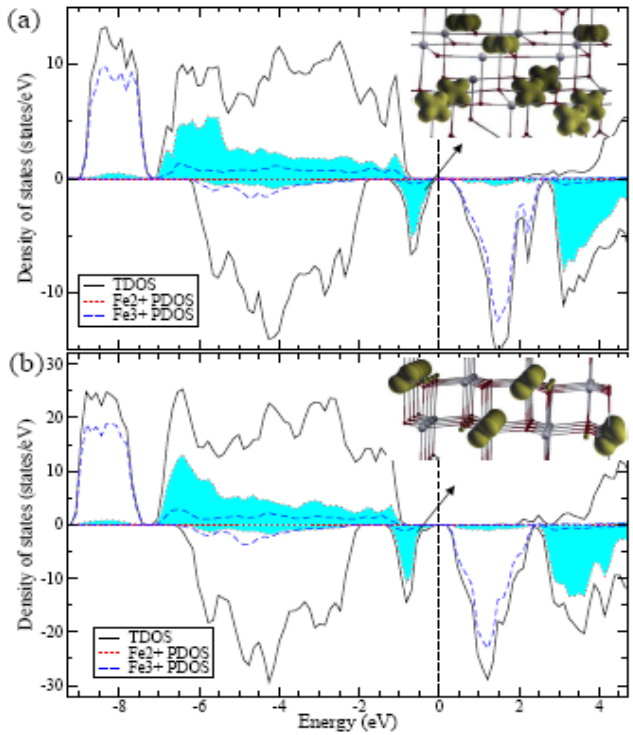


RUS Measurements in Magnetic Field



Optical Properties of $LuFe_2O_4$: Musfeldt Group, University of Tennessee

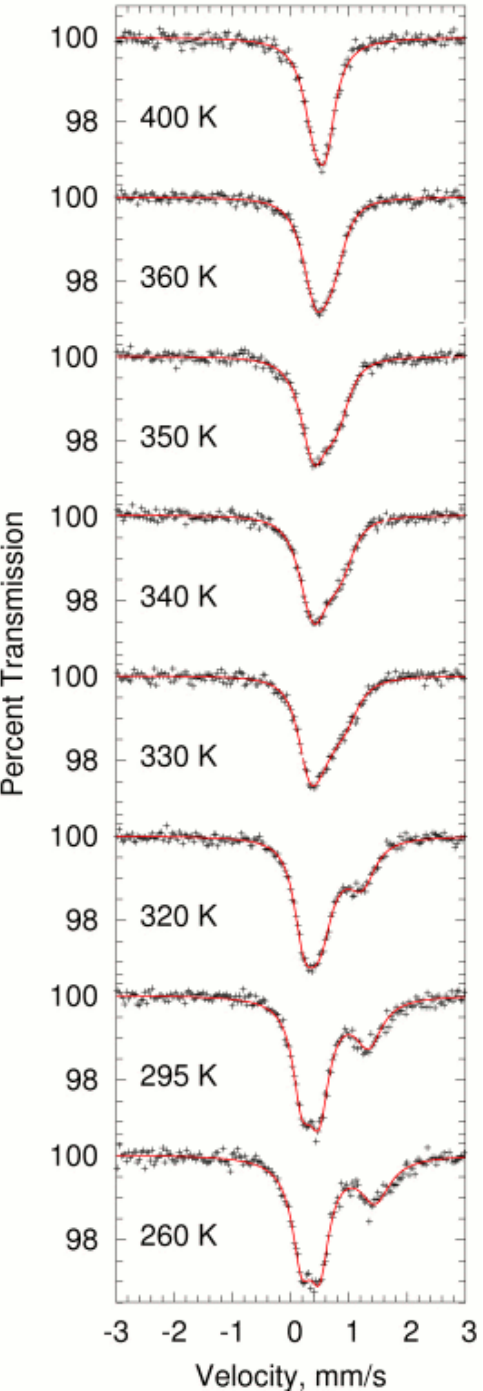


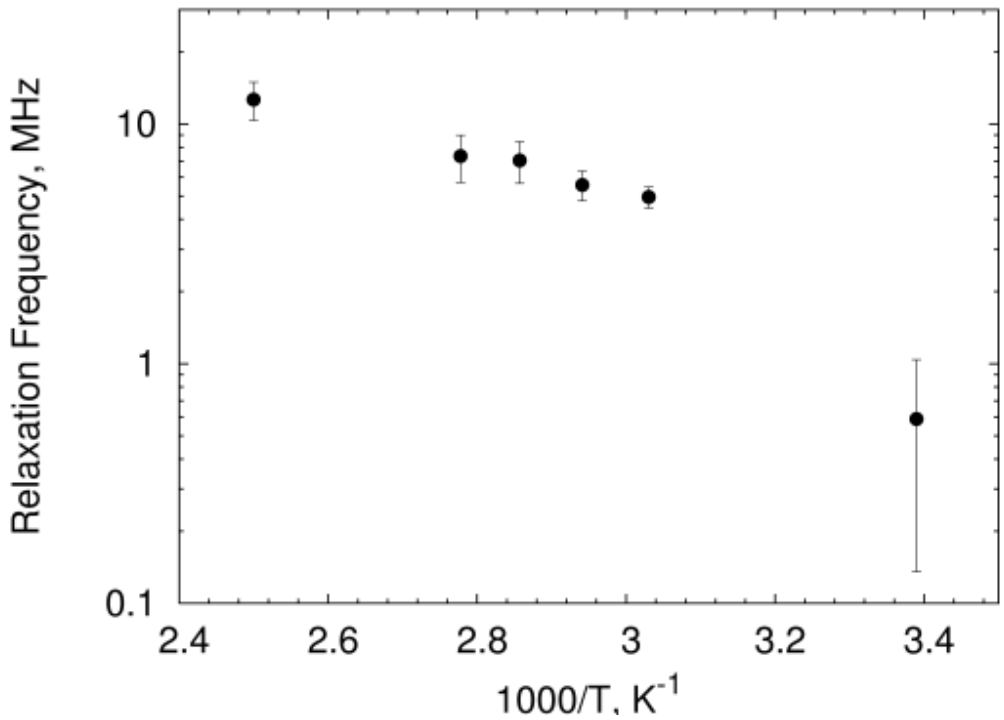


Xiang and Whangbo, PRL (2007)

- Optical properties are dominated by excitations in the minority spin channel
- √3 x √3 and chain structures have similar density of states pictures. Possibility of extracting domain distribution information via temperature dependence of 1.5 eV excitation.
- Magneto-optical work in progress.

Mössbauer Spectroscopy (R. Hermann)





Assuming 50% Fe^{2+} and 50% Fe^{3+} is compatible with the spectra.

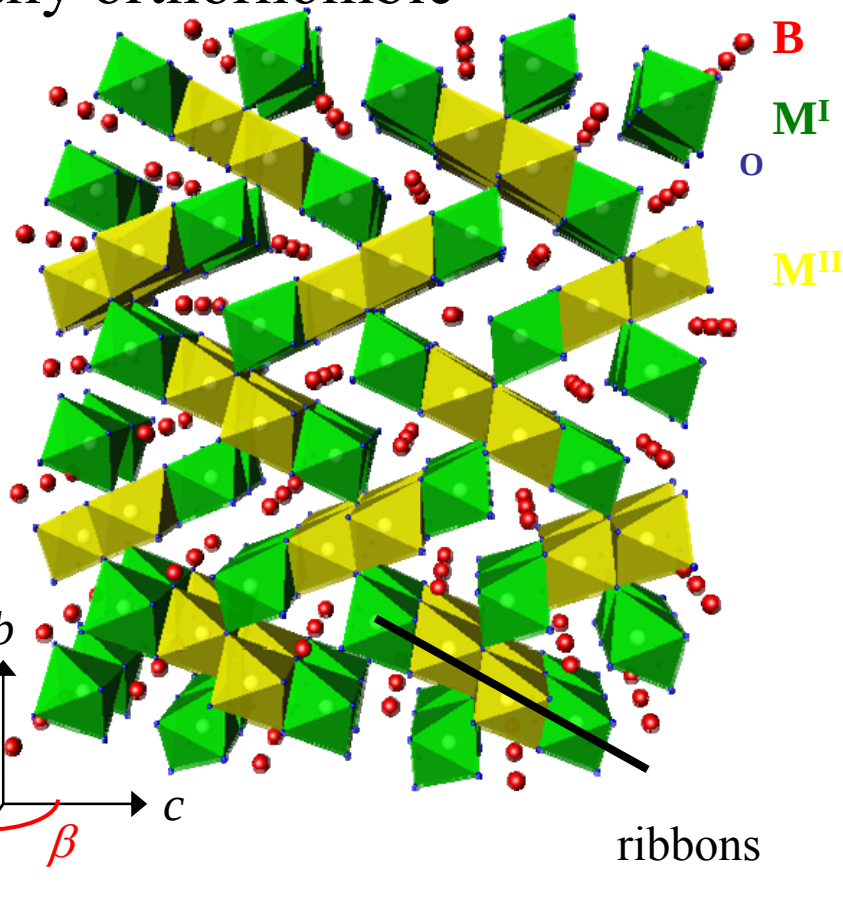
Upon heating, the charge order vanishes with an increase in the electron hopping frequency.

