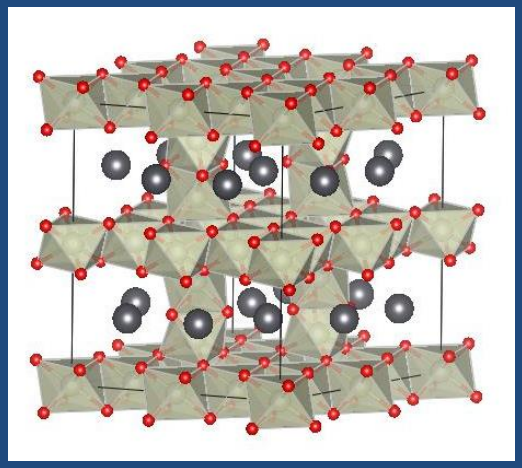
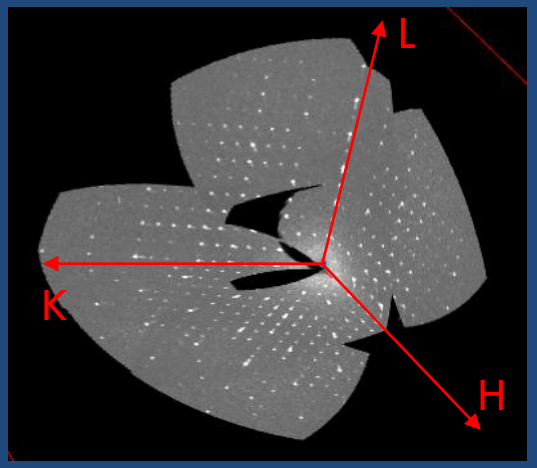
Investigating the Potential Verwey Transition in $Pb_3Rh_7O_{15}$ with Synchrotron X-rays





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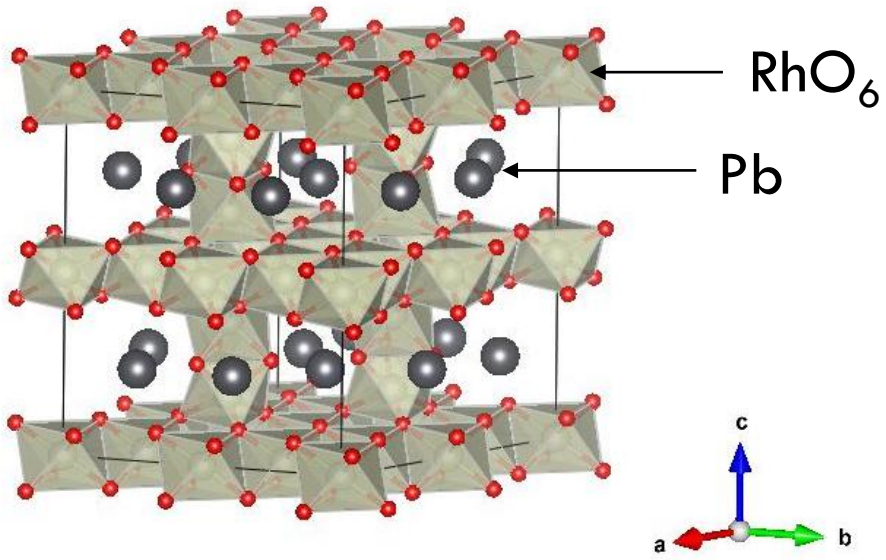
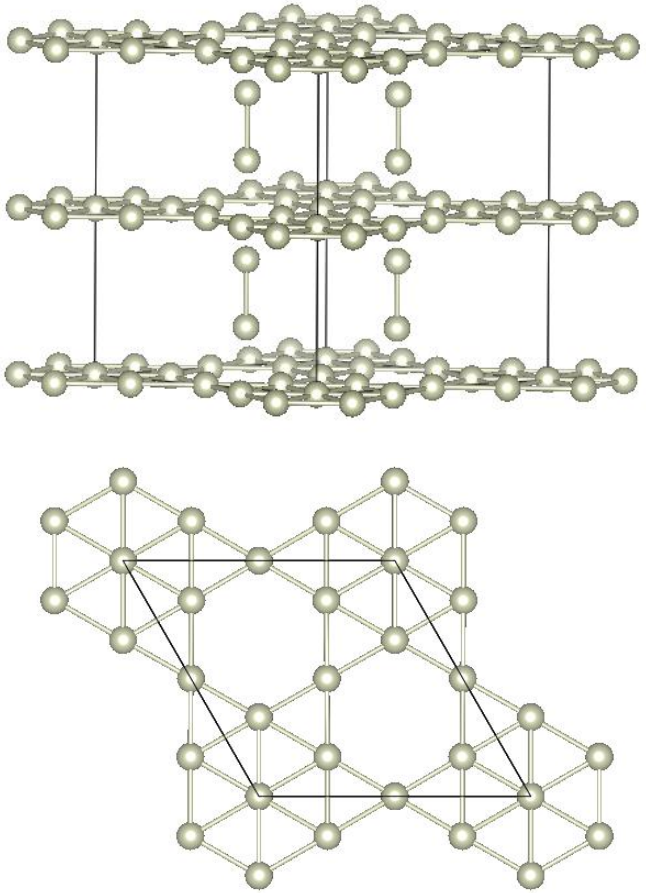
May 30, 2017

