

Stoichiometry and crystal quality in $\text{LuFe}_2\text{O}_{4-\delta}$ and $\text{YbFe}_2\text{O}_{4-\delta}$

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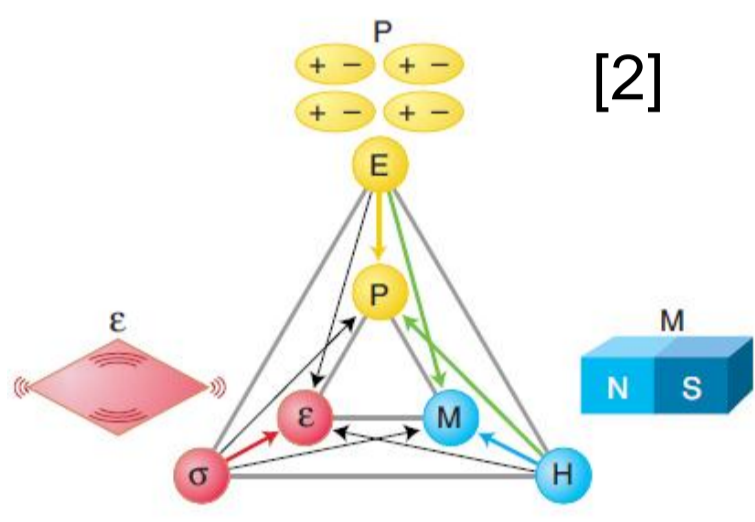
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Motivation

→ complex coupling between **electricity** and **magnetism (Magnetoelectric coupling)** where a system can become polarized by a magnetic field and vice versa.

Multiferroic's

→ which allow **ferroelectricity** through charge order (CO), with particular interest in $\text{LuFe}_2\text{O}_{4-\delta}$ (LFO) since the discovery of interesting magnetic and electrical characteristics.

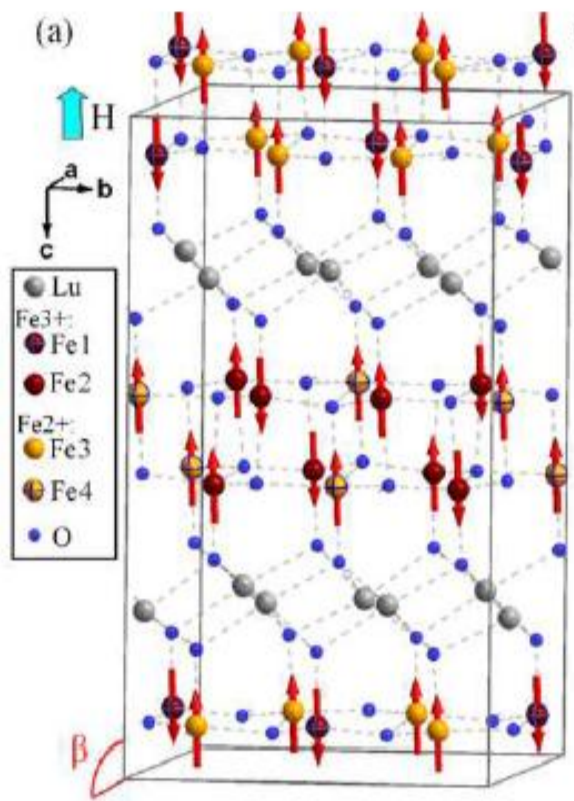


This has led to the investigations of other members of the $R\text{Fe}_2\text{O}_4$ series (R=rare earth)

Structure

The rhombohedral $R\text{Fe}_2\text{O}_{4-\delta}$ (R = Lu, Yb, Y, Tm, Ho and Er) system:

- triangular Fe bilayers separated by Lu monolayers.
- Average valance $\text{Fe}^{2.5+}$
- $\text{Fe}^{2+}/\text{Fe}^{3+}$ CO



(a) Refined monoclinic crystal structure $C2/m$ of charge ordered LFO. The ferrimagnetic high-field spin order and $\text{Fe}^{3+}/\text{Fe}^{2+}$ charge order is represented by arrows and different colors respectively [3].

The specific CO configuration in the bilayers was initially thought to produce a ferroelectric polarization due to an imbalance of Fe^{2+} and Fe^{3+} in the two layers of the bilayer [4]. However our recent investigations indicate that the CO configuration is LFO is actually non-polar [3].

Crystal Growth

Recent studies on LFO report large differences in crystal quality based on oxygen stoichiometry [5]. A systematic study is needed:

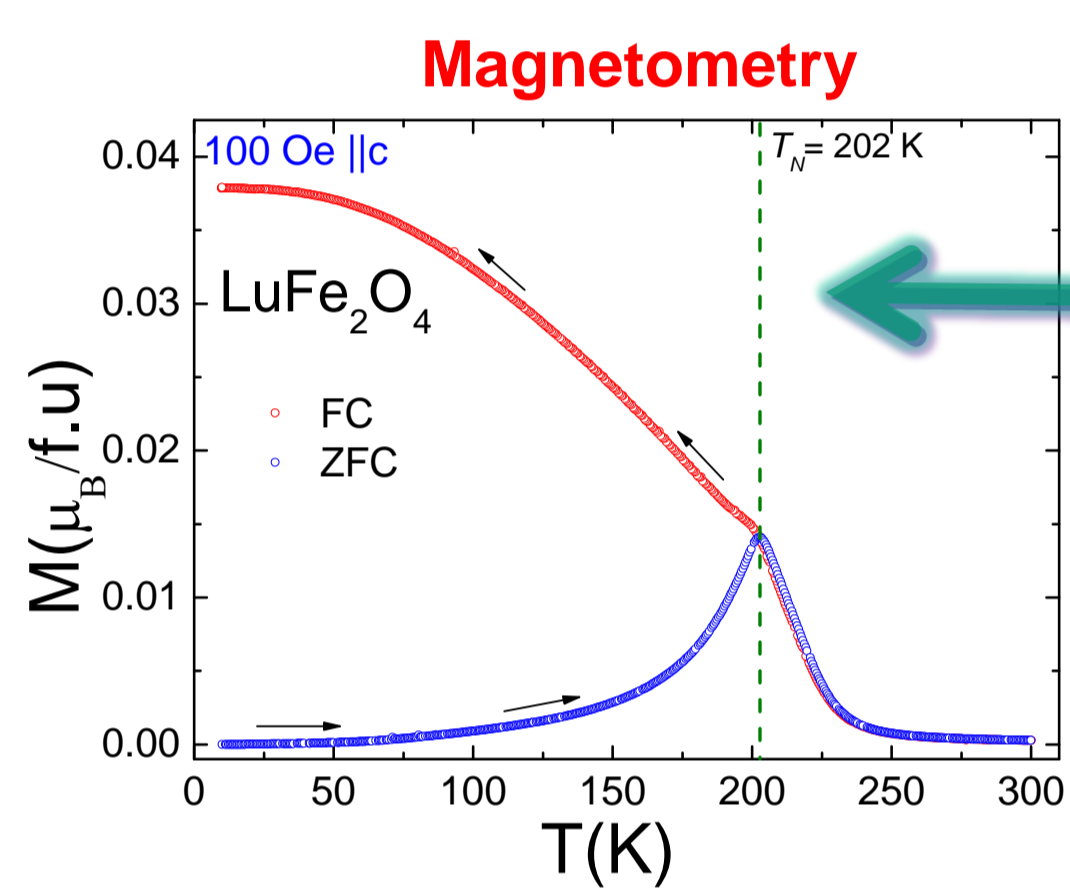
→ Off stoichiometric crystals without long range magnetic order present broad transitions compared to sharp transitions of near stoichiometric crystals.

→ Crystal growth of LFO and $\text{YbFe}_2\text{O}_{4-\delta}$ (YbFO) via optical floating zone method using gas ratios of $\text{CO}/\text{CO}_2=1:3$ and $\text{CO}/\text{CO}_2=1:5$ to tune O-stoichiometry and study property changes.