Below 260 K the hopping is slower than resolvable, ie than 0.1 MHz.

Fe_2OBO_3

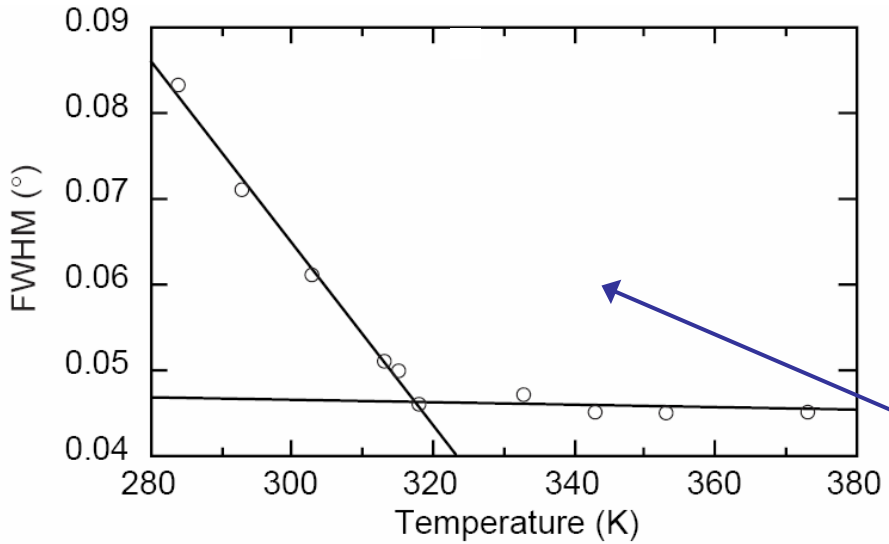
Warwickite type $M^{I}M`^{II}OBO_3$ usually orthorhombic

Two structurally distinct metal sites with octahedral coordination (**I**, **II**)



Fe_2OBO_3

→ monoclinic distortion below 317 K



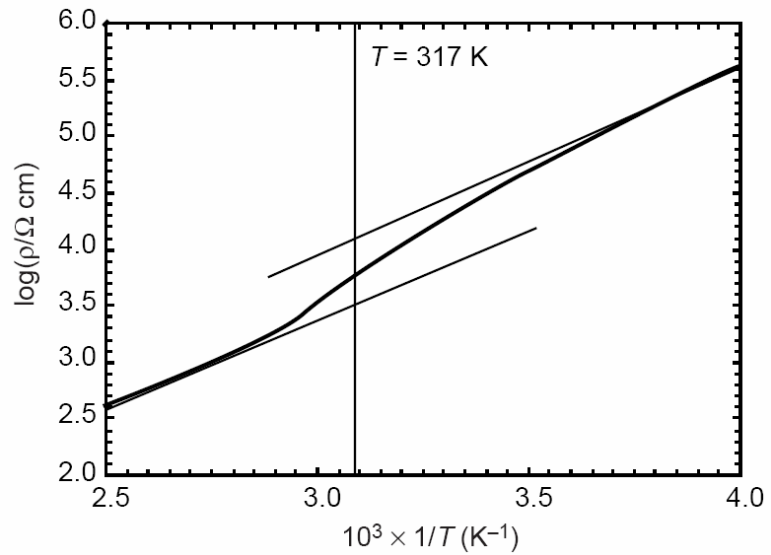
[Attfield *et al.*, Nature **396**, 655 (1998)]

Half-width of the combined monoclinically split (102)/(–102) doublet

Fe_2OBO_3

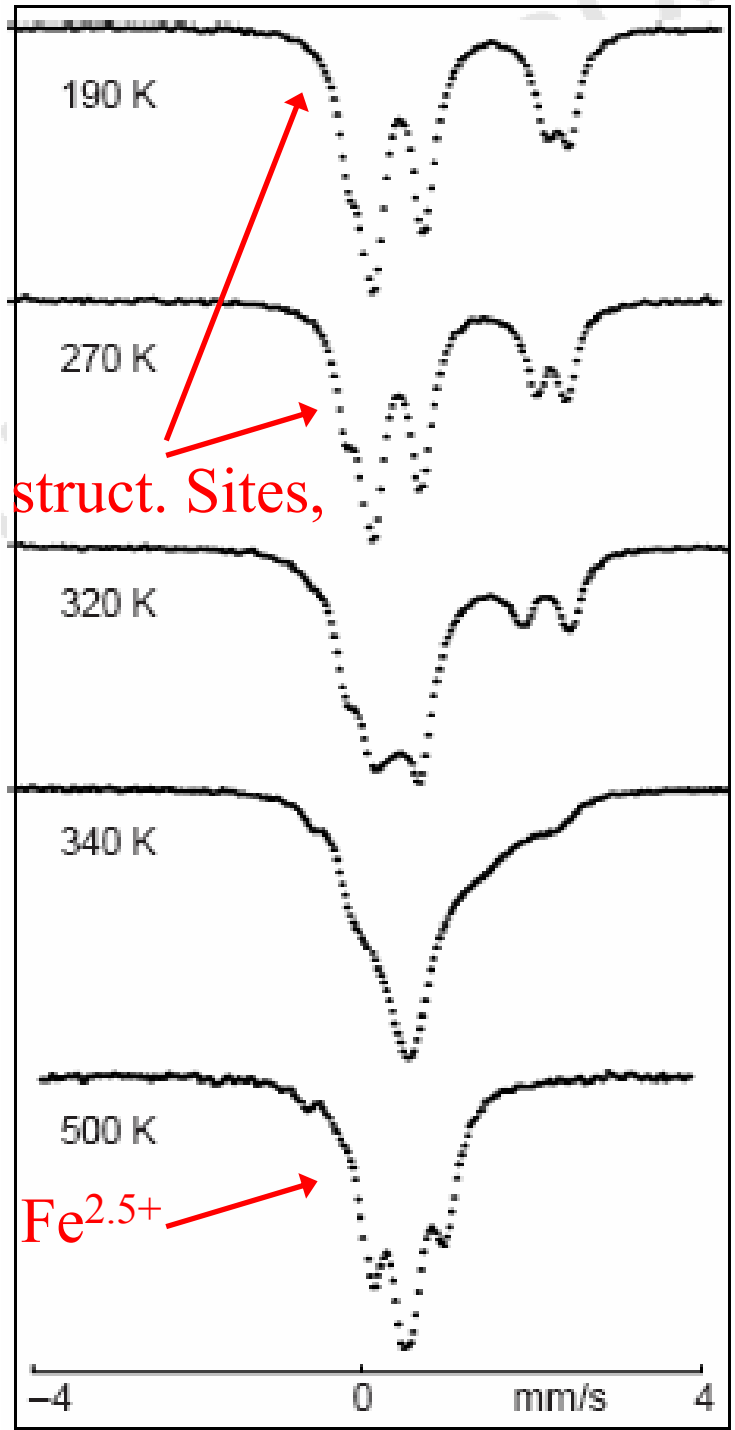
Charge order surmised based on Mössbauer spectroscopy and resitivity:

Four doublets assigned to Fe^{2+}/Fe^{3+} on two struct. Sites, no discernible hopping



Rapid hopping on two structural sites: $Fe^{2.5+}$

[Attfield *et al.*, Nature **396**, 655 (1998)]