CAP Congress, Queen's University, Kingston ON

Introduction to $Pb_3Rh_7O_{15}$



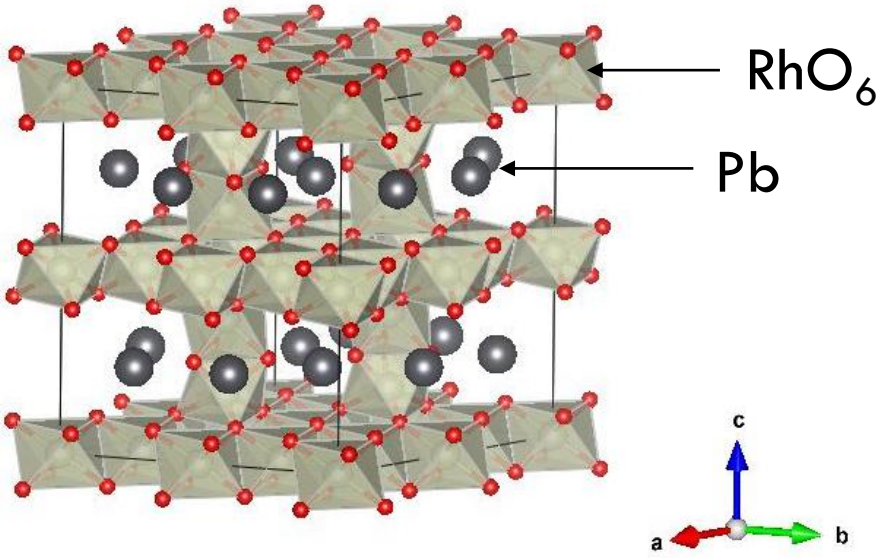
Simplified Structure (Rh Only):

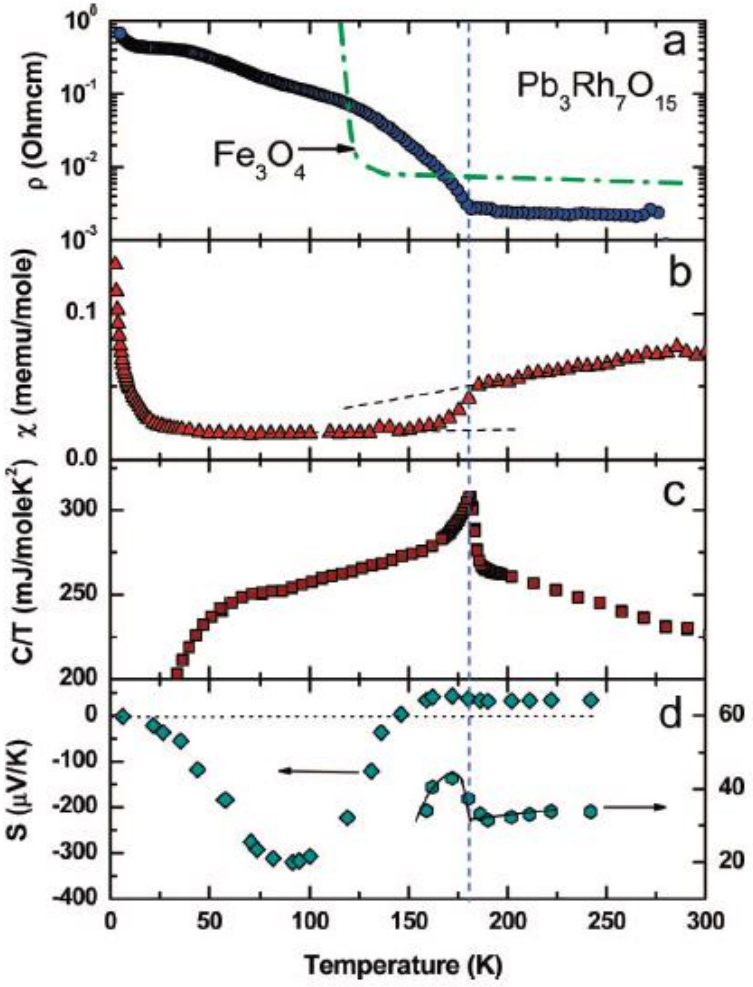


- Mixed valence: $Pb_3[Rh^{3+}]_4[Rh^{4+}]_3O_{15}$
- Hexagonal crystal structure ($P6_3/mcm$)