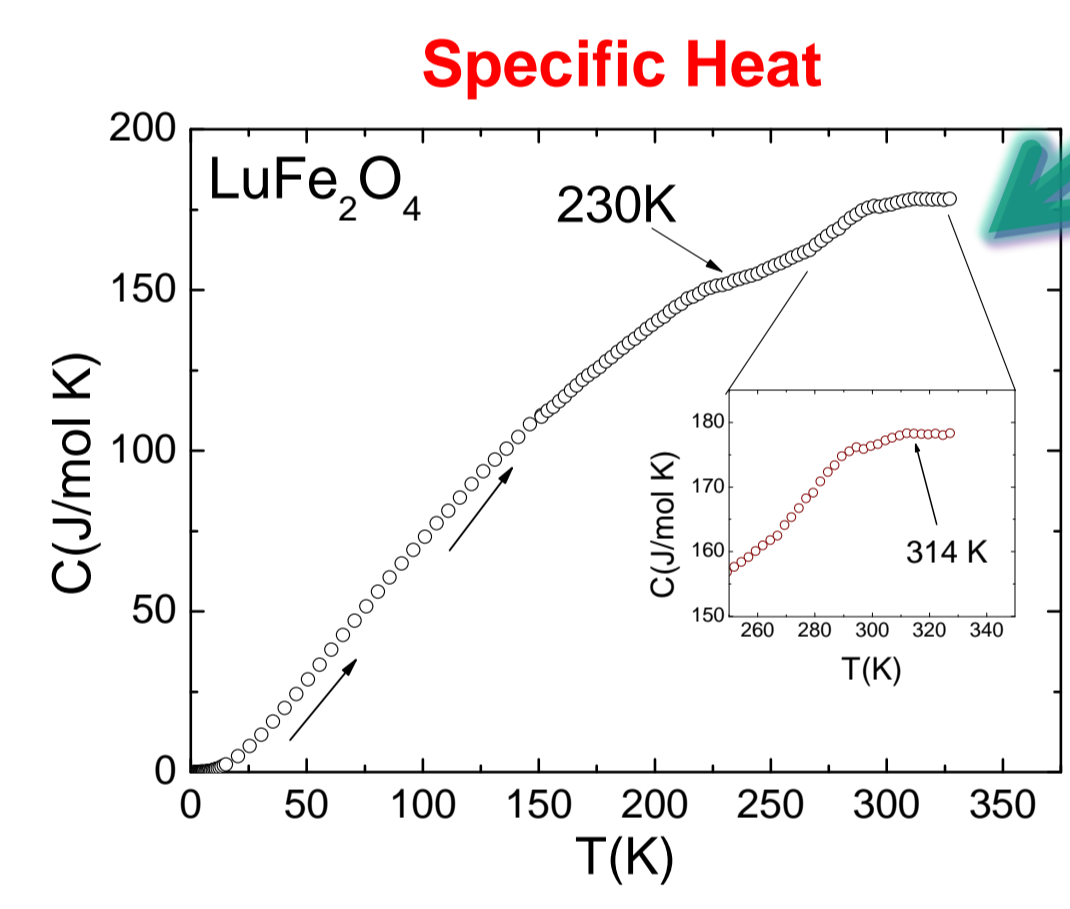
YbFe_2O_4 crystal

LuFe_2O_4 crystal

$\text{LuFe}_2\text{O}_{4-\delta}$ → $\text{CO}/\text{CO}_2=1:3$



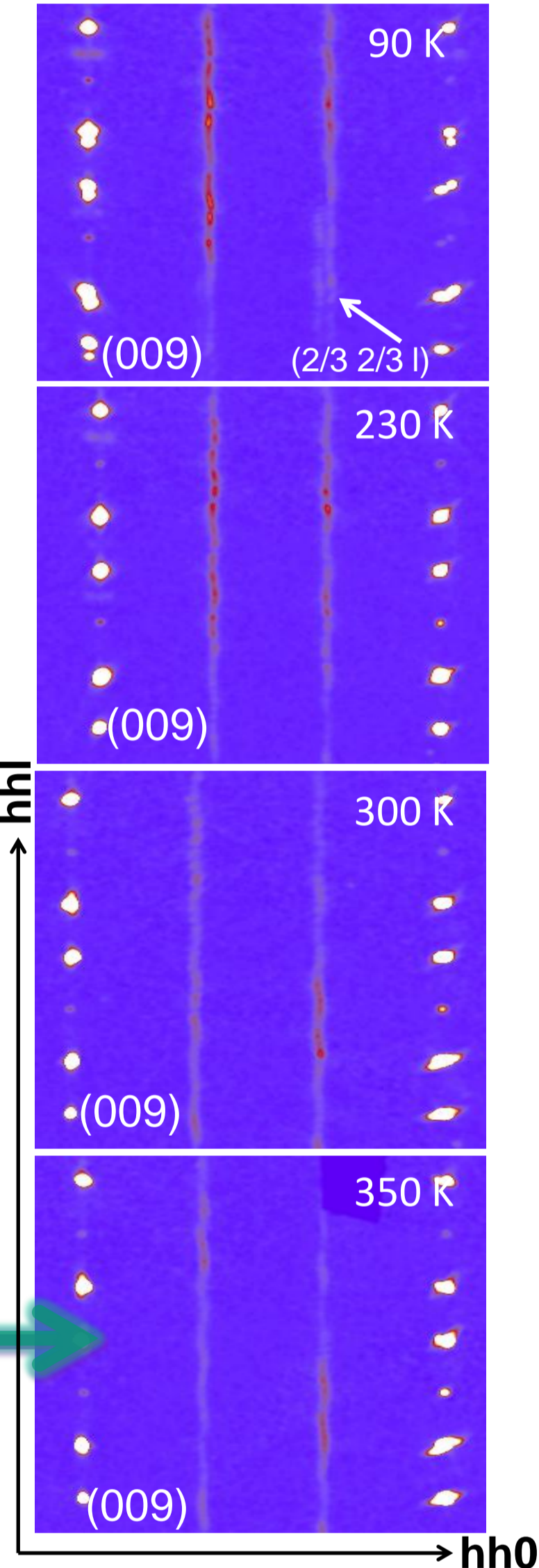
Very broad ferrimagnetic transition at 202 K, no evidence of the previously reported transition at 175 K [6].



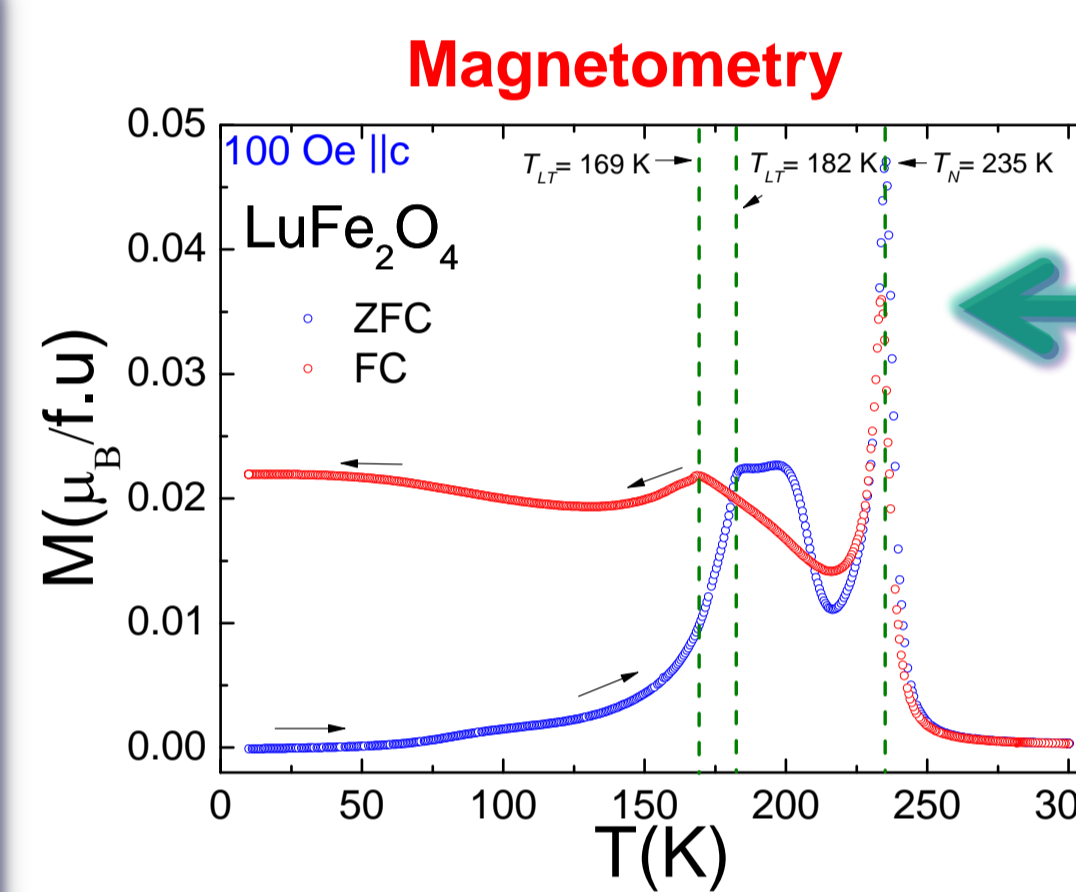
Smeared out magnetic transition and only a small peak at the CO transition.