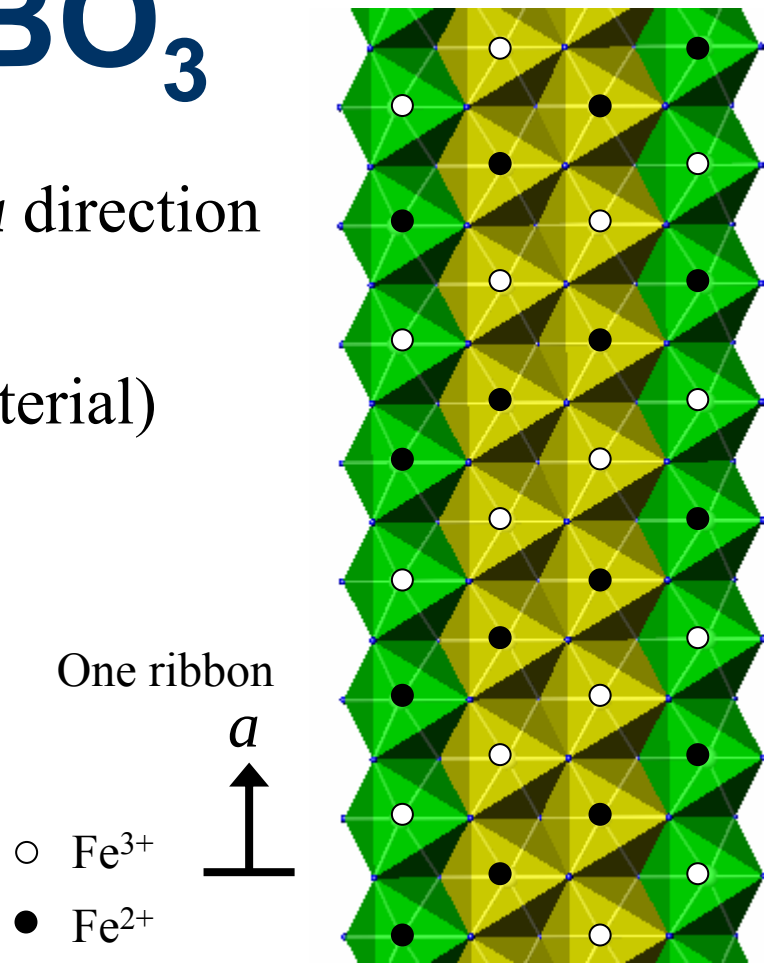


Fe_2OBO_3

Should lead to unit cell doubling in ***a*** direction
[weak (*h*+0.5 *k* *l*) reflections]

not observed (on polycrystalline material)

- No superstructure observed &
- Resistivity feature associated with CO very broad



possible charge order model
[Attfield *et al.*, Nature **396**, 655 (1998)]

→ Single-crystal study highly desirable

Single crystals of Fe_2OBO_3

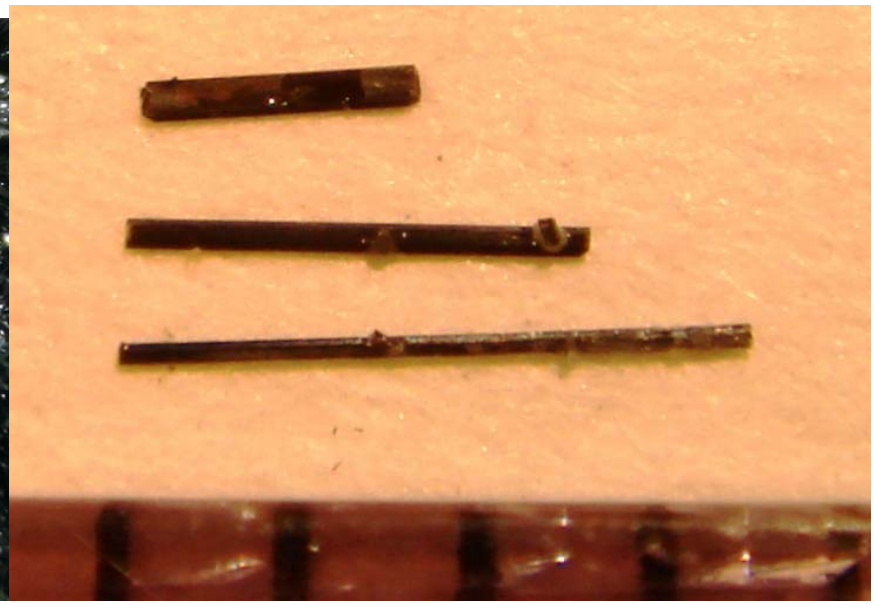
Try flux growth in Fe – B – O system

Starting point : growing $FeBO_3$ from

$Fe_2O_3 – B_2O_3 – PbO – PbF_2$ flux

[following Kotrobova *et al.*,
J. Crystal Growth **71**, 607 (1985)]

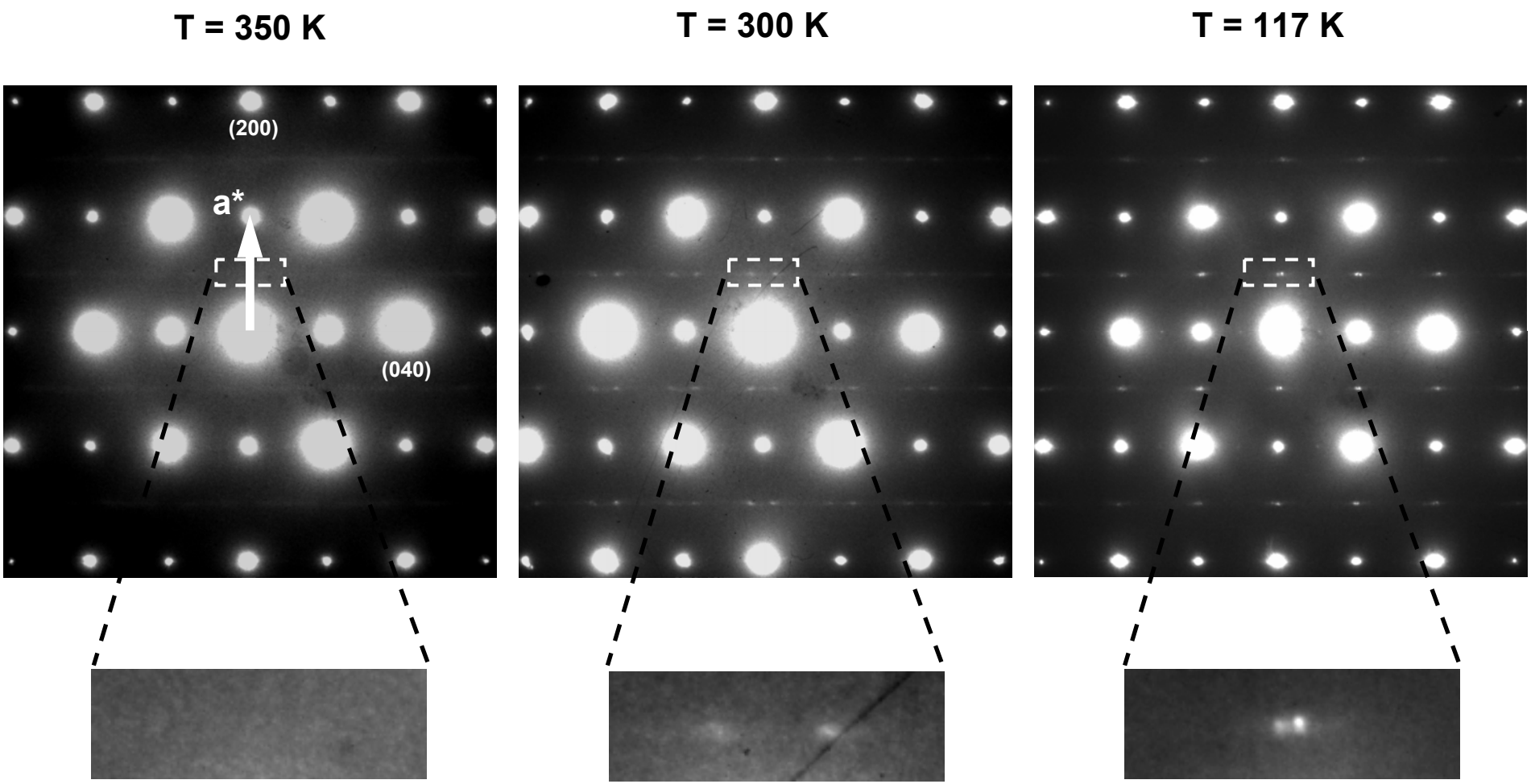
Then tune growth parameters to favor crystallisation of Fe_2OBO_3