$a = b = 10.35$ Å
$c = 13.28$ Å

Introduction to $Pb_3Rh_7O_{15}$



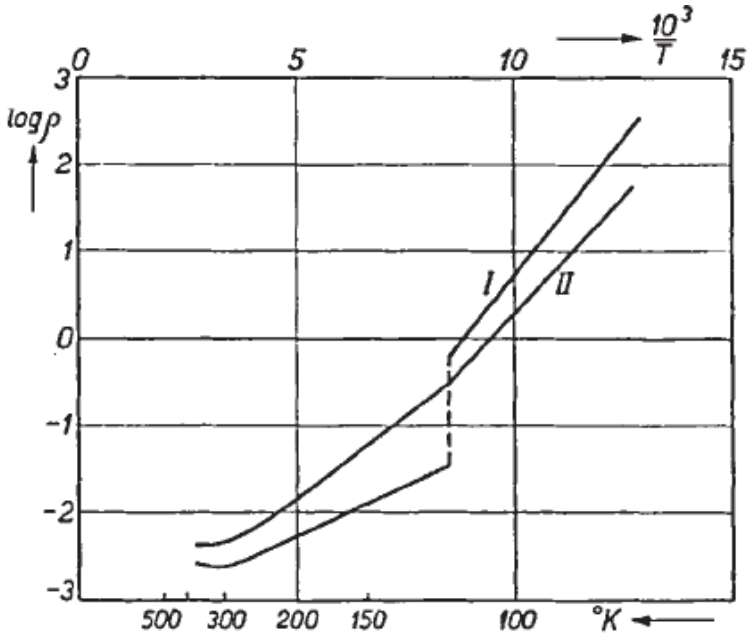


- Mixed valence: $Pb_3[Rh^{3+}]_4[Rh^{4+}]_3O_{15}$
- Hexagonal crystal structure ($P6_3/mcm$)
- Evidence of phase transition at Tc ~ 180 K

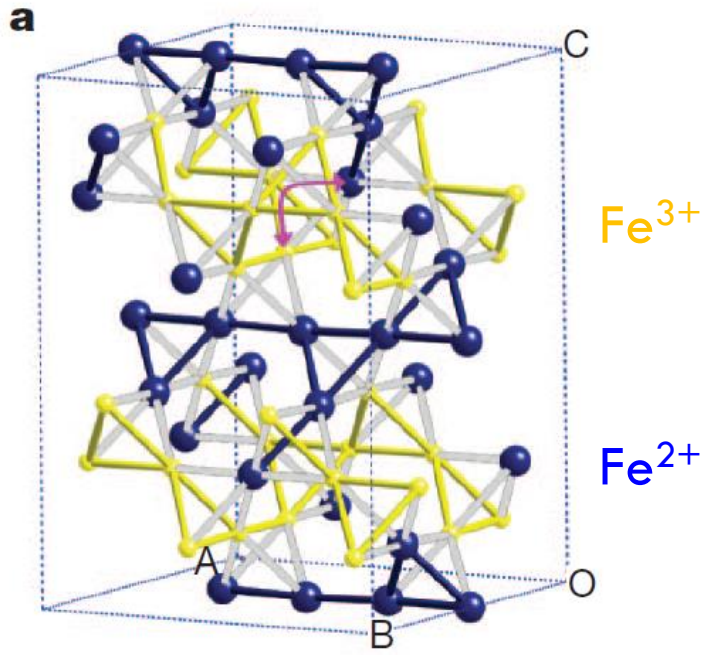
H. Mizoguchi et al, Chem. Mater. (2009)

The Verwey Transition

- Metal-to-insulator transition driven by the development of charge order
- First observed in magnetite (Fe_3O_4): Fe^{2+}/Fe^{3+} order below $T_V \sim 125$ K



