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Prediction of ferroelectric order in $PbCrO_3$

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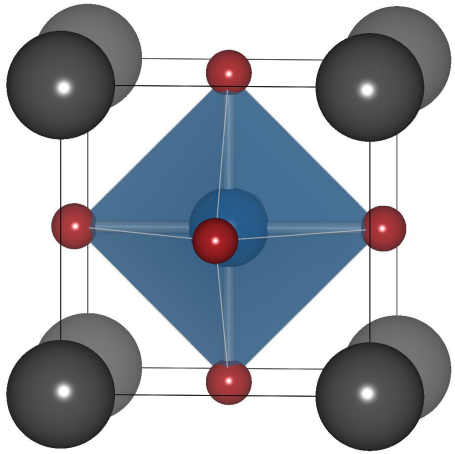
$PbCrO_3$ – an introduction



- perfect cubic perovskite
  G-type antiferromagnet

Roth, DeVries, *J. Appl. Phys.* **38** (1967), 951

- semiconductor

Chamberland, Moeller, *J. Solid State Chem.* **5** (1972), 39

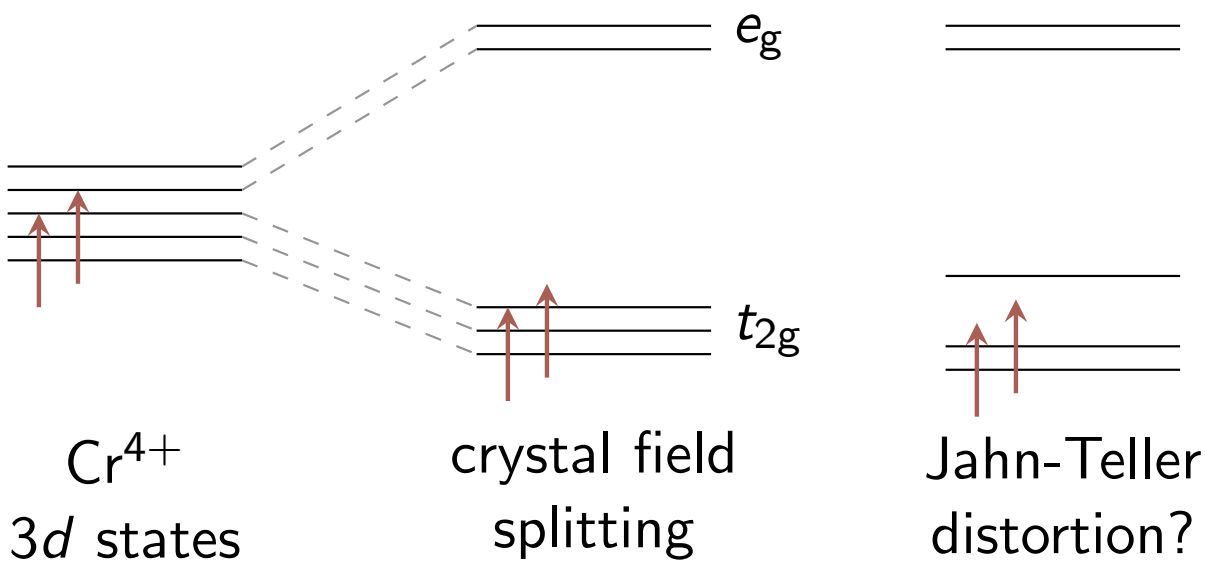
- large volume collapse

Xiao, *et al.*, *PNAS* **107** (2010), 14026

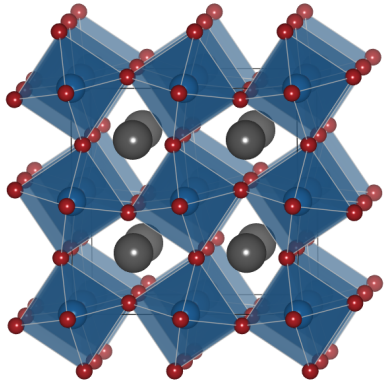
- spin reorientation
  weak ferromagnetism

Arévalo-López, *et al.*, *Inorg. Chem.* **48** (2009), 5434

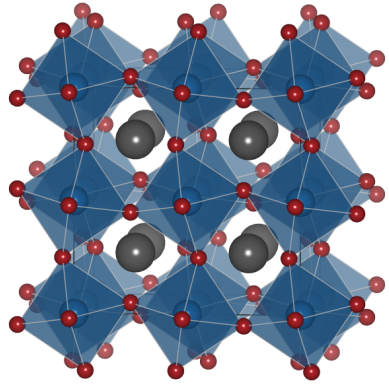
Semiconducting ground state?