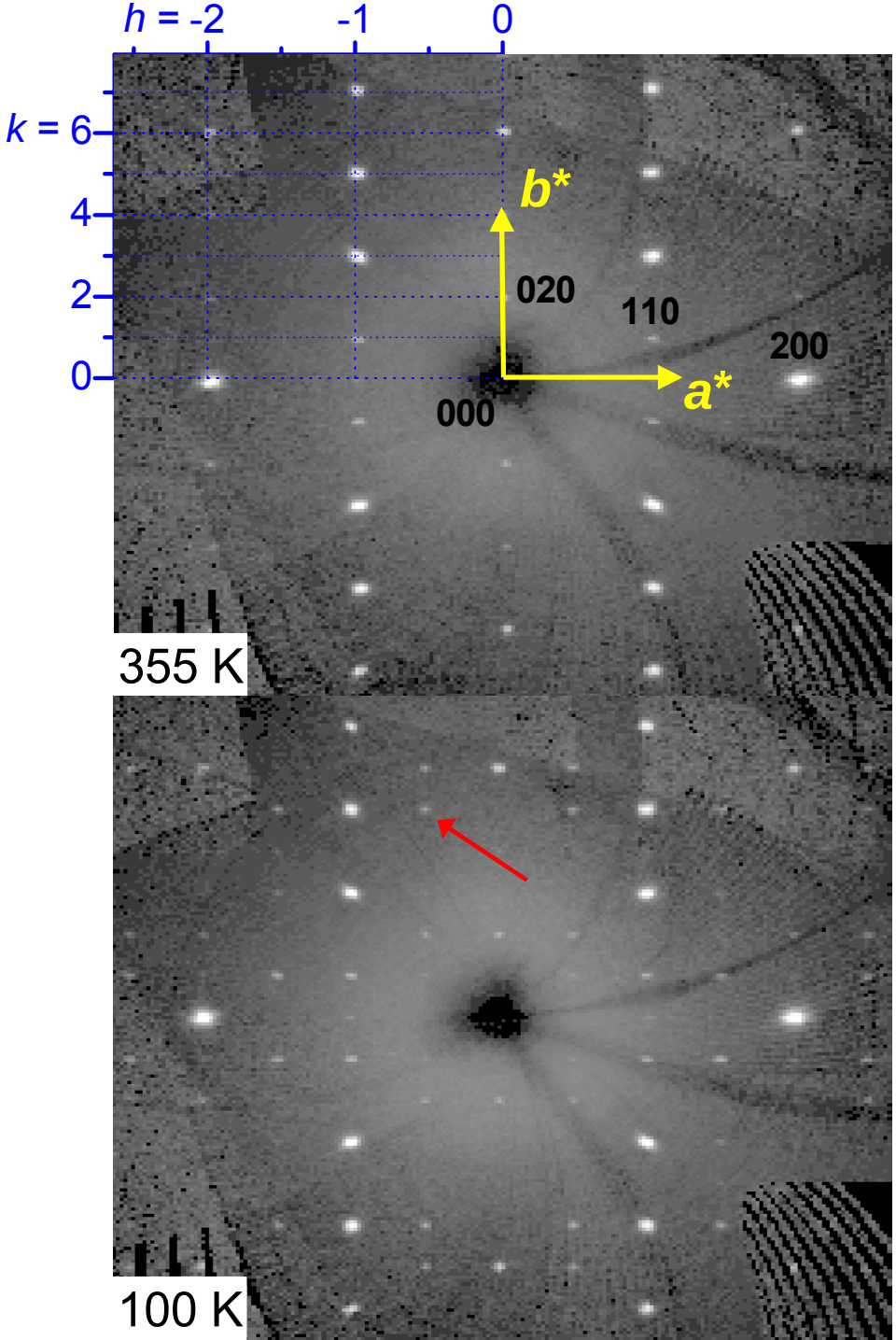
Fe_2OBO_3 crystallised as **thin needles** (||*a*) of weight **up to ~1 mg**

Phase confirmed by powder x-ray diffraction (and various phys. propert.)

Fe_2OBO_3 : electron diffraction ([001] zone)

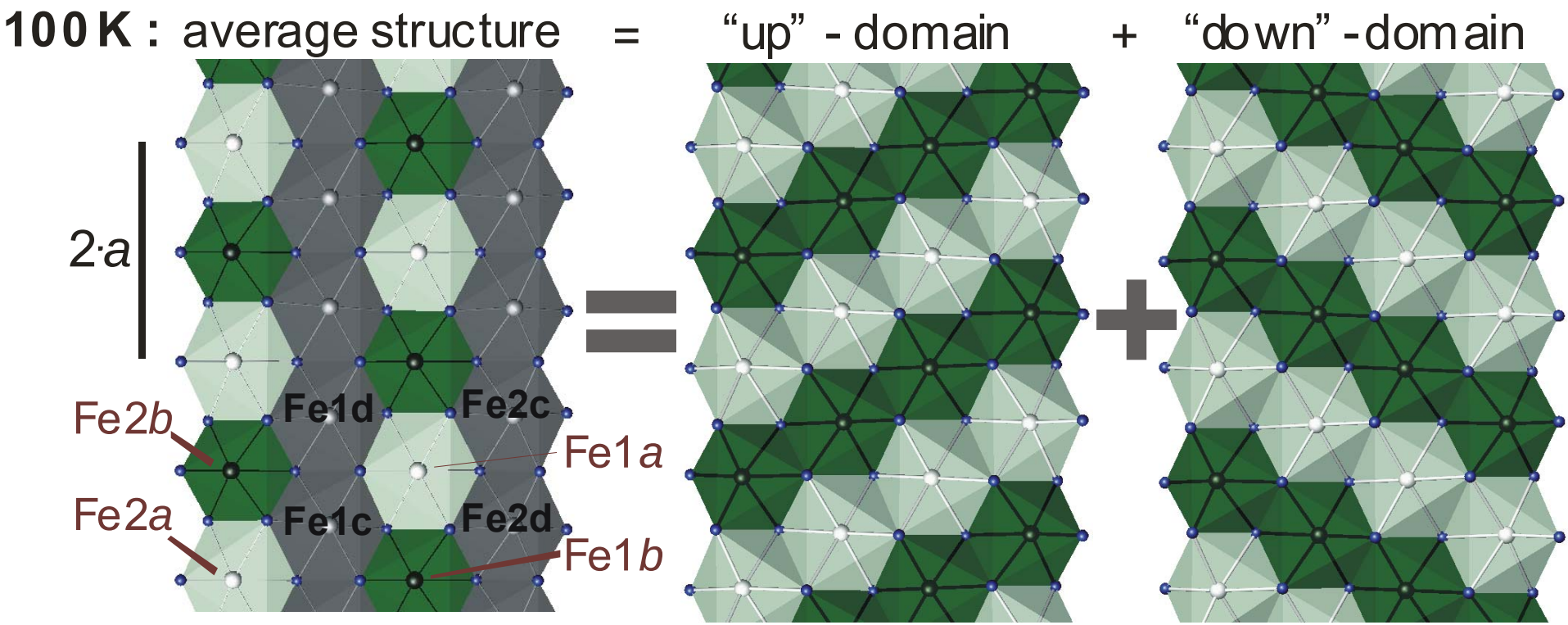


Experiments performed by Jing Tao on Urbana TEM

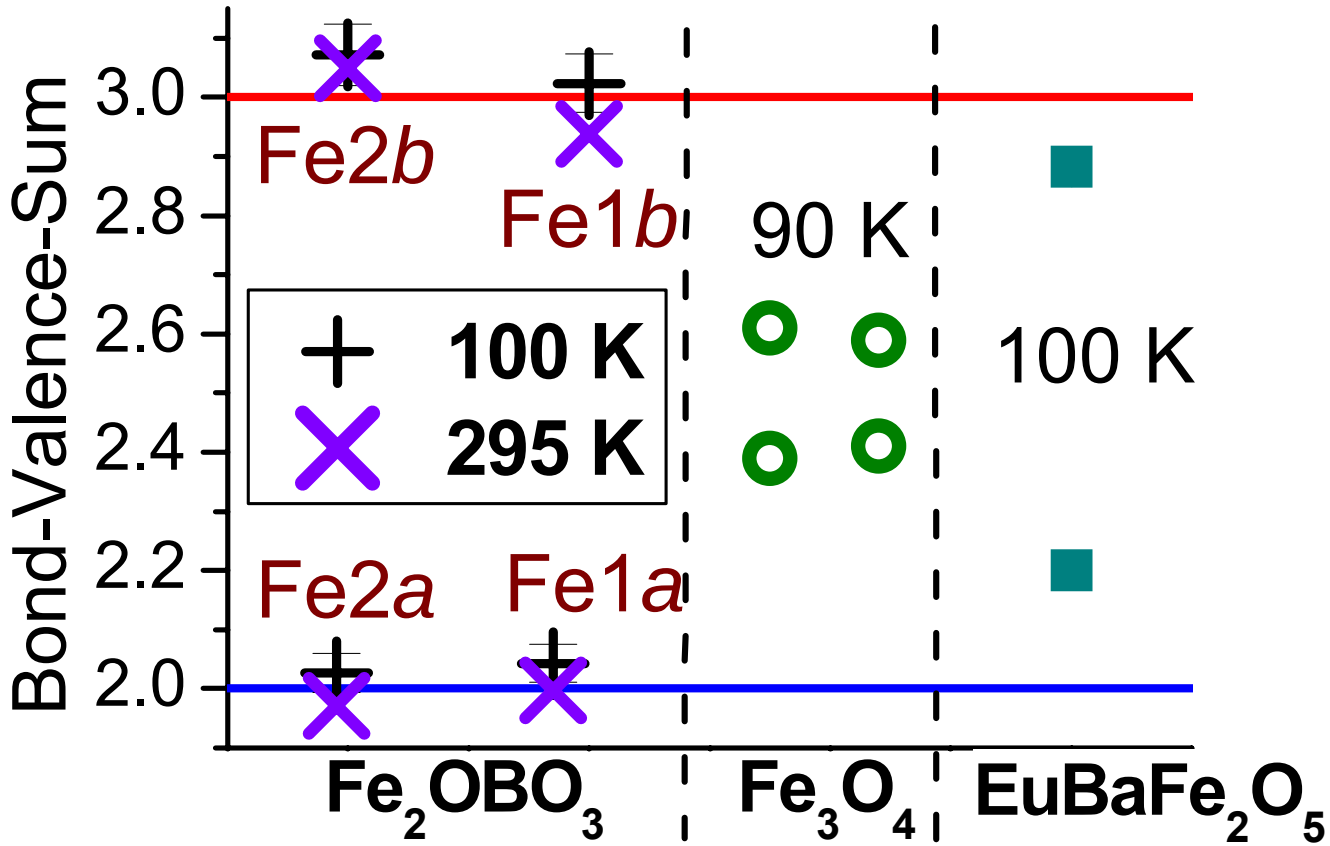


X-ray diffraction:
Doubling of unit cell
along a at low *T*

Structure refinement



Fe_2OBO_3 seems best example so far of ionic charge order



"…the inductive effect of the antagonistic bond…"

