Unconventional metallic osmates

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- Non-centrosymmetric metals: so what’s new?
  1. LiOsO$_3$: Ferroelectric-like structural phase transition driven by entropy
     
  2. Pb$_2$CoOsO$_6$: Multiferroic-like structural phase transition driven by magnetic frustration
Collaborators

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**High pressure synthesis & bulk measurements**

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**Neutron powder diffraction**

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**X-ray diffraction**

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**Convergent beam electron diffraction**

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**High pressure studies of crystal stability**

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**First-principles electronic structure calculations**

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Non-centrosymmetric metals

- Metals which lack spatial inversion symmetry: \( H(\mathbf{r}) \neq H(-\mathbf{r}) \)

- Non-centrosymmetric superconductors:
  - e.g. CePt\(_3\)Si, Li\(_2\)Pd\(_3\)B, NbReSi, LaNiC\(_2\), etc

States do not have well-defined parity;

can have mixed spin-singlet and spin-triplet superconducting pairing
Non-centrosymmetric metals

- Bands split by Dresselhaus–Rashba antisymmetric spin-orbit coupling:

\[ H_{SO} = \alpha (\nabla V \times \mathbf{k}) \cdot \mathbf{s} \]

Spin changes direction around the Fermi surface

- Physical consequences:
  - optical activity
  - anisotropic thermopower
  - skyrmions
  - Weyl semi-metals

~ 30 non-centrosymmetric metals, of which only 3 are oxides

Osmium oxide compounds

- Chemically highly versatile
- Stable oxides: OsO$_2$, OsO$_4$
- Examples:
  - KOs$_2$O$_6$ (Os$^{5.5+}$, 5$d^{2.5}$) Superconductor ($T_c = 9.5$ K)
  - Ba$_2$NaOsO$_6$ (Os$^{7+}$, 5$d^1$) FM insulator with moment $\sim 0.2 \mu_B$
  - Cd$_2$Os$_2$O$_7$, NaOsO$_3$ (Os$^{5+}$, 5$d^3$) Slater-type (?) metal-insulator transitions
1. LiOsO$_3$

Phase transition at 140 K

LiOsO$_3$

Powder neutron diffraction on WISH, ISIS

- Continuous phase transition
- Strain is secondary order parameter → primary order parameter is symmetry-breaking
- Primary structural instability is a shift in the Li ions by 0.5 Å along $c$
- Loss of centre of symmetry and formation of ‘polar’ axis below $T_s$ (R-3c → R3c)
- No evidence for magnetic order
Convergent-beam electron diffraction observed and simulated for R-3c and R3c structures.
Calculated electronic structure

DFT-GGA (WIEN2K)
• First-order structural transitions can involve only strain

• Second-order structural transitions usually involve a change in internal symmetry other than mere strain

\[ F = F_0 + \frac{1}{2} aP^2 + \frac{1}{4} bP^4 + \frac{1}{2} \lambda \epsilon P^2 + \frac{1}{2} C_{el}\epsilon^2 \ldots \]

• To be classed as a "ferroelectric metal", the phase transition must:
  (i) be continuous
  (ii) involve loss of inversion symmetry
  (iii) be accompanied by appearance of a polar axis

• Previous candidate "ferroelectric metals" (subsequently dismissed):
  \((V_3Si, Nb_3Sn)\quad Cd_2Re_2O_7\quad BaTiO_{3-\delta}\)
Ferroelectricity in LiNbO$_3$, LiTaO$_3$ (and LiOsO$_3$)

LiNbO$_3$: $T_s = 1480$ K
LiTaO$_3$: $T_s = 940$ K
LiOsO$_3$: $T_s = 140$ K

$T > T_s$ (R-3c) $T < T_s$ (R3c)

Abrahams et al., JPCS 34, 521 (1973)
LiOsO$_3$ Summary

- Order–disorder transition drives structural transition
- “Ferroelectric metal” à la Anderson & Blount
- Possible because polar displacements of Li almost entirely decoupled from conduction states on Os & O
2. \( \text{Pb}_2\text{CoOsO}_6 \)
Monoclinic crystal system

\[ a = 5.64, \quad b = 5.58, \quad c = 7.82 \text{ Å}, \quad \beta = 89.8^\circ \]

centrosymmetric space group \( P2_1/n \)

Double perovskite: \( A_2B B'O_6 \)
Spin-polarised bands from DFT in GGA

c.f. localized states:

Co\(^{2+}\) (3\(d^7\))
Os\(^{6+}\) (5\(d^2\))

\(t_{2g}\)
\(e_g\)

\(e_g\)
\(t_{2g}\)
• Single magnetic transition
  simultaneous order of Co & Os

• Magnetic structure is frustrated
  (no inversion symmetry)

• Magnetic order is coupled to lattice
  removes crystal centre of symmetry
  \( P2_1/n \rightarrow Pn \)

- Propagation vector \( \mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2}) \)
Pb$_2$CoOsO$_6$ Summary

- Magnetic frustration drives structural transition to non-centrosymmetric structure
- Analogous to a type-II multiferroic transition
- Both Os and Co states contribute to Fermi level