E. J. W. Verwey, Nature (1939)

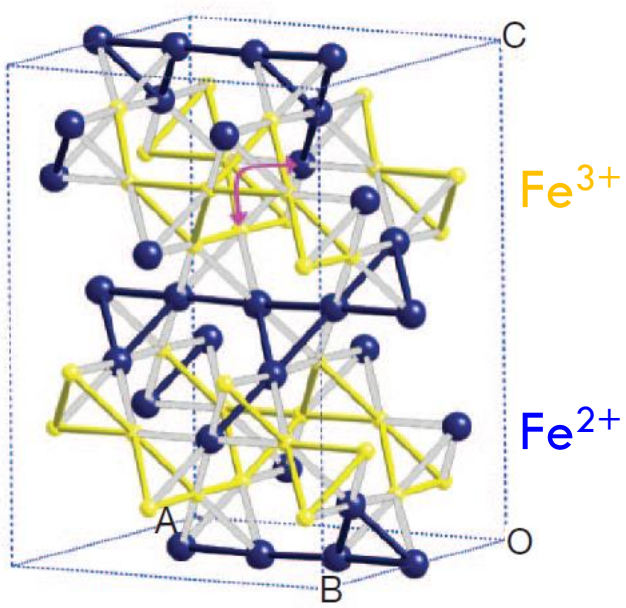


$(Fe_3O_4 = Fe^{3+}[Fe^{2.5+}]_2O_4)$

M. S. Senn et al, Nature (2012)

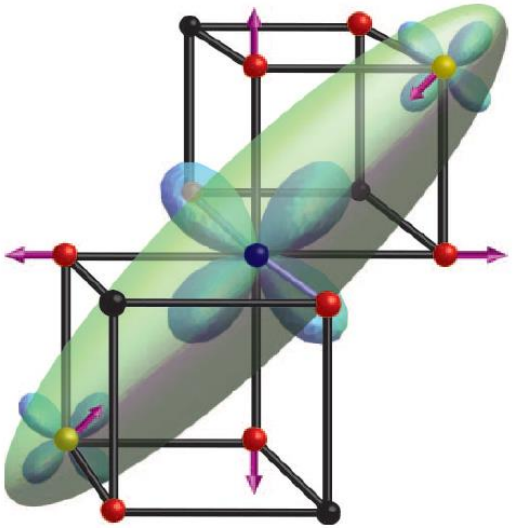
The Verwey Transition

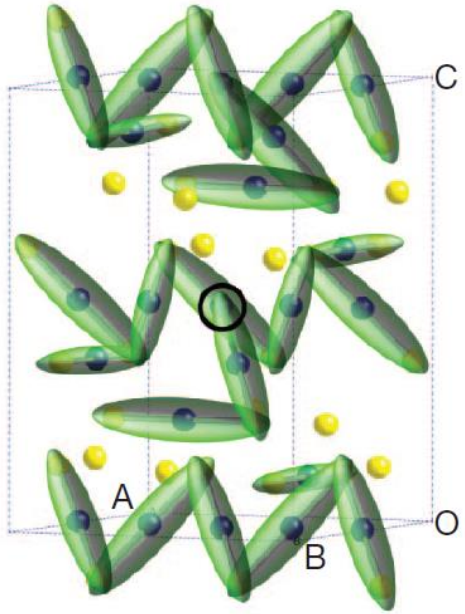
- Determining low temperature structure of magnetite = 73 year problem!



Fe^{3+}

Fe^{2+}





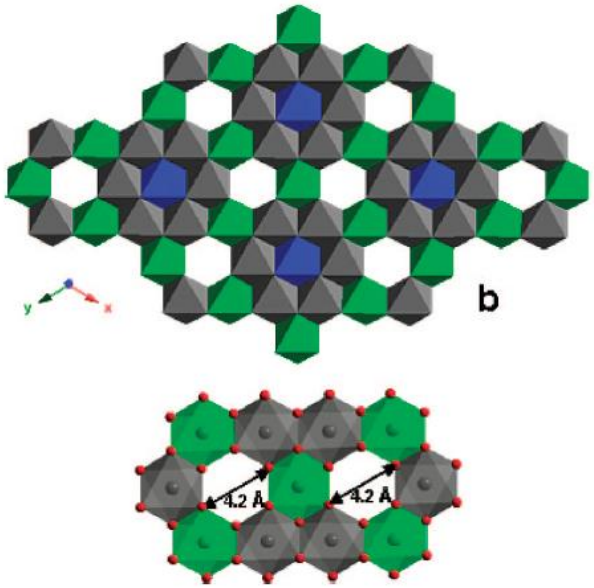
M. S. Senn et al, Nature (2012)

- Charge order → Jahn Teller distortion → 3 site "Trimeron" ordering

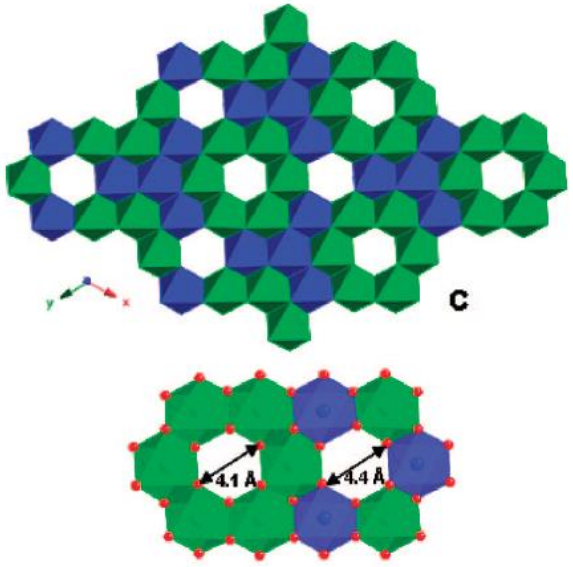
Potential charge order in $Pb_3Rh_7O_{15}$?

- Rh^{3+}/Rh^{4+} charge order patterns predicted by lattice energy calculations [*Muller-Buschbaum (2007)*] and bond valence sum analysis [*Mizoguchi et al (2009)*]

(High Temperature)



(Low Temperature)



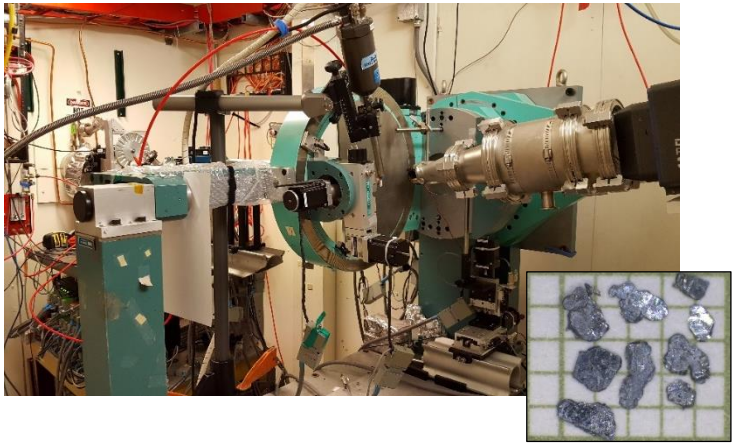
Green = Rh^{4+}
Blue = Rh^{3+}
Grey = Intermediate