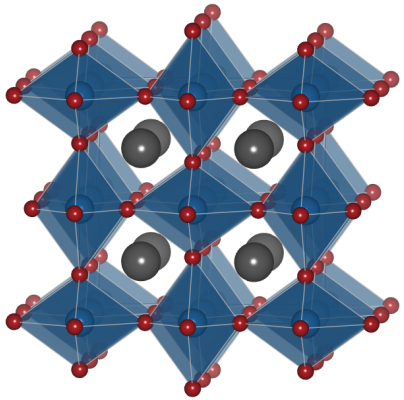
Distortions of the oxygen octahedra



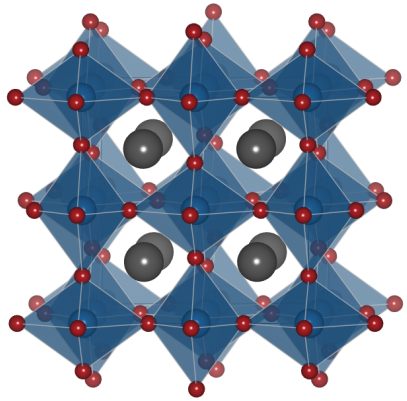
M_3^+ $a^0a^0c^+$



R_4^+ $a^0a^0c^-$



M_2^+ $a^0a^0c^0$



R_3^+ $a^0a^0c^0$

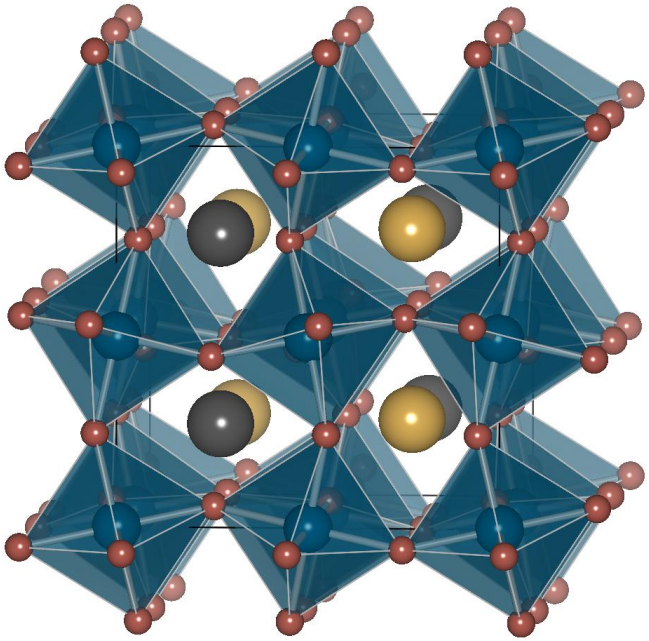
42 space groups

Carpenter, Howard, *Acta Cryst. B* **65**, 134 (2009)

Computational setup

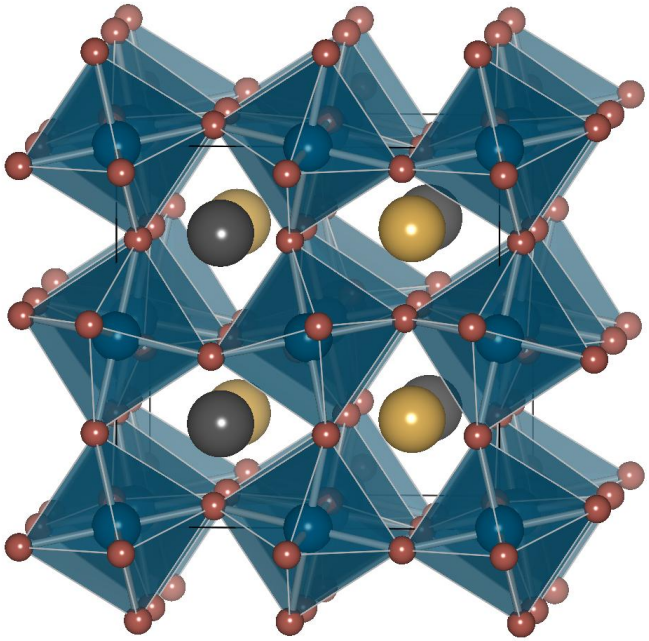
- PBE+U approach, Cr d states: $U = 4\,\text{eV}$, $J = 1\,\text{eV}$
- relaxed structure with HSE hybrid functional
- $8 \times 8 \times 8$ **k**-point mesh
- plane-wave cutoff 600 eV
- fix to experimental volume