Single crystal x-ray data (SCXR) → no 3D charge order, only diffuse superstructure lines along the $(1/3\ 1/3\ 1)$.

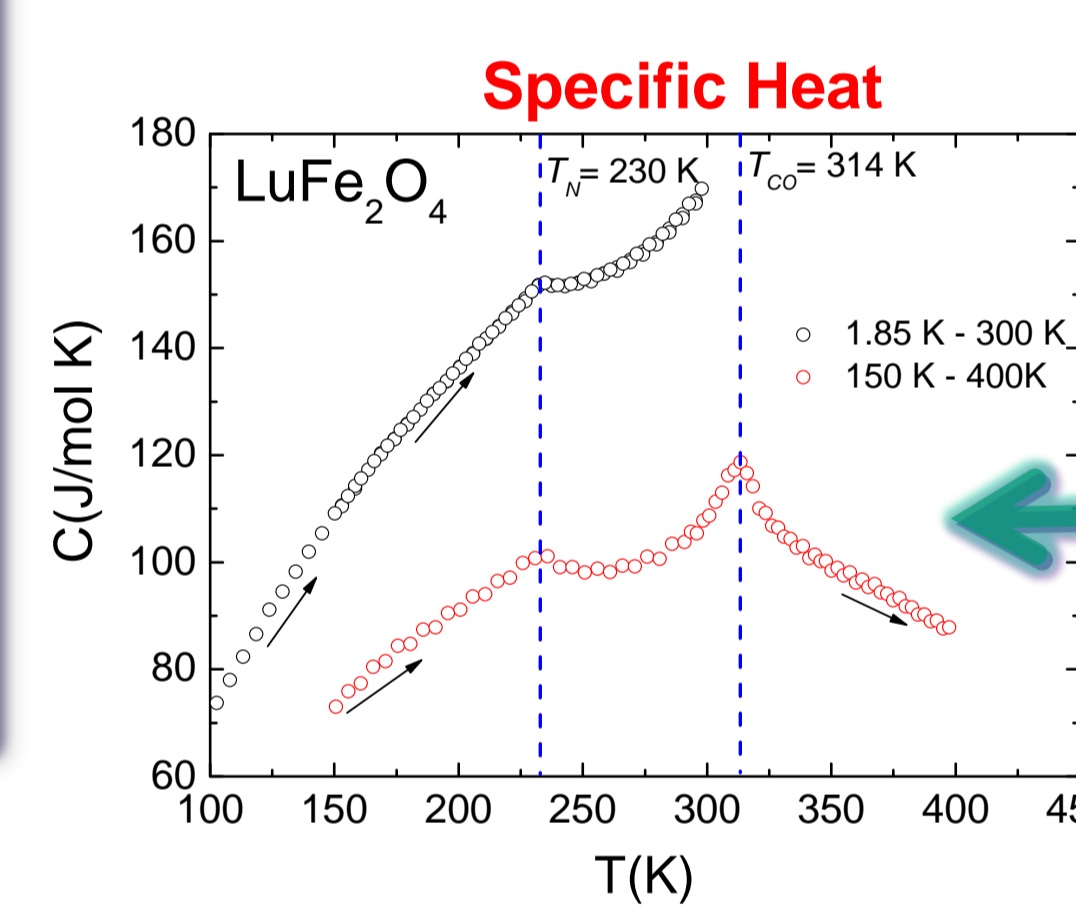
Single Crystal X-Ray Diffraction



$\text{LuFe}_2\text{O}_{4-\delta}$ → $\text{CO}/\text{CO}_2=1:5$



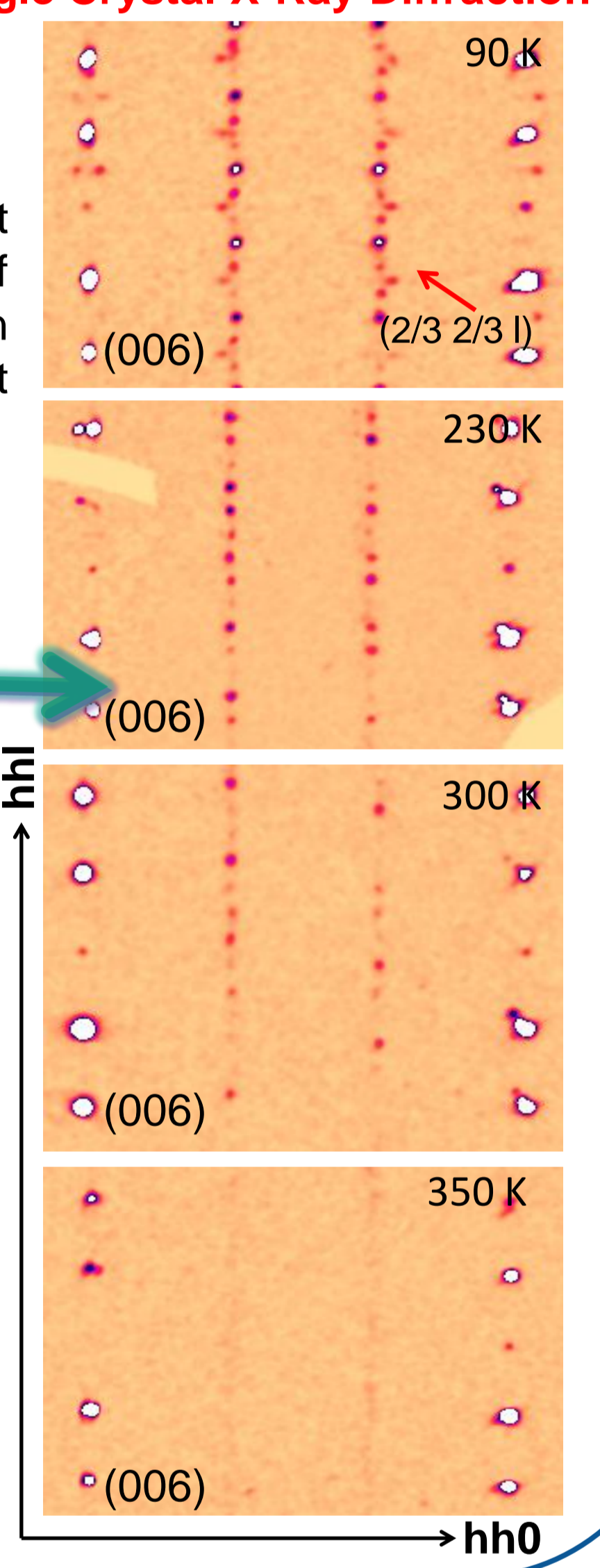
Sharp magnetic transition at $T_N = 235$ K. Indication of further transition at 175 K on cooling in good agreement with Christianson *et al.* [6].