H. Mizoguchi et al, Chem. Mater. (2009)

Experimental Details

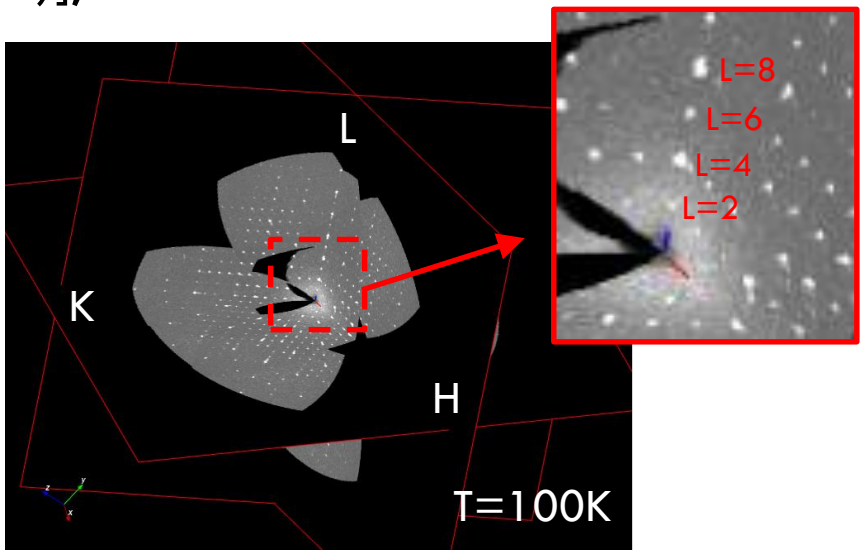
Can we find evidence of Rh^{3+}/Rh^{4+} charge order?

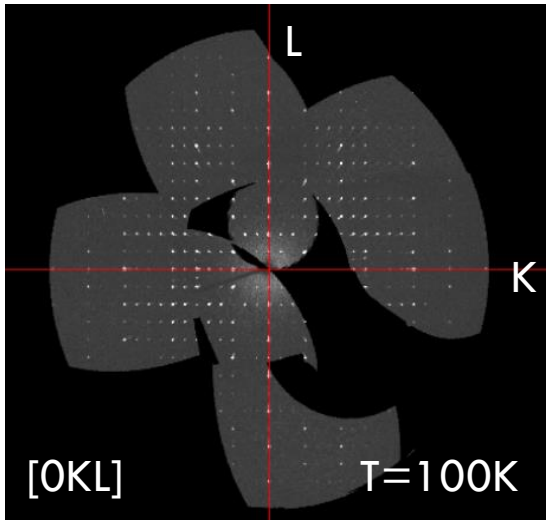
- Single crystal samples of $Pb_3Rh_7O_{15}$ (flux growth methods, PbO flux)
- Single crystal x-ray diffraction (McMaster)
- Synchrotron x-ray scattering (Cornell)
  - Beamline A2 at CHESS
  - High energy diffraction
  - Resonant scattering at Rh K-edge (E_i = 23.22 keV, 1s → 5p)



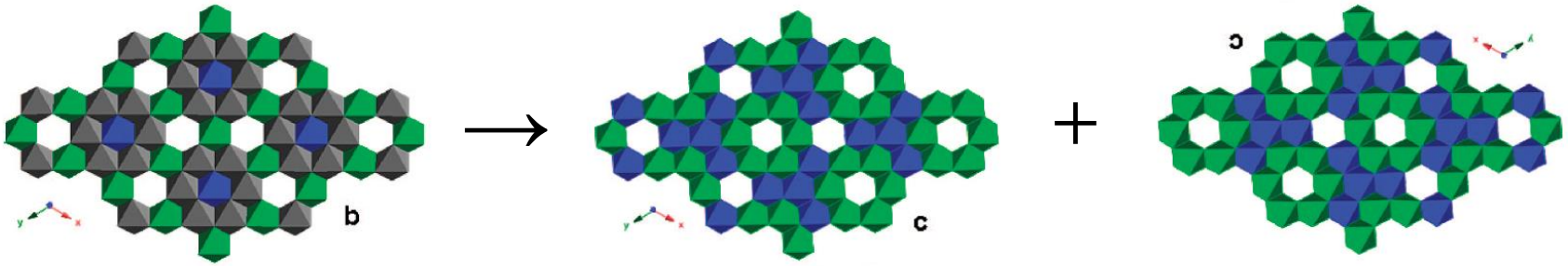
A Complex Crystal Structure (Pt. 1)

- Low temperature crystal structure previously measured [*Mizoguchi et al (2009)*], but never solved…