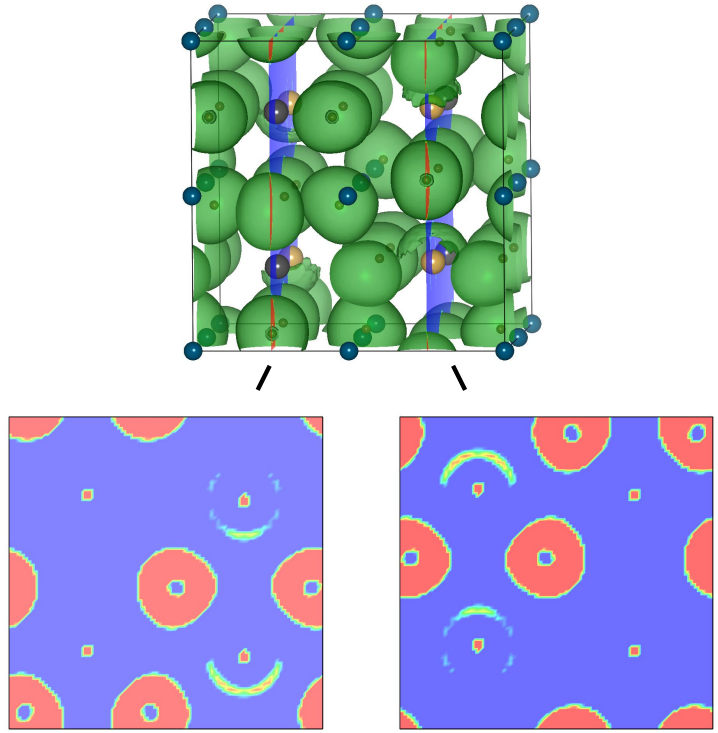
Ground-state structure



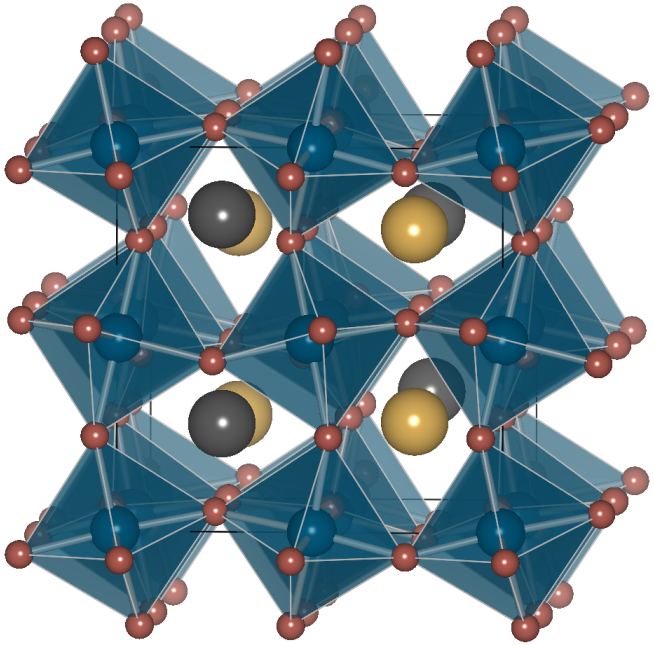
- $a^+a^+c^- \Rightarrow c/a = 0.995$
- Cr t_{2g} states filled
- charge-order of Pb^{2+} and Pb^{4+}
- antipolar shift of Pb^{2+}