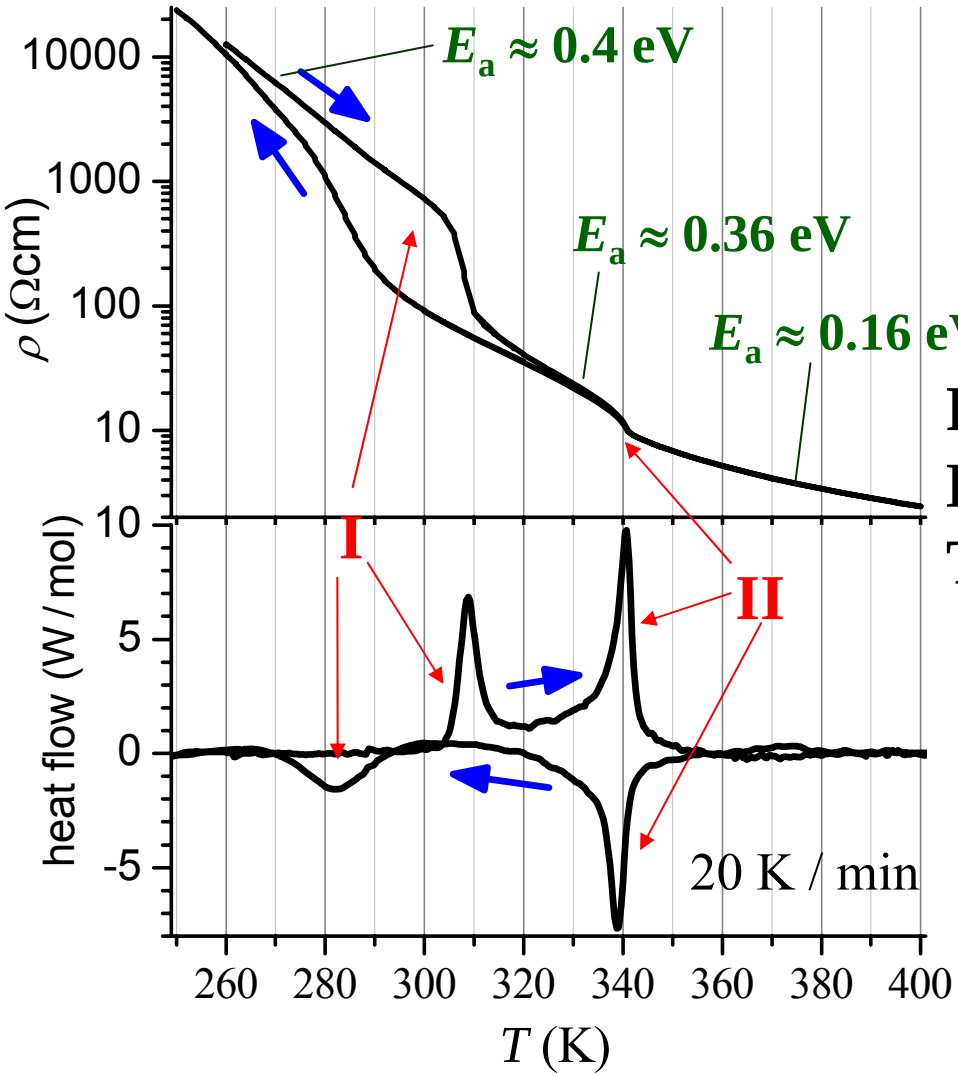
F. Menil, J. Phys. Chem. Solids 46, 763 (1985)

From Art Sleight:

In $EuBaFe_2O_5$, the impact of the Eu and Ba would be to increase Fe-O covalency relative to Fe_3O_4. In Fe_2OBO_3, the impact of B would be to increase ionicity relative to Fe_3O_4. And I am convinced that it is this increased ionicity that gives basically the ideal values in Fe_2OBO_3.