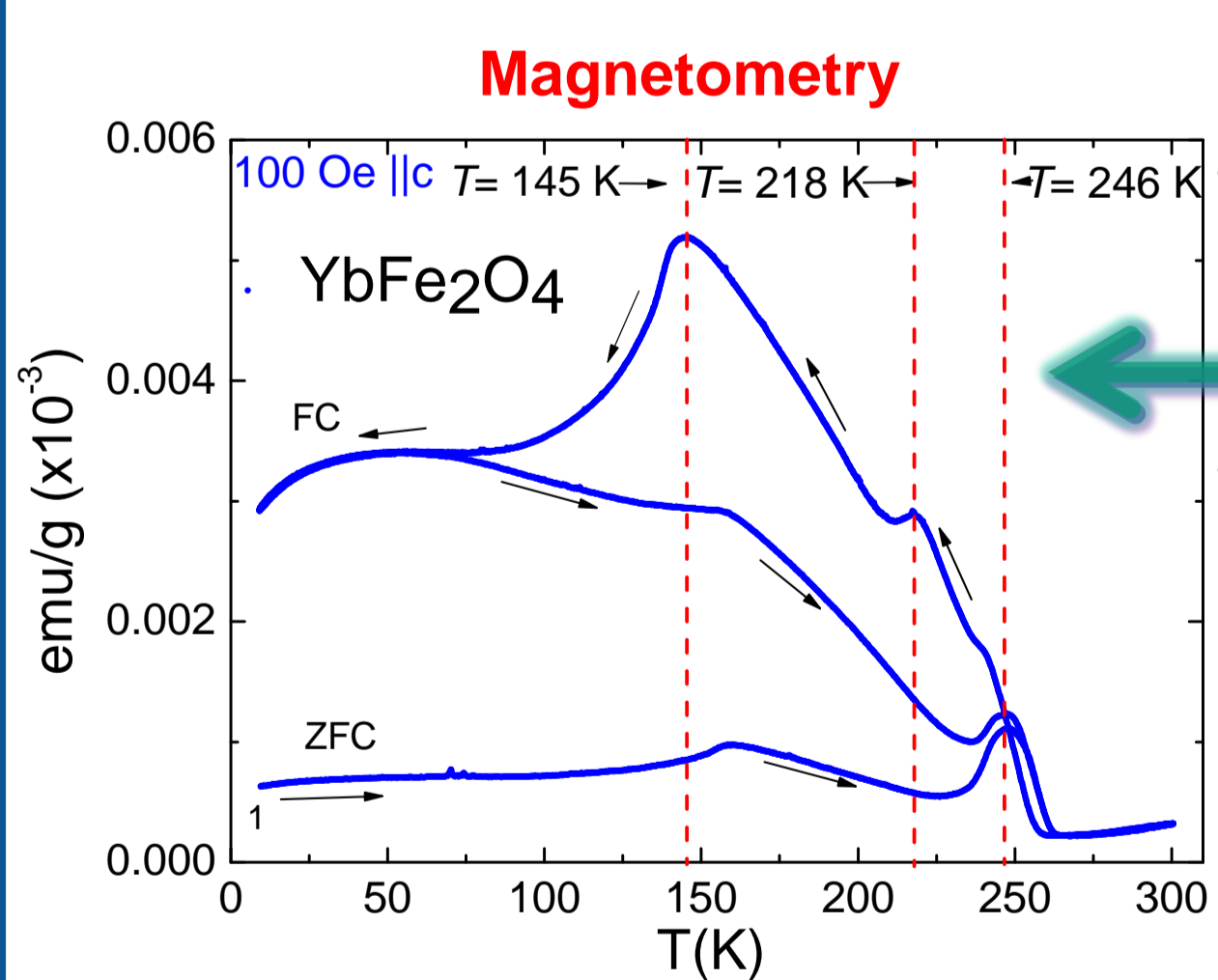
SCXR reveals 3D CO superstructure at 90 K up to 300 K. At $T=350$ K the CO is destroyed and only weak diffuse lines are left.

Two sharp transitions, much more defined than that of the (1:3) crystal. In particular the onset of CO at $T_{CO}=317$ K, which correlates nicely with the SCXR data.