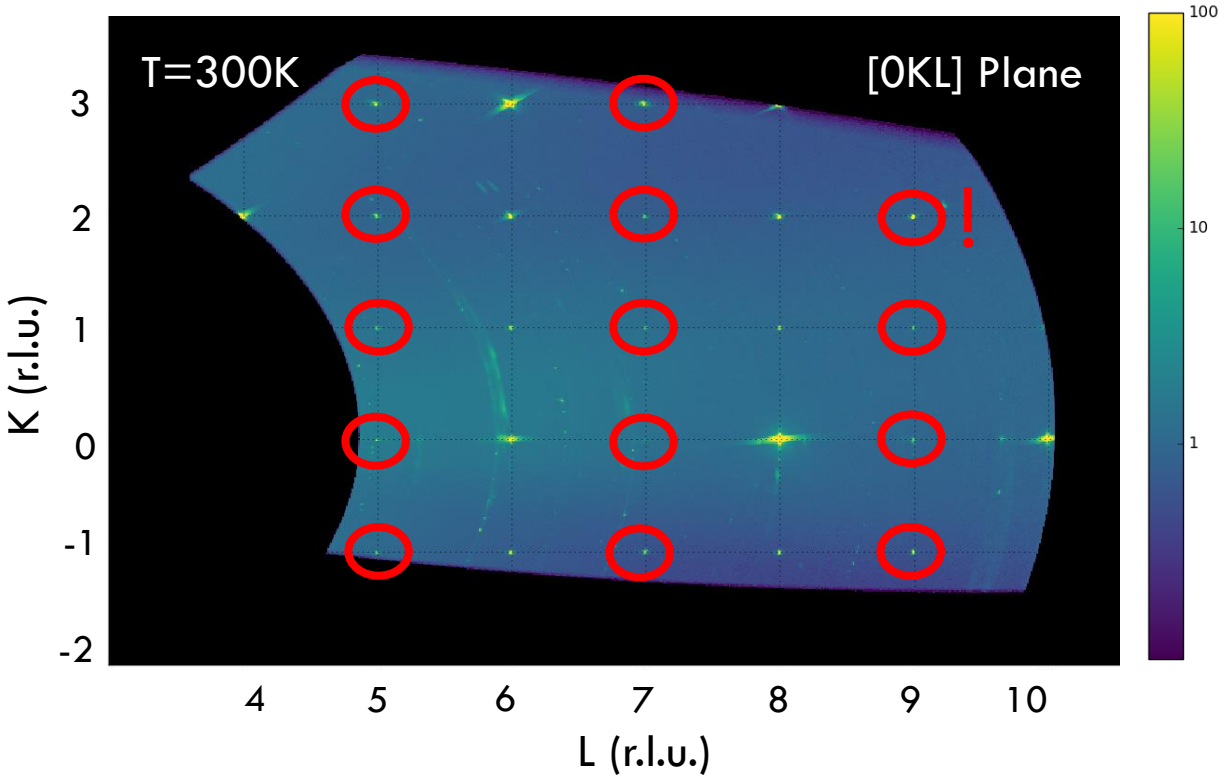


- Preliminary refinements point to trigonal structure with merohedral twinning



A Complex Crystal Structure (Pt. 2)

- High flux synchrotron measurements reveal structurally forbidden peaks, present above *and* below Tc



For space group $P6_3/mcm$:

No. 193

Reflection Conditions

(general)