Fe – O – T

Fe_2OBO_3 : intermediate phase

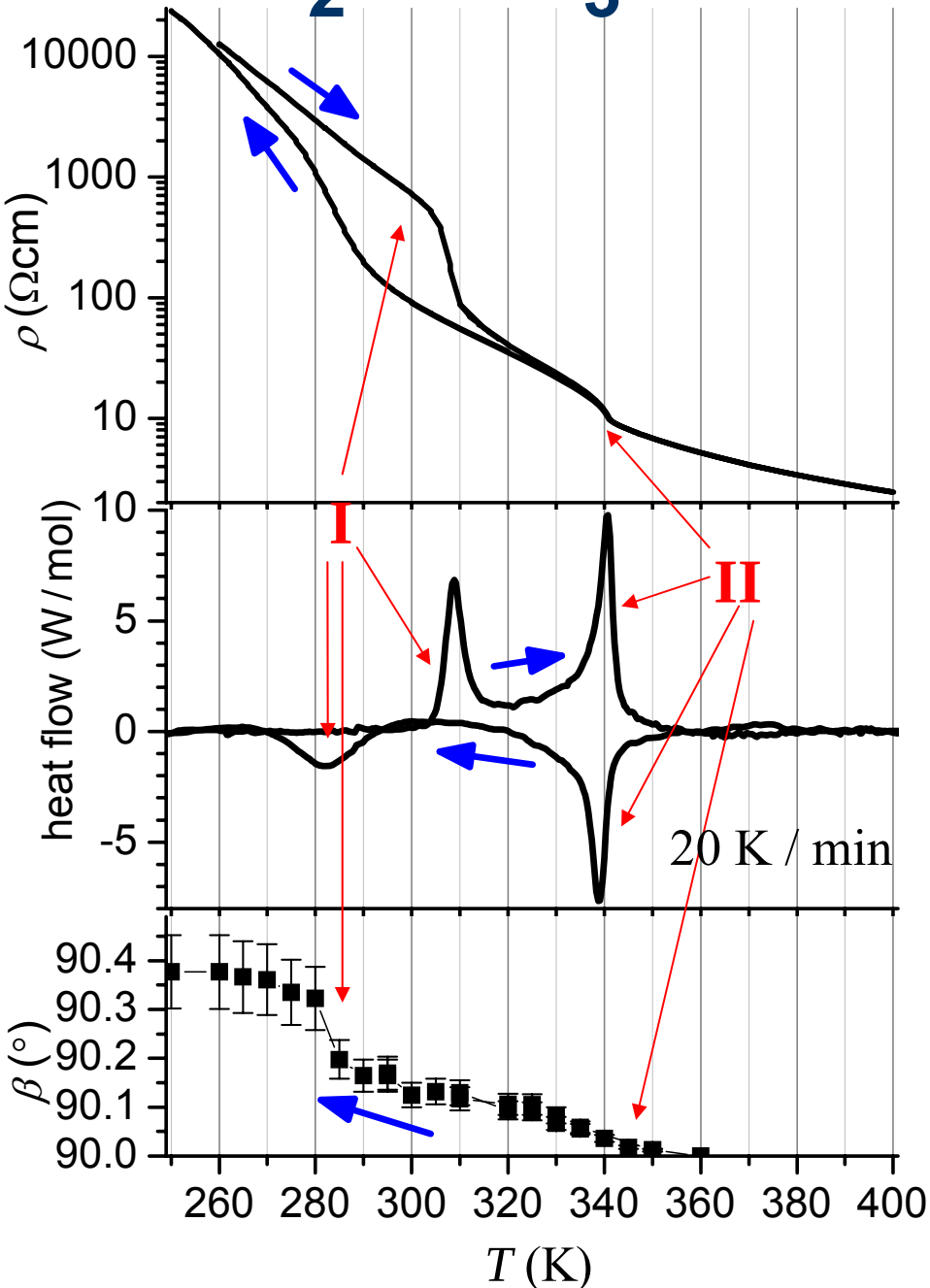


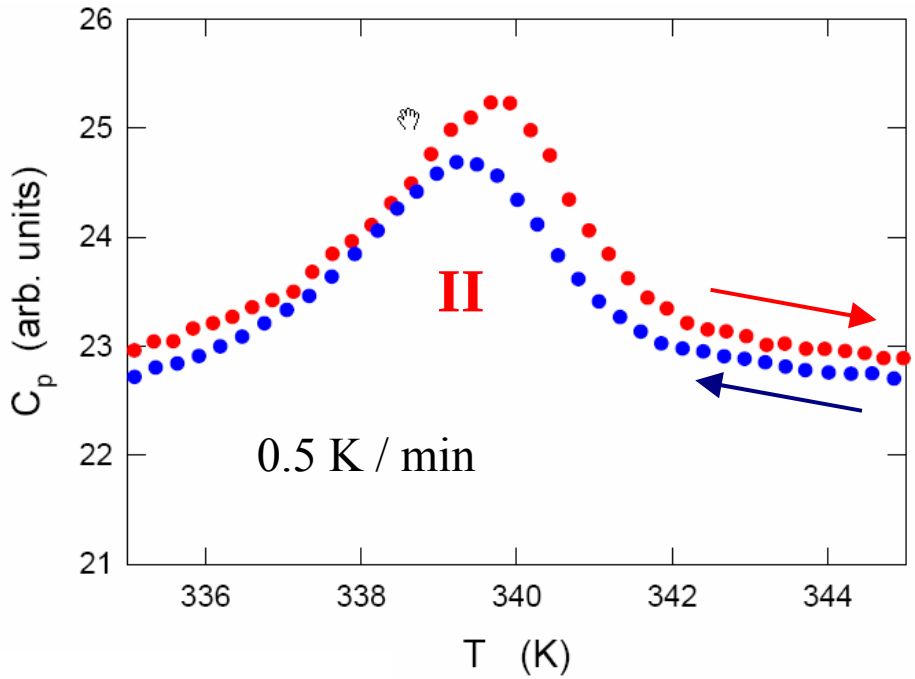
Activated transport :

$(\rho \propto e^{E_a/kT})$

Resistivity and
Differential scanning calorimetry :
Two phase transitions

Fe_2OBO_3 : intermediate phase



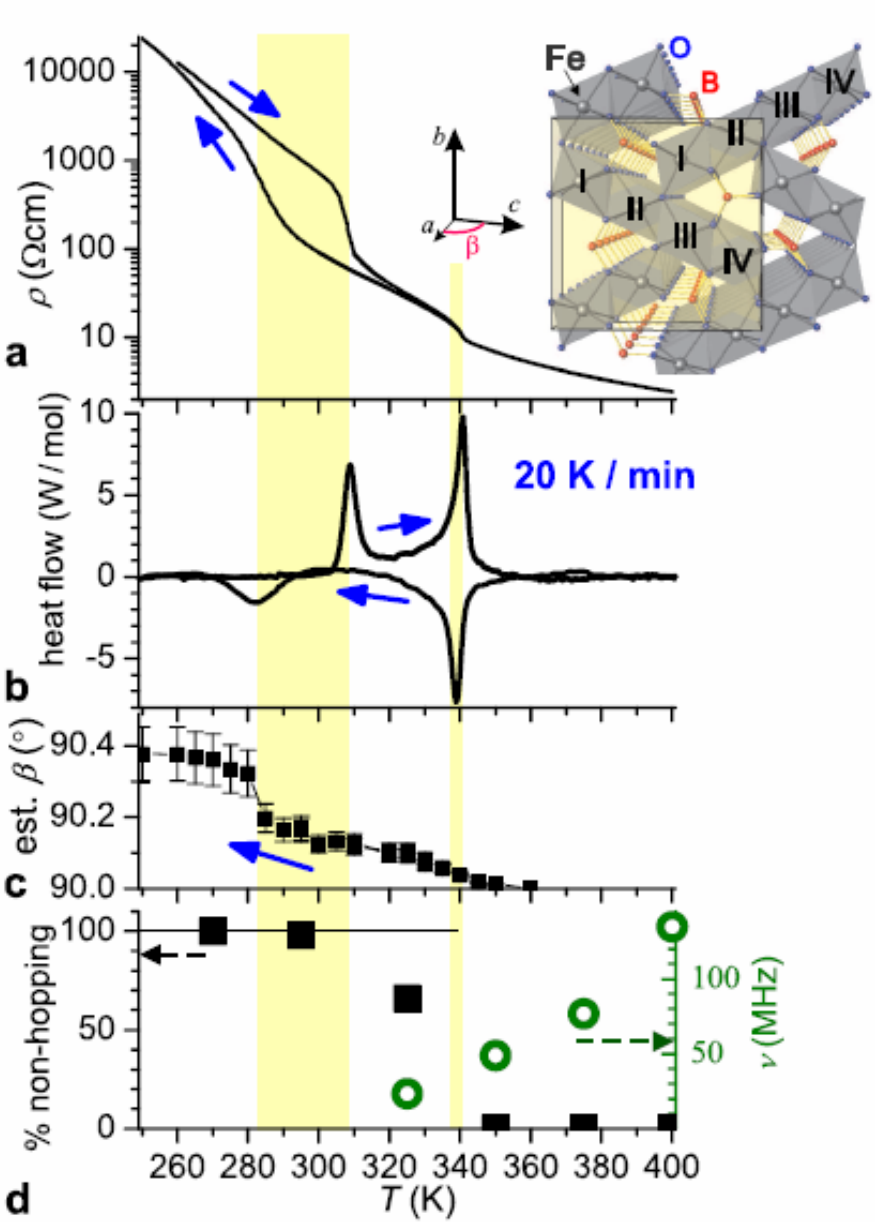


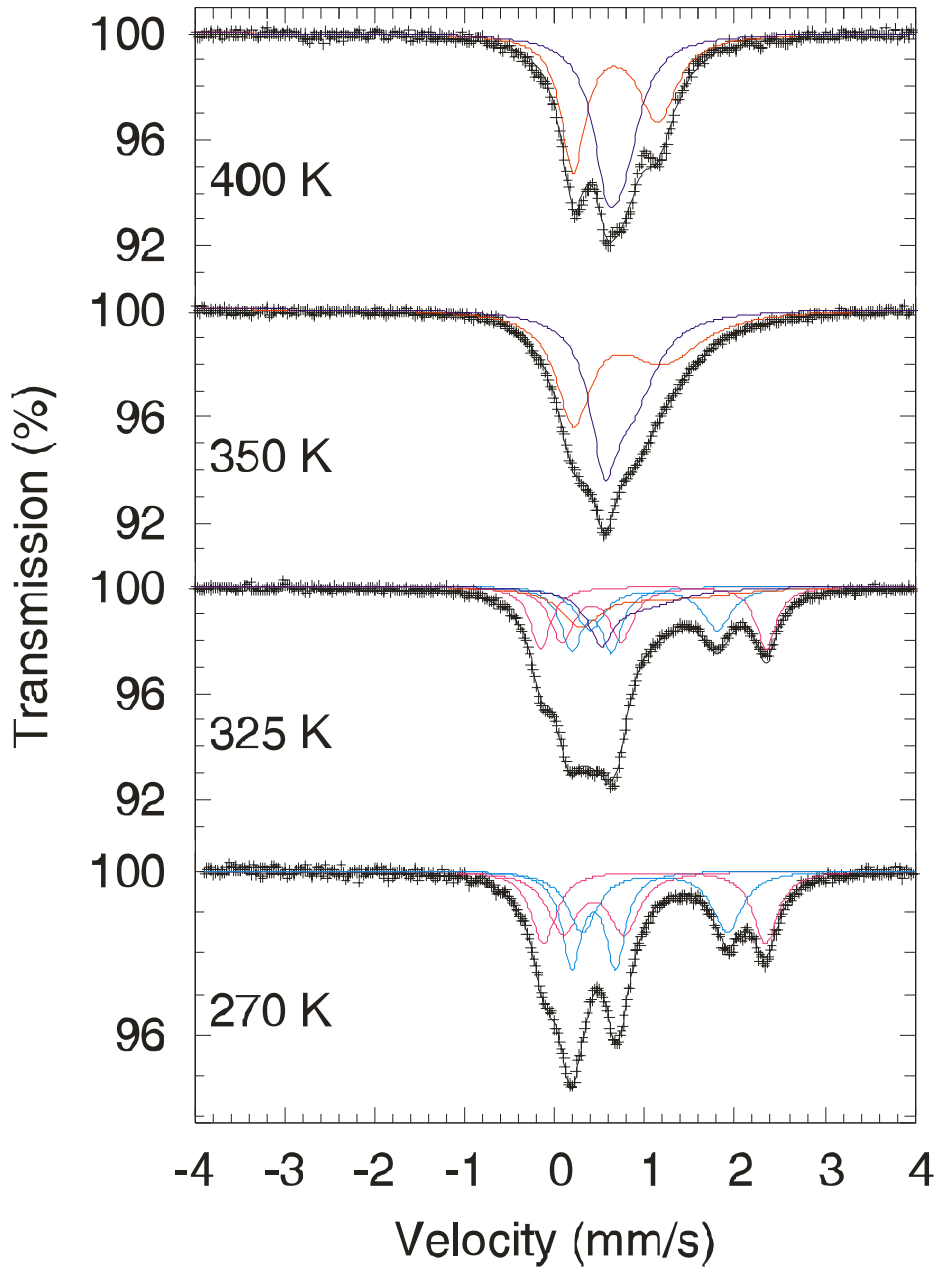
(Viji Varadarajan, Joe Brill, UK)

