Theoretical study of Ag- and Au-filled skutterudites.

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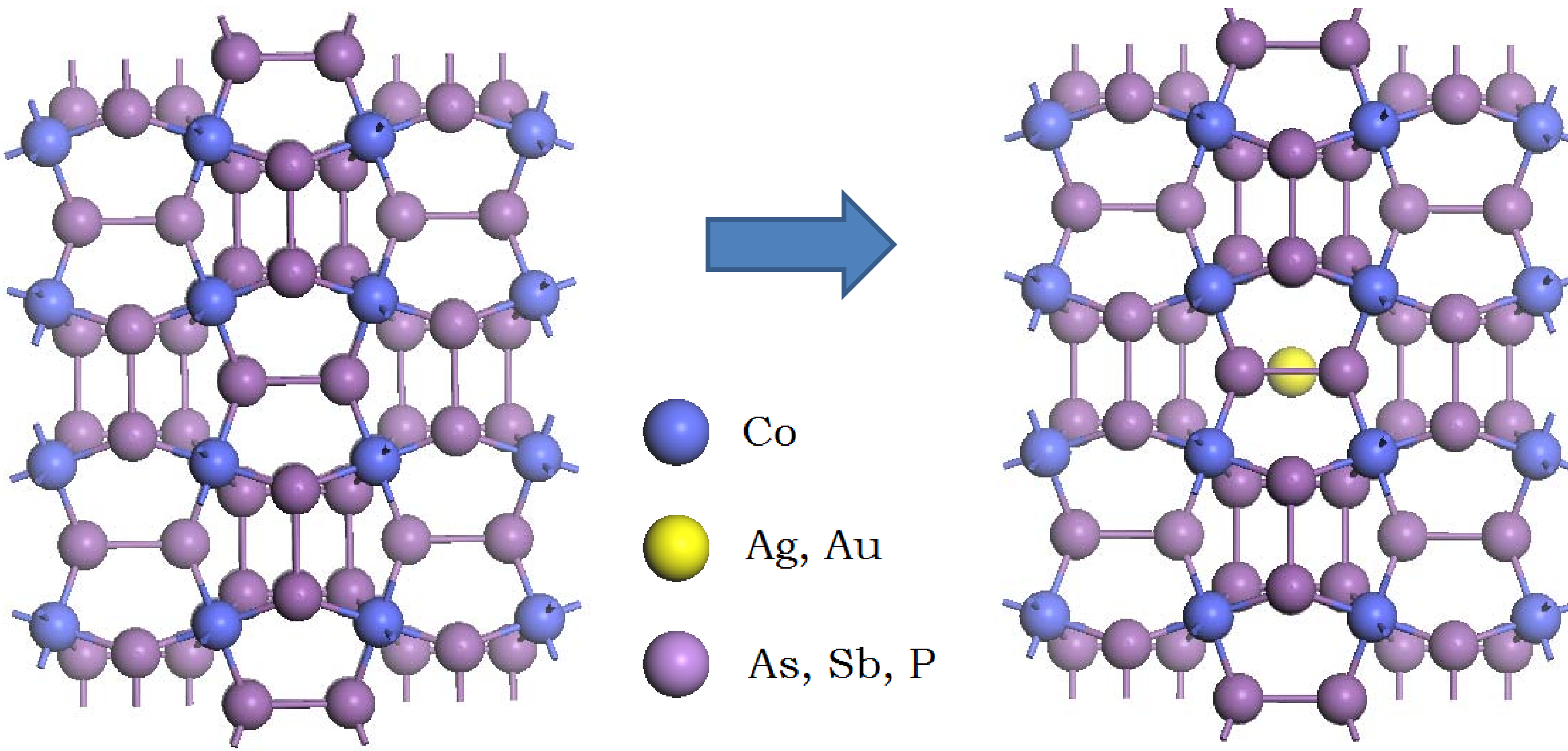
Goal of project.

To study the effect of Ag- and Au- filling in Co-based skutterudites, $CoAs_3$, $CoSb_3$, and CoP_3.



Why Ag, Au?

Light element filling has been of interest in recent years, and some studies have shown increased electrical performance in Na- and Ba- filled compounds.

Studies suggest that enhanced electrical properties are the cause, due to hybridization of s-orbitals of light elements with valence orbitals of Co.

Comparison of fillers.