Single Crystal X-Ray Diffraction

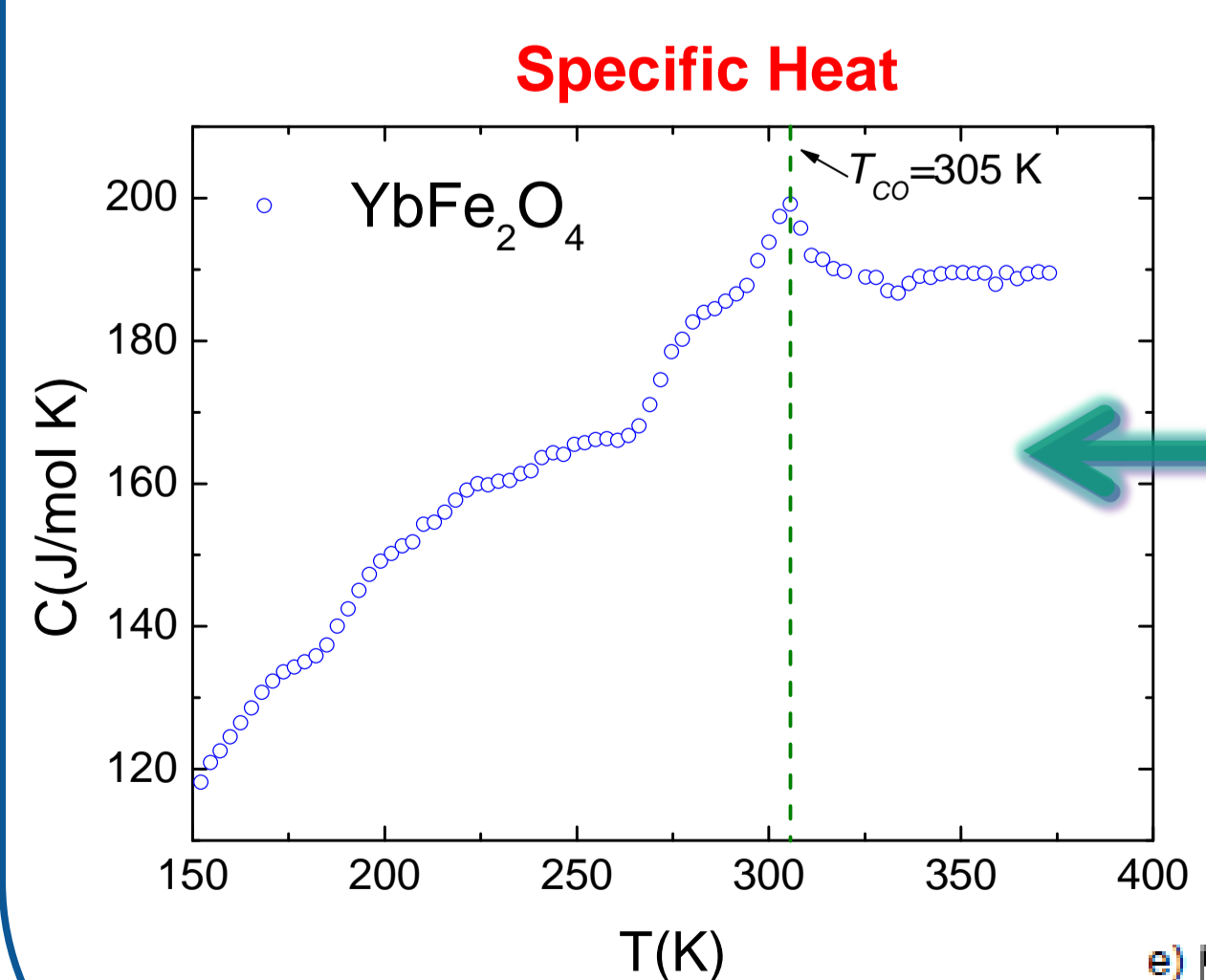


$\text{YbFe}_2\text{O}_{4-\delta}$ → $\text{CO}/\text{CO}_2=1:3$



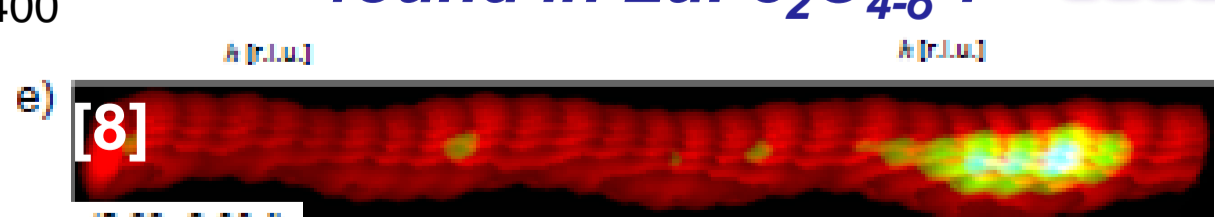
- Magnetic transition similar to that seen in LFO but shifted to 246 K.
- Transitions at 218 K, 145 K and low temperatures require more detailed investigation.

Mössbauer spectroscopy was carried out using a ^{57}Co source.