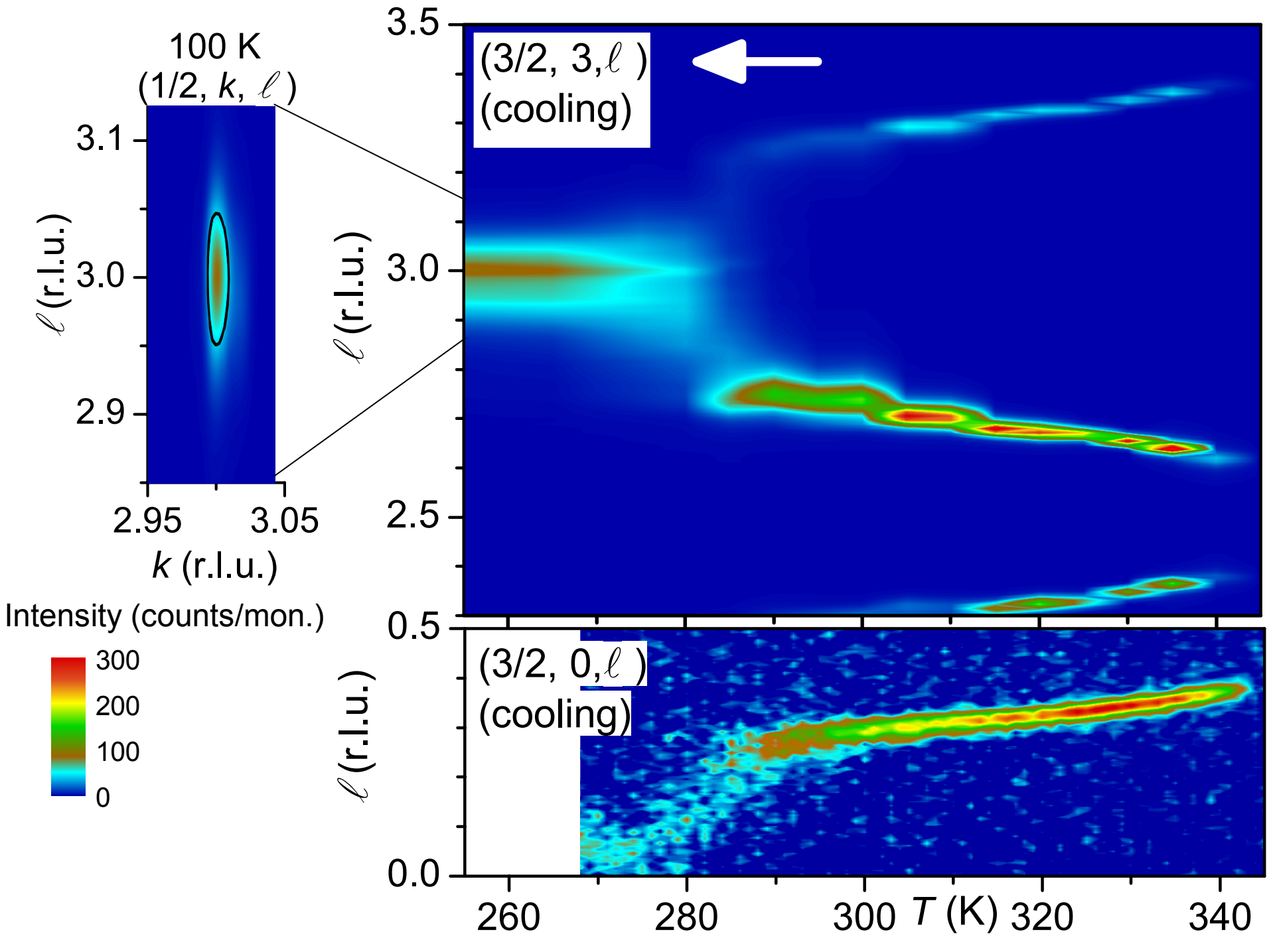
Hysteresis → **II** (weakly) first order too

