Using a Synchrotron to Explore the Potential Verwey Transition in Lead Rhodium Oxide

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1. McMaster University, 2. Trent University, 3. Oak Ridge National Laboratory, 4. Cornell High Energy Synchrotron Source

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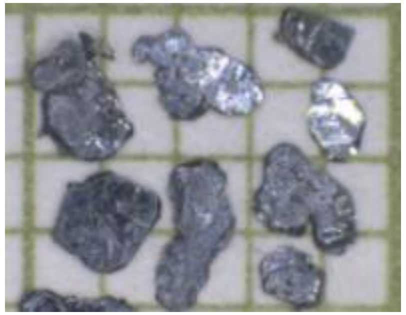
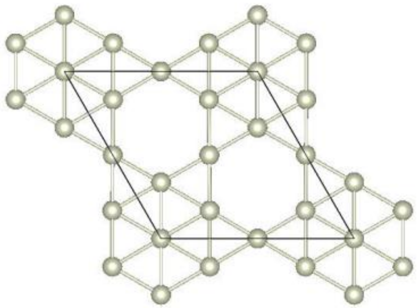
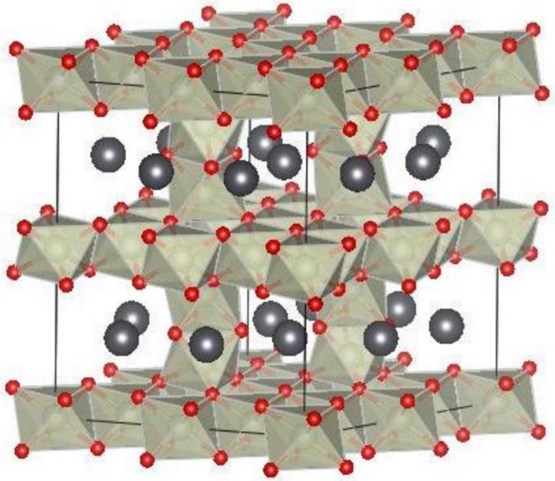
Lead Rhodium Oxide

- $Pb_3Rh_7O_{15}$
- Mixed Valence compound: $Pb_3[Rh^{3+}]_4[Rh^{4+}]_3O_{15}$
- Transition metal
- Space group: $P6_3/mcm$
- Hexagonal crystal structure
  - Lattice constants: a = b = 10.35Å, c = 13.28Å