Ground-state structure



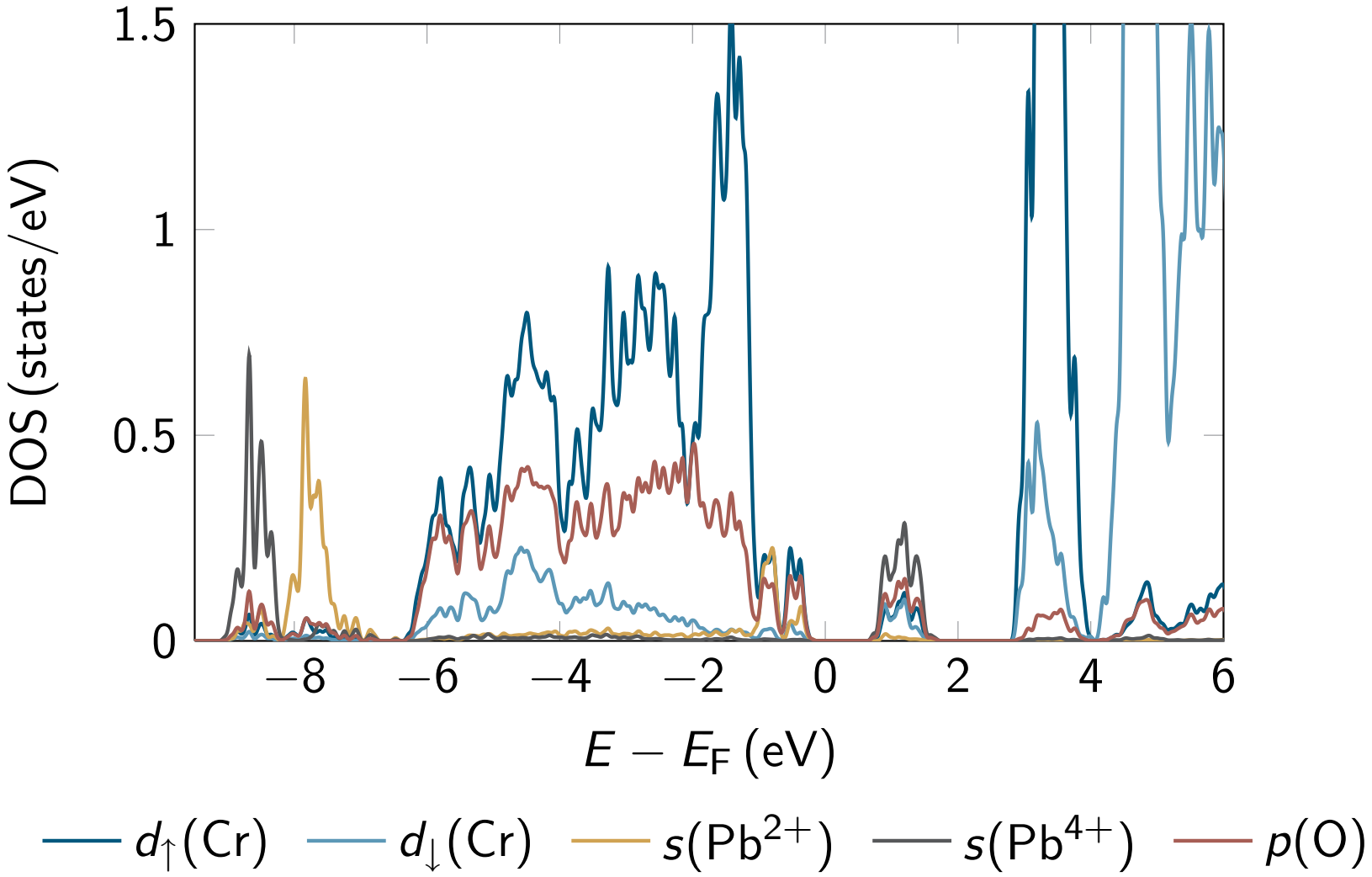


Ferroelectric order possible?