Structurally, **II** is monoclinic-orthorhombic transition

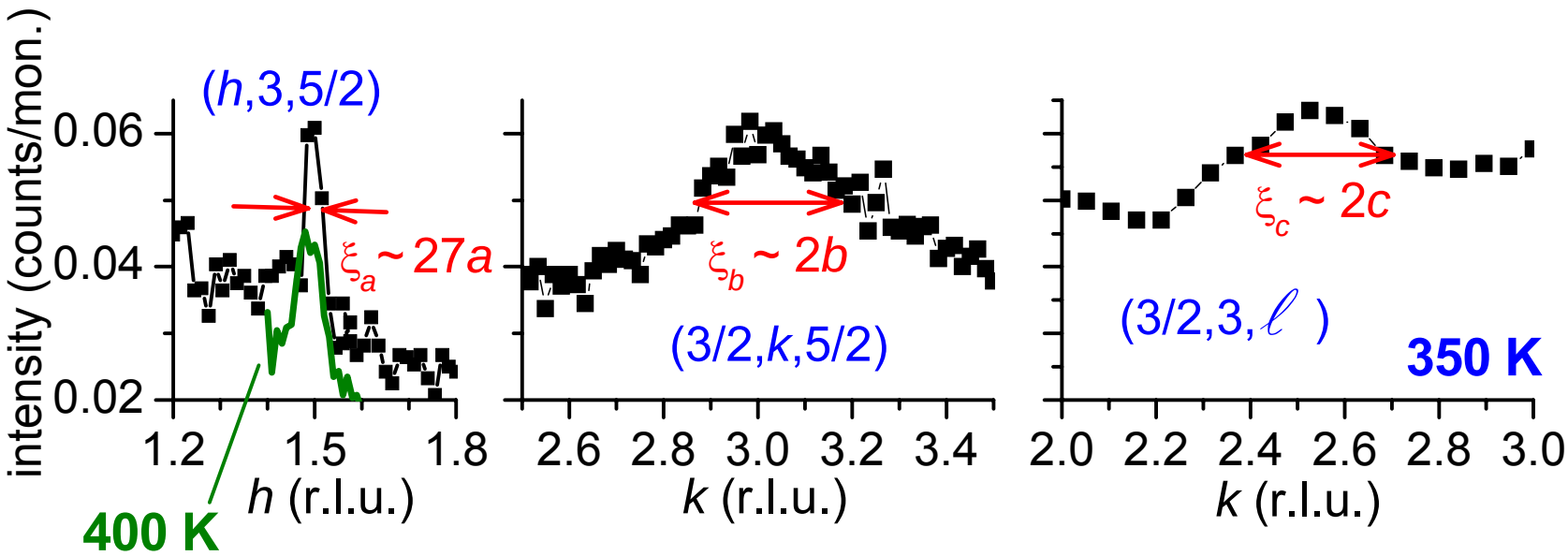
Fe_2OBO_3 : intermediate phase

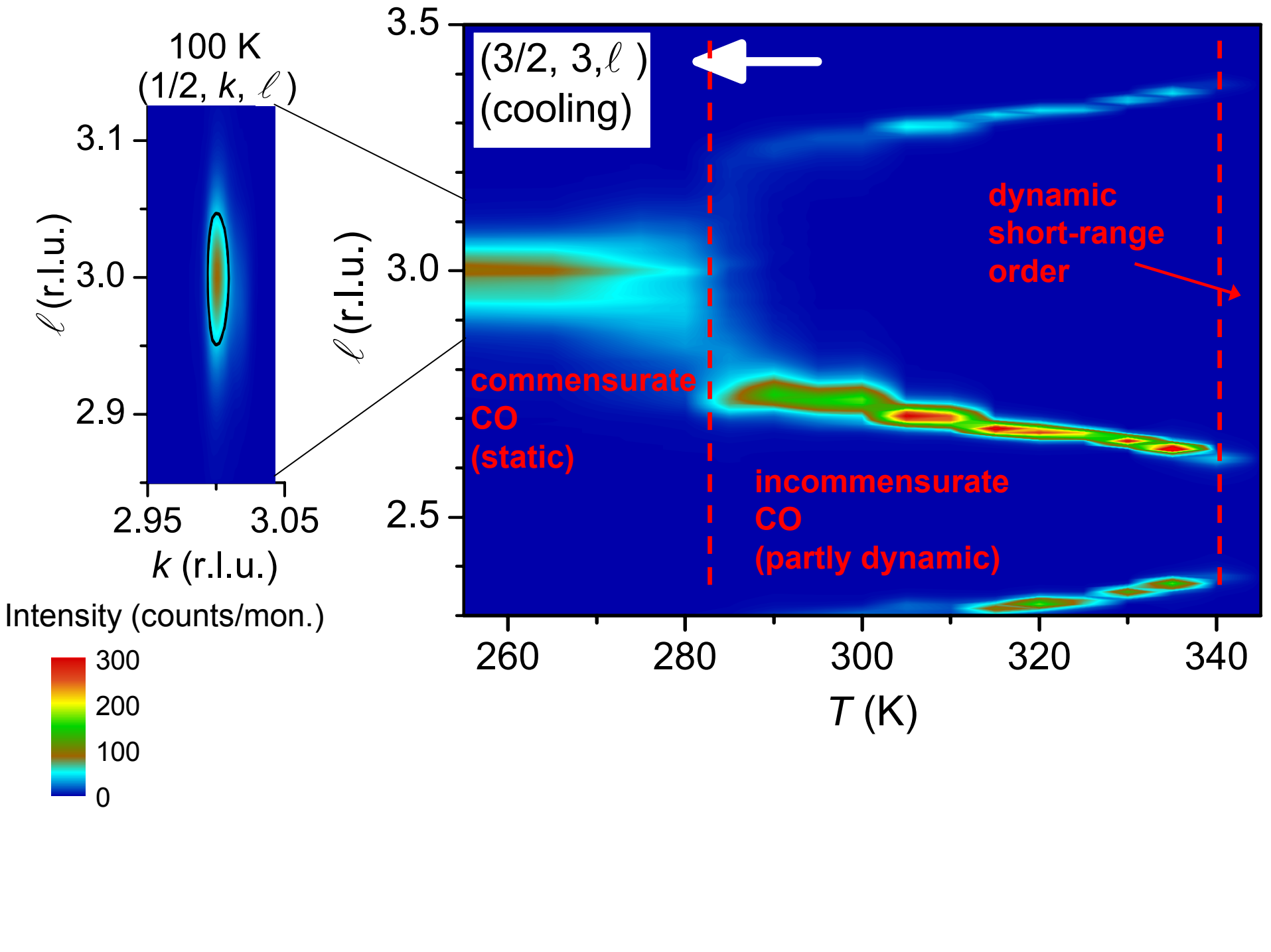




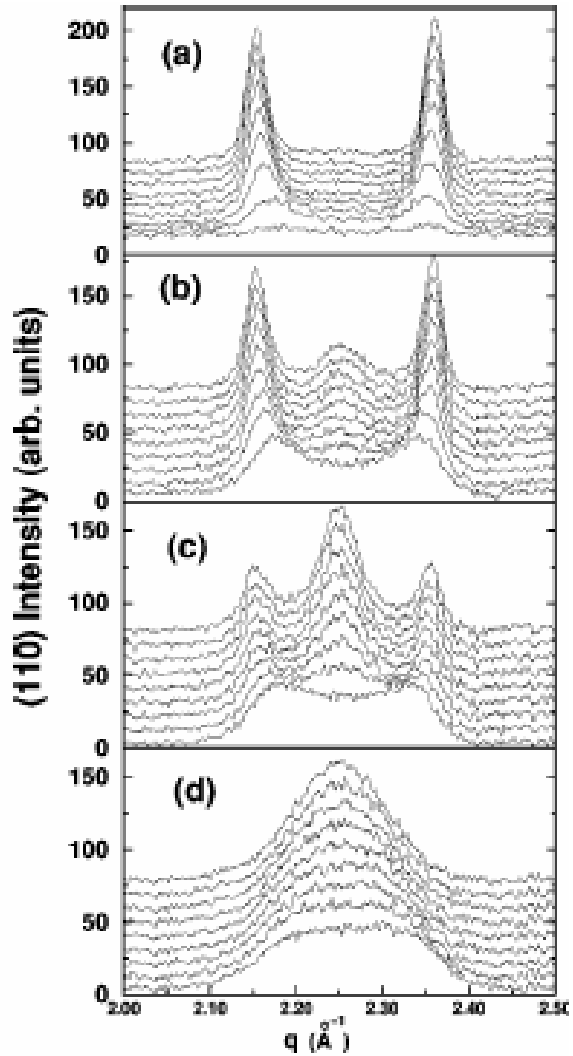

100 K
(1/2, k, ℓ)
3.1
3.0
2.9
ℓ (r.l.u.)
2.95
3.05
k (r.l.u.)
Intensity (counts/mon.)
300
200
100
0
3.5
3.0
2.5
0.5
0.0
ℓ (r.l.u.)
(3/2, 3, ℓ)
(cooling)
(3/2, 0, ℓ)
(cooling)
260
280
300
T (K)
320
340

Correlations Above CO Transition




100 K
(1/2, k, ℓ)
3.1
3.0
2.9
ℓ (r.l.u.)
2.95
3.05
k (r.l.u.)
Intensity (counts/mon.)
300
200
100
0
3.5
3.0
2.5
ℓ (r.l.u.)
(3/2, 3, ℓ)
(cooling)
dynamic
short-range
order
commensurate
CO
(static)
incommensurate
CO
(partly dynamic)
260
280
300
320
340
T (K)

Incommensurate Phase Belongs to Class of Phenomena Known as “Modulated Phases“



Cu-Au 50-50 at. %

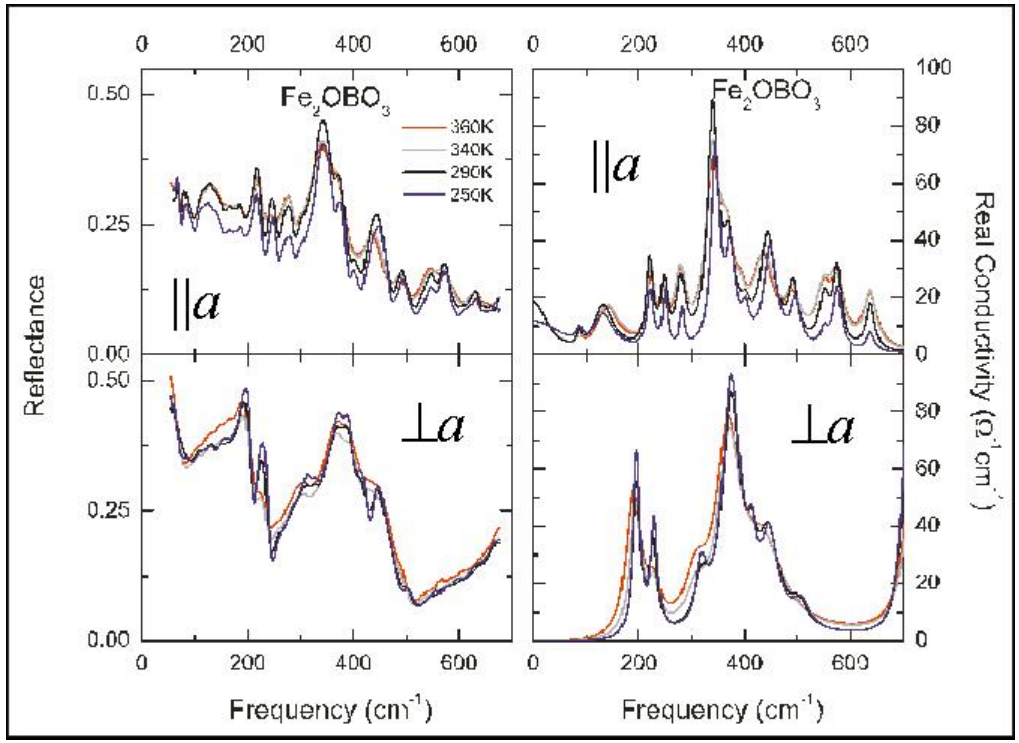
- Above 410 °C stable phase disordered
- Below 385 °C equilibrium phase CuAu I, in which Cu and Au occupy alternating atomic Layers
- Between these 2 transition temperatures CuAu orders into a one dimensional long Period superlattice called CuAu II, which consists of a periodic array of antiphase boundaries with an average modulation wavelength approx. 10 times the size of the underlying CuAu cell

Malis, Ludwig, PRB **60**, 14675 (1999)

“the origin of the modulated phase is still under debate”

Future Work

Optics – Willie Padilla, Boston College



"Switching" Effects in IV curves -- Ana Akrap, L. Forro, EPFL

Impedance Spectroscopy, search for ferroelectricity

TEM work

Summary

$LuFe_2O_4$

- Oxygen stoichiometry strongly affects physical properties
- Observation of thermal anomaly at 330 K
- 3D magnetic structure solved
- New phase transition observed at 180 K

Fe_2OBO_3

- Crystal growth of Fe_2OBO_3
- Found C.O. superstructure reflections
- Showed that Fe_2OBO_3 is best example to date of ionic C.O.
- Found the incommensurate phase, assigned it to the same class of phenomena as the CuAu II "modulated phase"

Papers: M. Angst, et al. PRL **99**, 086403 (2007); M. Angst, et al. cond-mat: 0707.3127