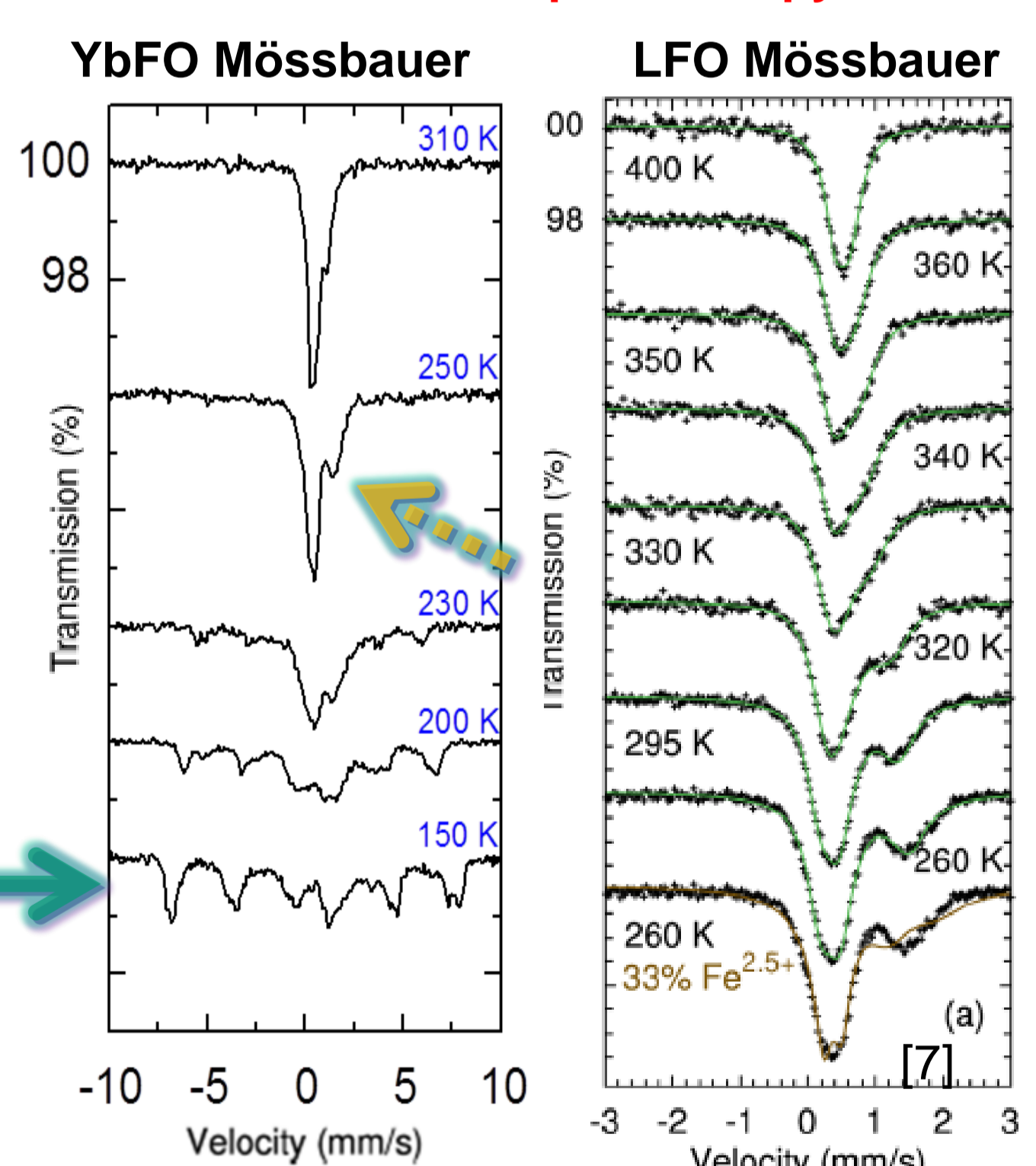


Charge order transition similar to that seen in the specific heat data of LFO with slightly lower temperature.

CDW or will better stoichiometric crystals show similar 3D CO found in $\text{LuFe}_2\text{O}_{4-\delta}$?



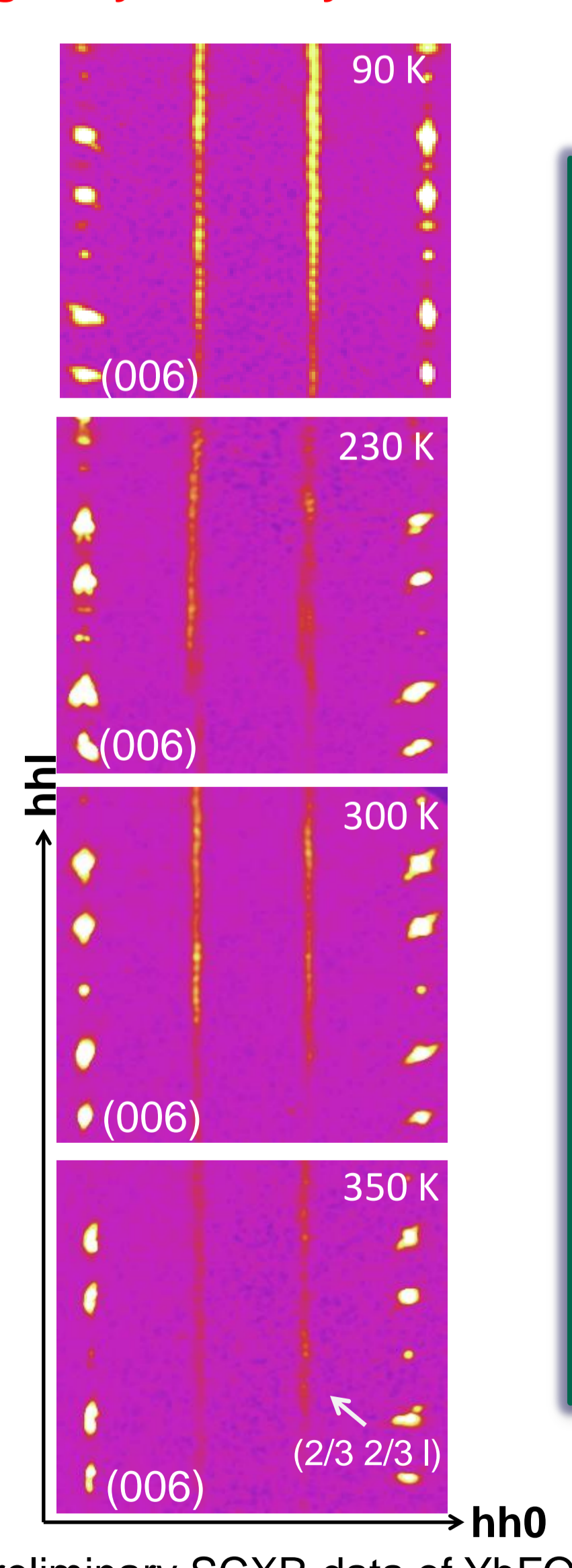
Mössbauer Spectroscopy



YbFO Mössbauer data reveals similar Fe^{2+} and Fe^{3+} splitting between 250 K and 310 K as the LFO data [7].

Hearmon *et al.* [8] describes charge ordering as incommensurate charge density waves (CDW).