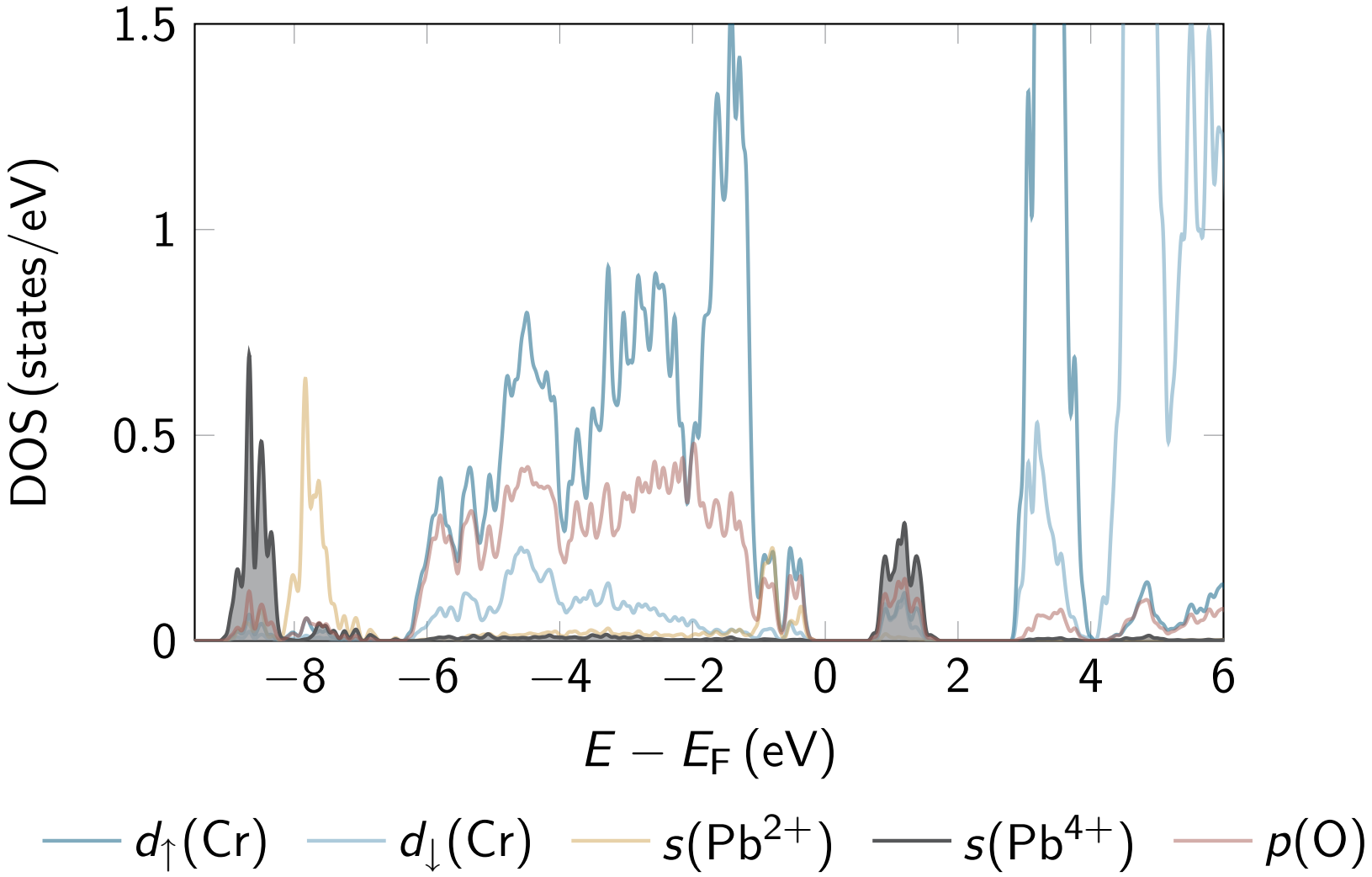


- tilting of octahedra $a^+a^+c^-$
- almost cubic $c/a = 0.998$
- polar displacement of Pb ions
- polarization $20.8\,\mu\mathrm{C/cm^2}$
- Cr ions in center of octahedra