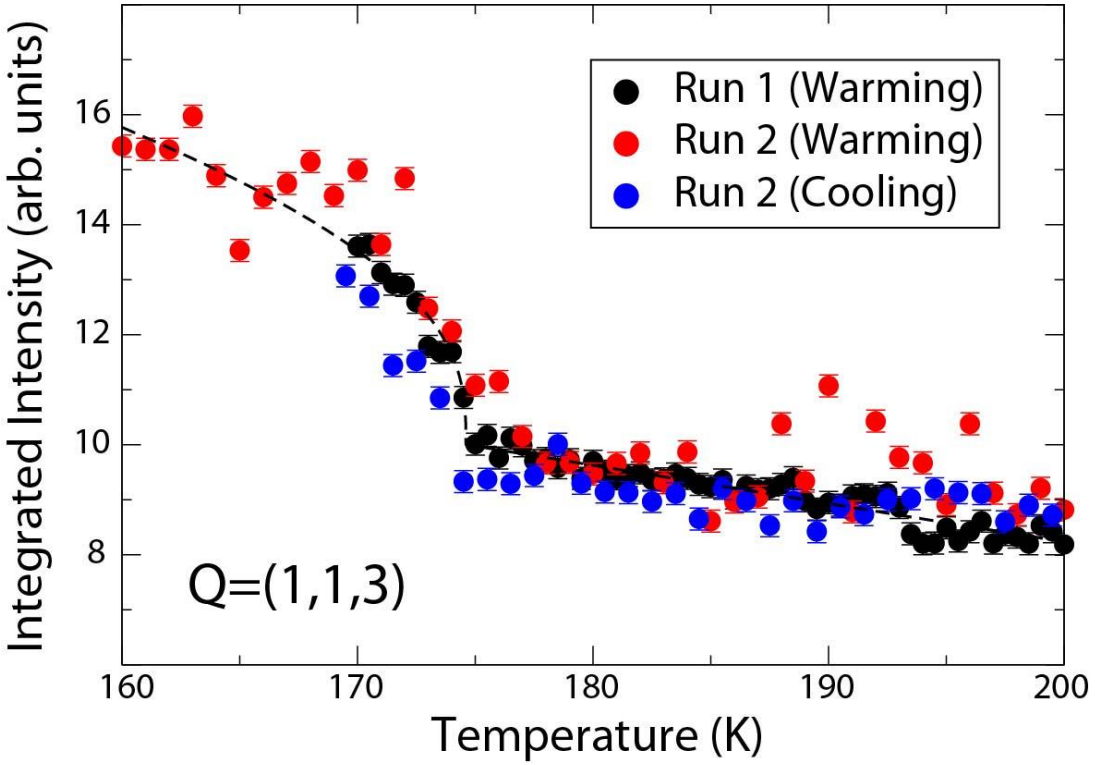
$0kl$: $l = 2n$ X

$h0l$: $l = 2n$ X

$00l$: $l = 2n$ X

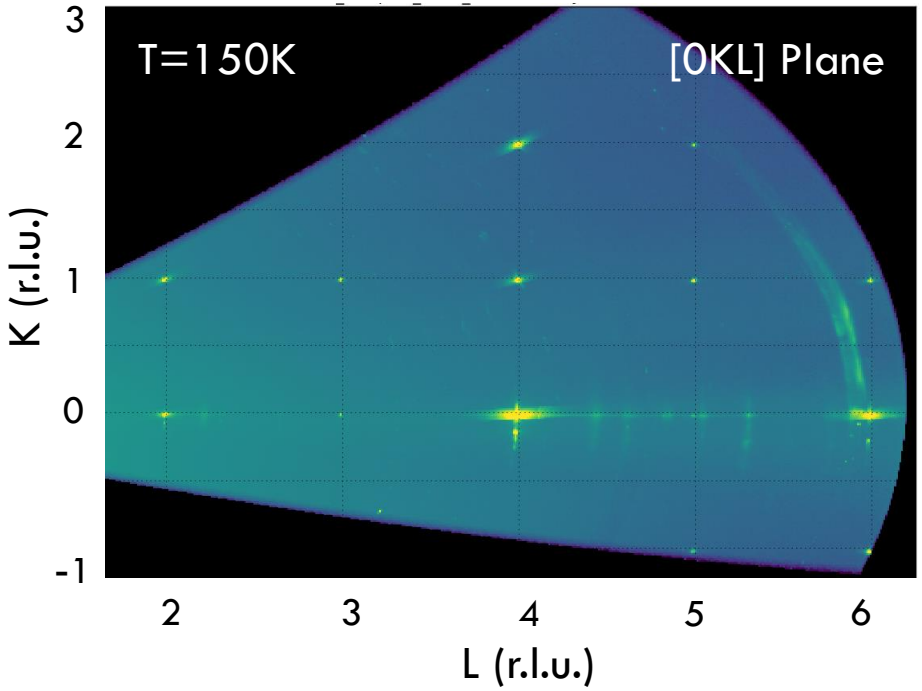
- No systematic absences → screw-axis and glide-plane symmetries broken

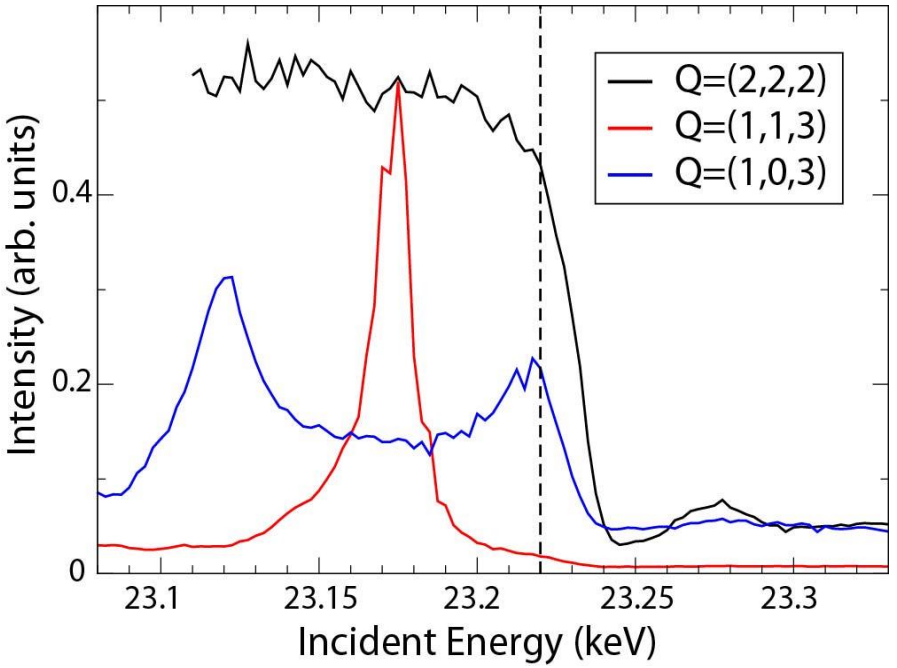
Structural Phase Transition at Tc



- Evidence of continuous structural phase transition at Tc ~ 174.6 ± 1.0 K

Resonance Behaviour at Rh K-edge





- Tune incident energy to Rh K-edge at 23.22 keV → No new superlattice peaks appear
- Structural peaks display rich energy dependence, theoretical modelling underway