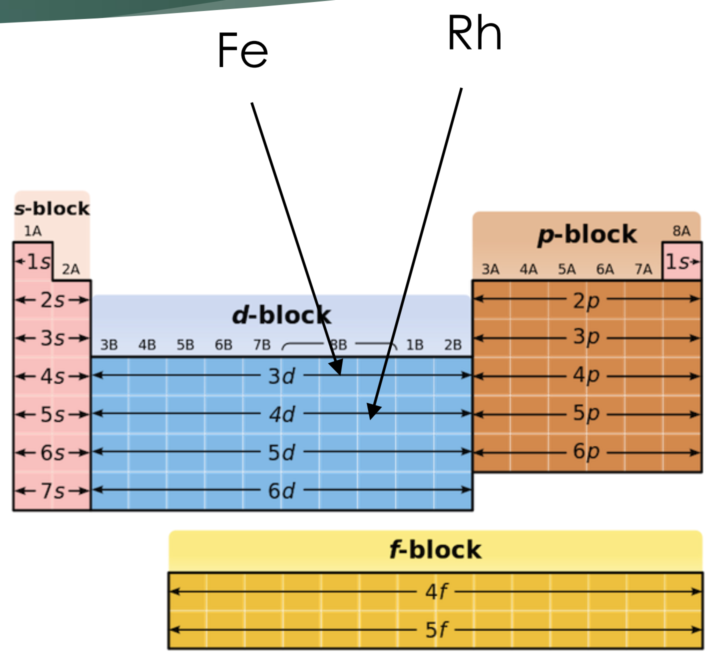






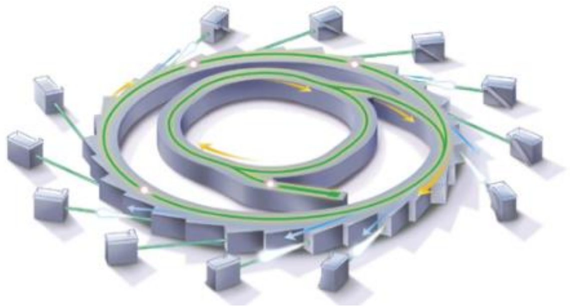
Verwey Transition

- A type of phase transition: properties change rapidly/discontinuously
- Electrical resistivity increases, charge ordering occurs
- Magnetite (Fe_3O_4) – 3d transition metal, T_V ~ 125K
- Lead rhodium oxide – 4d transition metal, change in space group at ~185K (H. Mizoguchi et al, 2009)
- Use synchrotron to determine charge ordering below ~185K
- Would be first 4d or 5d transition metal oxide Verwey Transition



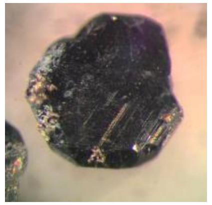
Synchrotron X-rays

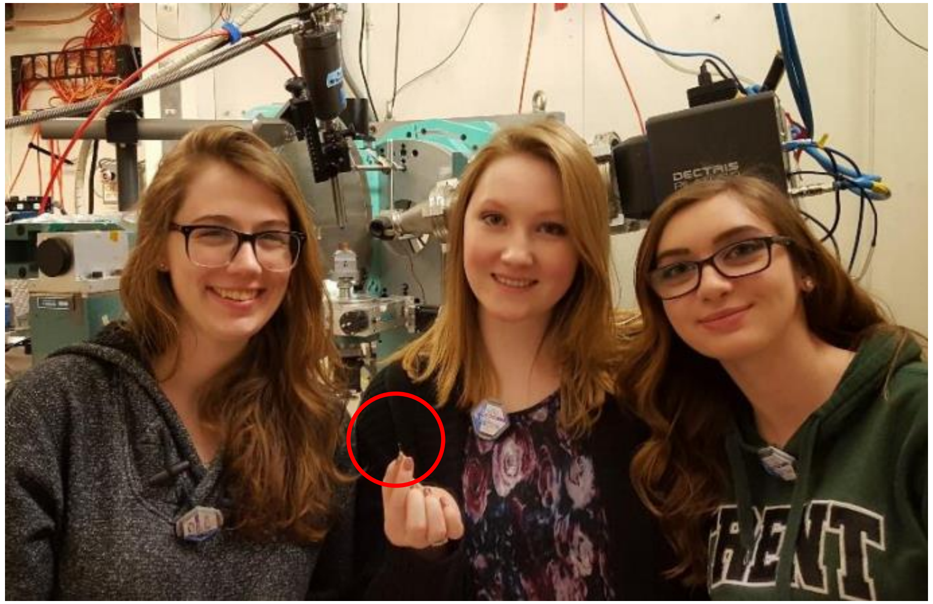
- Electron changes direction, energy is emitted
- Faster electron means higher energy emitted
- X-ray wavelengths can be achieved if electron is moving fast enough
- Synchrotron accelerates electrons, then changes their direction periodically, producing X-rays
- The X-rays are directed towards beamlines



Cornell High Energy Synchrotron Source

- Travelled to Ithaca, NY to use Cornell High Energy Synchrotron Source (CHESS) beamline A2
- 99.9999995% speed of light
- Circumference: 768m
- Week long experiment, with the first day being used to mount the crystal and align the beam properly