Single Crystal X-Ray Diffraction



Preliminary SCXR data of YbFO.

$\text{YbFe}_2\text{O}_{4-\delta}$ → $\text{CO}/\text{CO}_2=1:5$

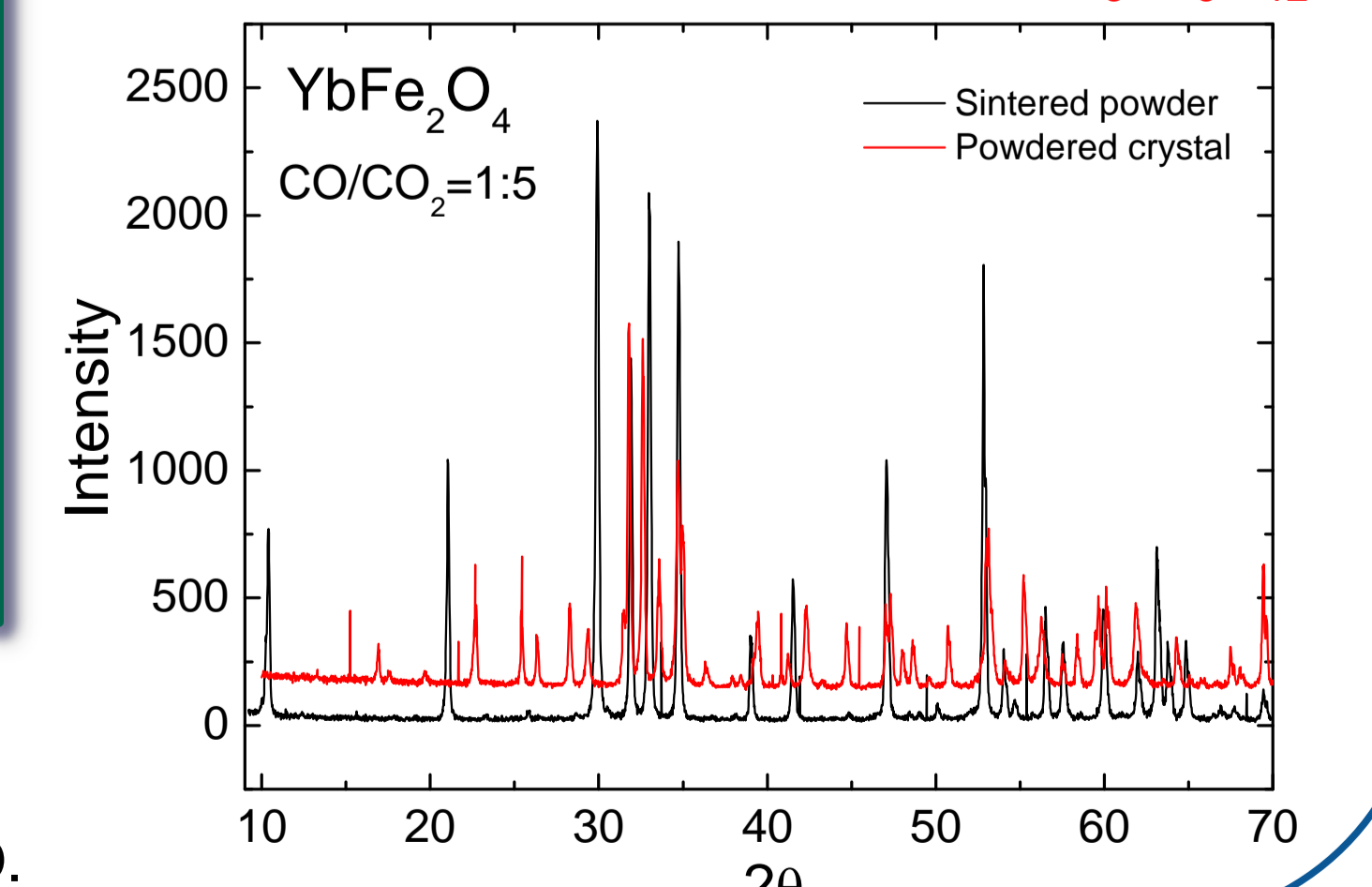
From LFO crystal growth- (1:5) gas ratio produced better stoichiometric crystals.

→ YbFO single phase powder synthesized in (1:3).

→ YbFO crystals grown in (1:5).

Powder x-ray confirmed single phase YbFO decomposed into 4 different phases:

- YbFe_2O_4
- YbFe_2O_3
- $\text{Yb}_2\text{Fe}_3\text{O}_7$
- $\text{Yb}_3\text{Fe}_5\text{O}_{12}$



Outlook

- Mössbauer analysis of YbFO- peak fitting.
- Neutron scattering experiments to uncover origins of multiple transition points shown in magnetization YbFO data.
- Refine YbFO SCXR data at low and higher temperatures measured.
- Determine true oxygen content in both types of LFO crystals and YbFO (1:3).
- Grow YbFO in $\text{CO}/\text{CO}_2 = 1:3.5$ to view stoichiometric changes.

Acknowledgement

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References

- [1] S.-W. Cheong and M. Mostovoy, *Nat. Mater.* **6**, 13 (2007).
- [2] Spaldin & Fiebig, *Science* **309**, 391 (2005).
- [3] de Groot *et al.*, *Phys. Rev. Lett.* in press; Preprint on arXiv: 1112.0978.
- [4] Ikeda *et al.*, *Nature* **436**, 1136 (2005).
- [5] de Groot *et al.*, *Phys. Rev. Lett.* **108**, 037206 (2012).
- [6] Christianson *et al.*, *PRL* **100**, 107601 (2008).
- [7] Xu *et al.*, *PRL* **101**, 227602 (2008).
- [8] Hearmon *et al.*, *Phys. Rev. B* **85**, 014115 (2012).