Summary and Conclusions

- $Pb_3Rh_7O_{15}$: first 4d candidate for Verwey transition
- Metal-to-insulator transition at Tc ~180 K, potentially driven by the development of Rh^{3+}/Rh^{4+} charge order

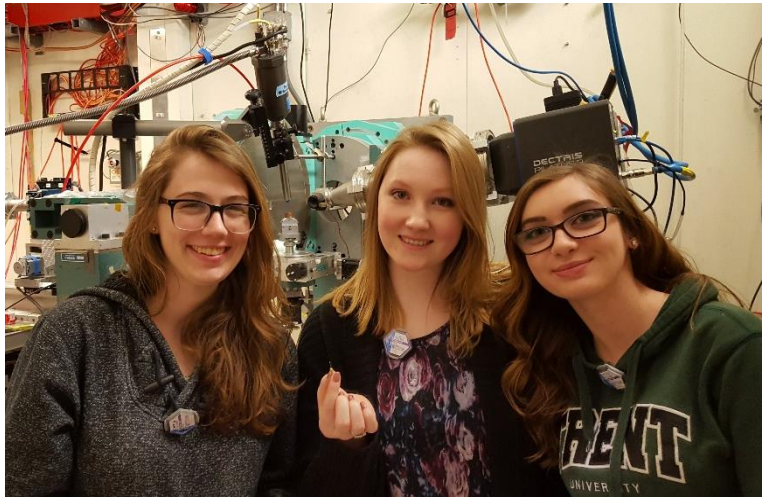
- Crystal structure of $Pb_3Rh_7O_{15}$ more complex than previously assumed (even at room T)
- Twinned trigonal crystal structure develops at low T
- Evidence of continuous structural phase transition at Tc ~180 K

- If present, charge order appears to be commensurate with lattice (no new superlattice peaks below Tc)

Acknowledgements

- Undergraduate student research experience project:
- Cassandra Thompson
- Lindsey Munro
- Melissa Van Bussel

- Primary funding provided by Trent VP Research Strategic Initiatives Fund



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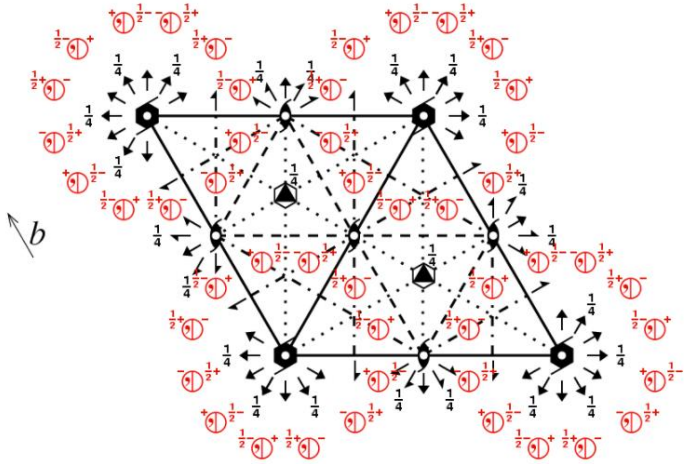
$P6_3/mcm$ Structural Model

$P6_3/mcm$ *$P\,6_3/m\,2/c\,2/m$* *6/mmm* No. 193



Symmetry Operators

1	x, y, z	1
2	$\bar{y}, x-y, z$	3^+ $(0, 0, z)$
3	$\bar{x}+y, \bar{x}, z$	3^- $(0, 0, z)$
4	$\bar{x}, \bar{y}, \frac{1}{2}+z$	2_1 $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
5	$x-y, x, \frac{1}{2}+z$	6_3^+ $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
6	$y, \bar{x}+y, \frac{1}{2}+z$	6_3^- $(0, 0, z)$ $[0, 0, \frac{1}{2}]$
7	$\bar{y}, \bar{x}, \frac{1}{2}+z$	c $(x, \bar{x}, z)$ $[0, 0, \frac{1}{2}]$
8	$\bar{x}+y, y, \frac{1}{2}+z$	c $(x, 2x, z)$ $[0, 0, \frac{1}{2}]$
9	$x, x-y, \frac{1}{2}+z$	c $(2x, x, z)$ $[0, 0, \frac{1}{2}]$
10	y, x, z	m (x, x, z)
11	$x-y, \bar{y}, z$	m $(x, 0, z)$
12	$\bar{x}, \bar{x}+y, z$	m $(0, y, z)$
13	$\bar{x}, \bar{y}, \bar{z}$	$\bar{1}$ $(0, 0, 0)$
14	$y, \bar{x}+y, \bar{z}$	$\bar{3}^+$ $(0, 0, z; 0, 0, 0)$

Reflection Conditions (general)

$0kl$: $l = 2n$

$h0l$: $l = 2n$

$00l$: $l = 2n$