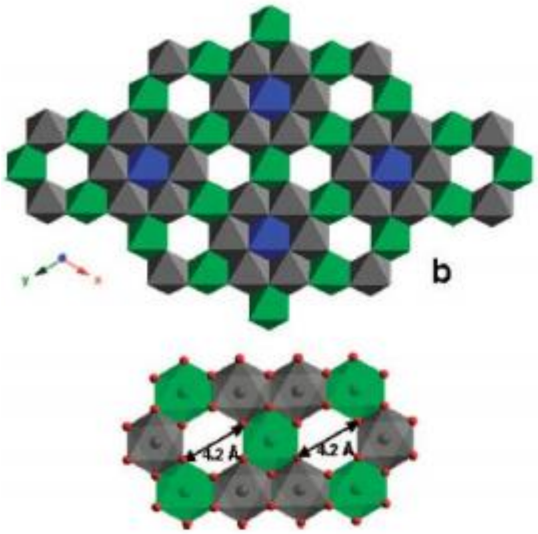
Details of the Experiment

- Beamline A2 can receive electromagnetic radiation of energies 5-70 keV
- Used 23.22 keV, K-edge for Rh
  - Energy required to eject an electron from the innermost shell
- Used liquid nitrogen stream to get sample to ~185K
  - Sometimes the mass would increase too much and sample would move, would need to realign
- Diffraction patterns produced in real-time

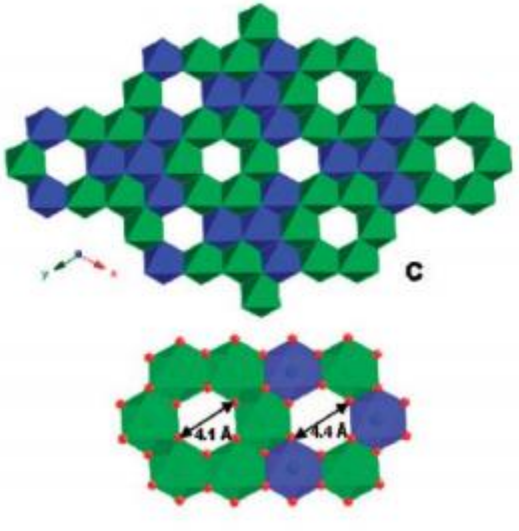
A2	1.5m CHESS Compact Undulator	Resonant & non-resonant scattering; Single crystals & thin films; High-energy powder diffraction and PDF; Reciprocal space mapping; low temperatures and custom sample environments	5-70 keV

Results of the Experiment

- Predicted charge ordering:



High Temperature

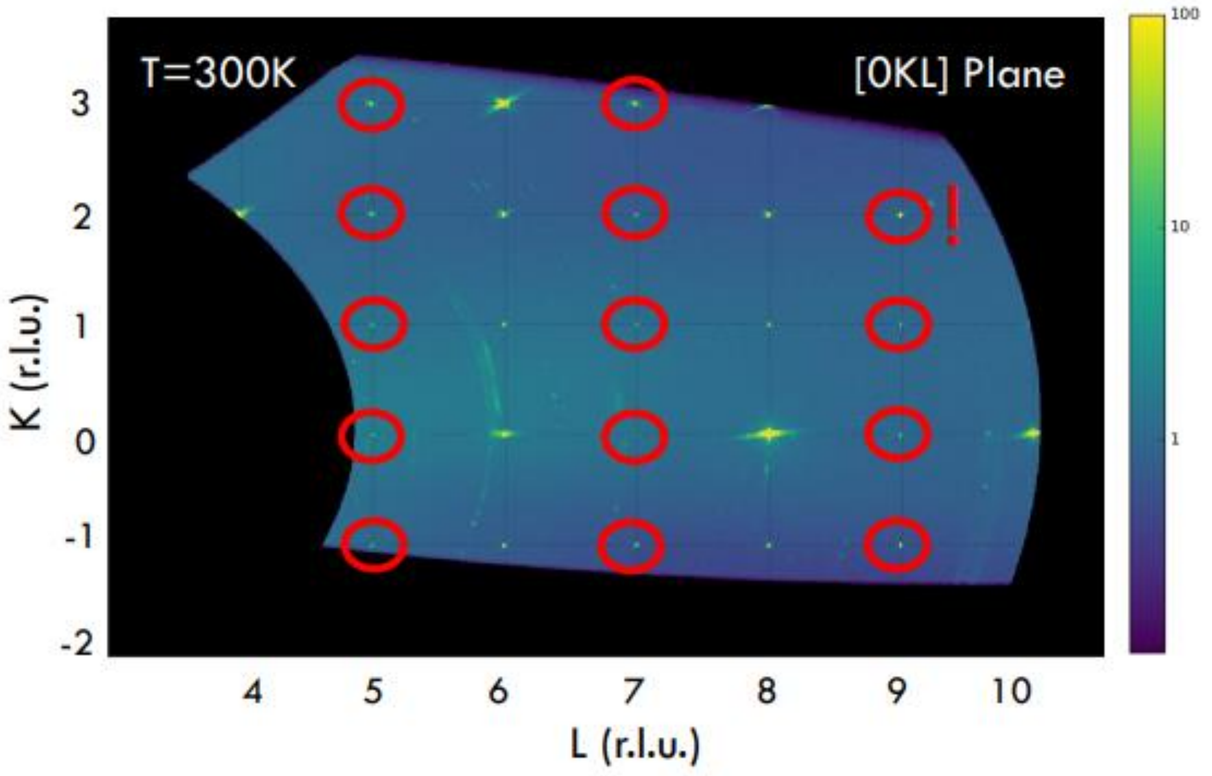


Low Temperature

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

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

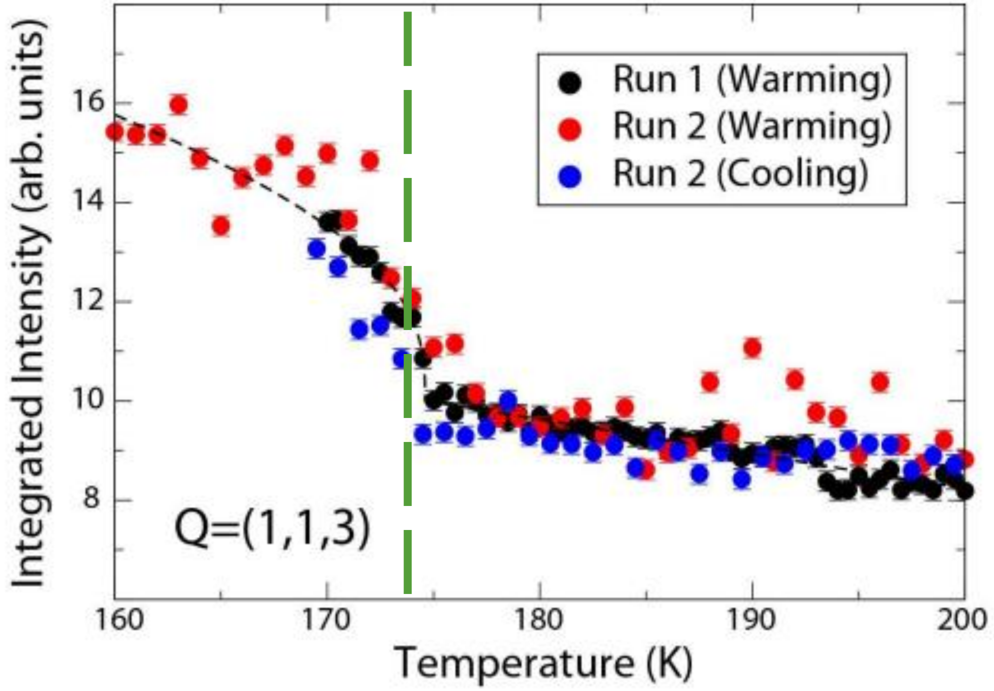
Results of the Experiment



- For the space group $P6_3/mcm$, peaks should only be occurring on this plane (0KL) at 2n
- But structurally forbidden peaks are present both below AND above ~185K
- This suggests that the structure of lead rhodium oxide is more complicated than originally predicted

Results of the Experiment

174.6 ± 1.0K



Results of the Experiment

- Charge ordering seen:

Summary and Conclusions

- Pb3Rh7O15 is the first 4d transition metal oxide candidate for a Verwey Transition, at ~175K
- The structure of lead rhodium oxide is more complex than predicted in 2009, at low and high temperatures
- At low temperatures (~175K), the crystal structure becomes twinned trigonal

Acknowledgments

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