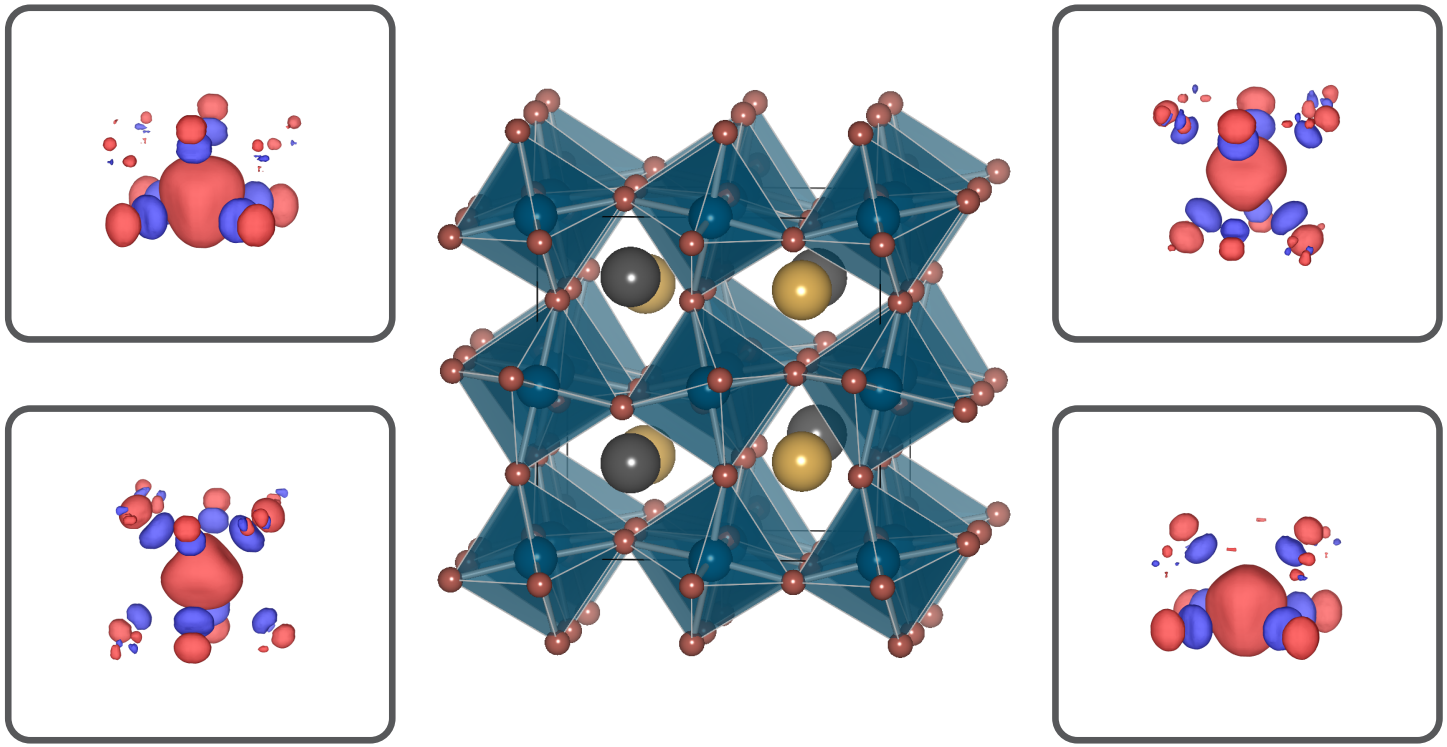
Atom resolved DOS



Atom resolved DOS

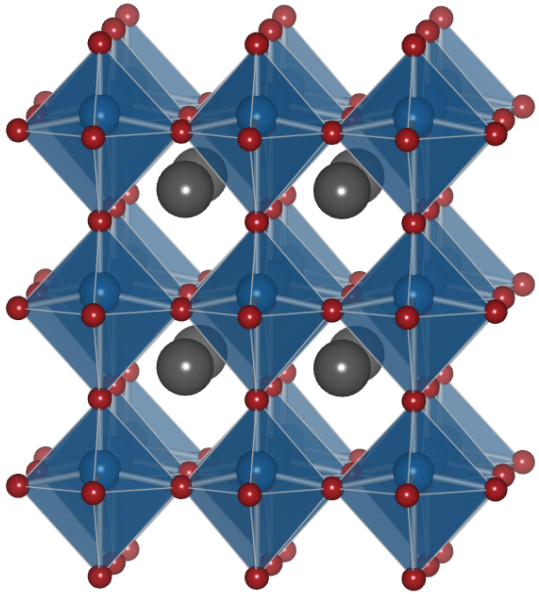


Charge order: Pb^{2+} vs. Pb^{4+}



What about the U dependence?

At small U different ground state!



- JT elongation out of plane
- checkerboard JT in plane
- polar displacement of Pb and Cr
- polarization 54 μC/cm^2
- large c/a ratio
- analogy to $PbVO_3$

Conclusions

- semiconducting states in $PbCrO_3$ identified
- two competing structures depending on size of U
- both allow for polar displacements

1. empty Pb orbitals hybridize
2. analogy to $PbVO_3$