	In	Na	La	Ag	Au
Radius (Å)	2	2.23	2.47	1.75	1.79
Weight (amu)	114.8181	22.98977	138.9055	107.8682	196.9665
Electronic configuration	[Kr] $4d^{10}5s^2p^1$	[Ne] $3s^1$	[Xe] $5d^16s^2$	[Kr] $4d^{10}5s^1$	[Xe] $5d^{10}6s^1$

We hypothesize that these elements will interact electronically in a similar way to light elements, with additional effects caused by d-shell electrons.

Possible implications for thermal conductivity due to weight of atoms.

Computational details.

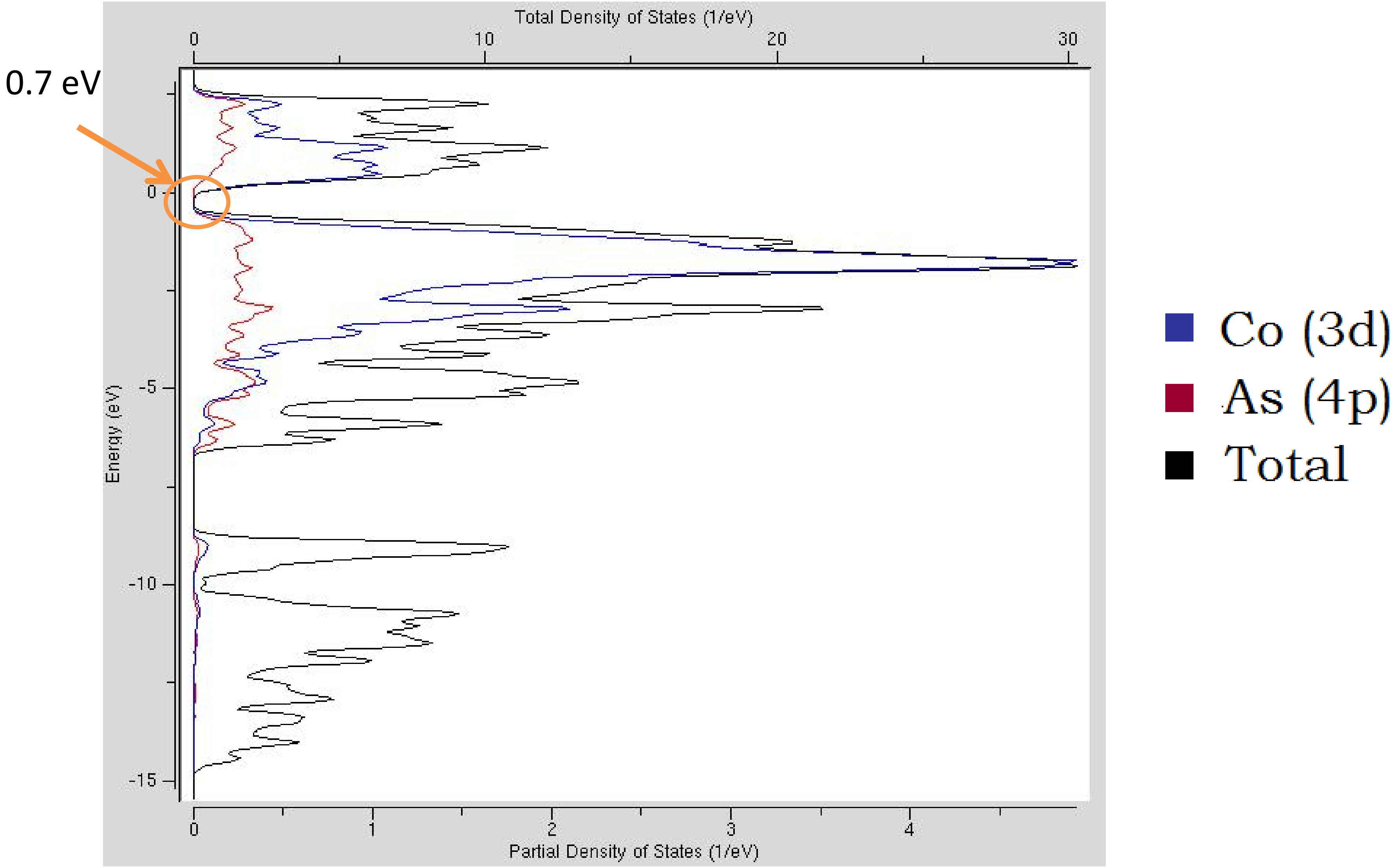
Used PAW method as implemented in *ab initio* DFT VASP.

PBE-GGA XC potential

20x20x20 k-point meshes
30x30x30

Emulated temperature by setting the electronic temperature for the electrons using Fermi smearing.

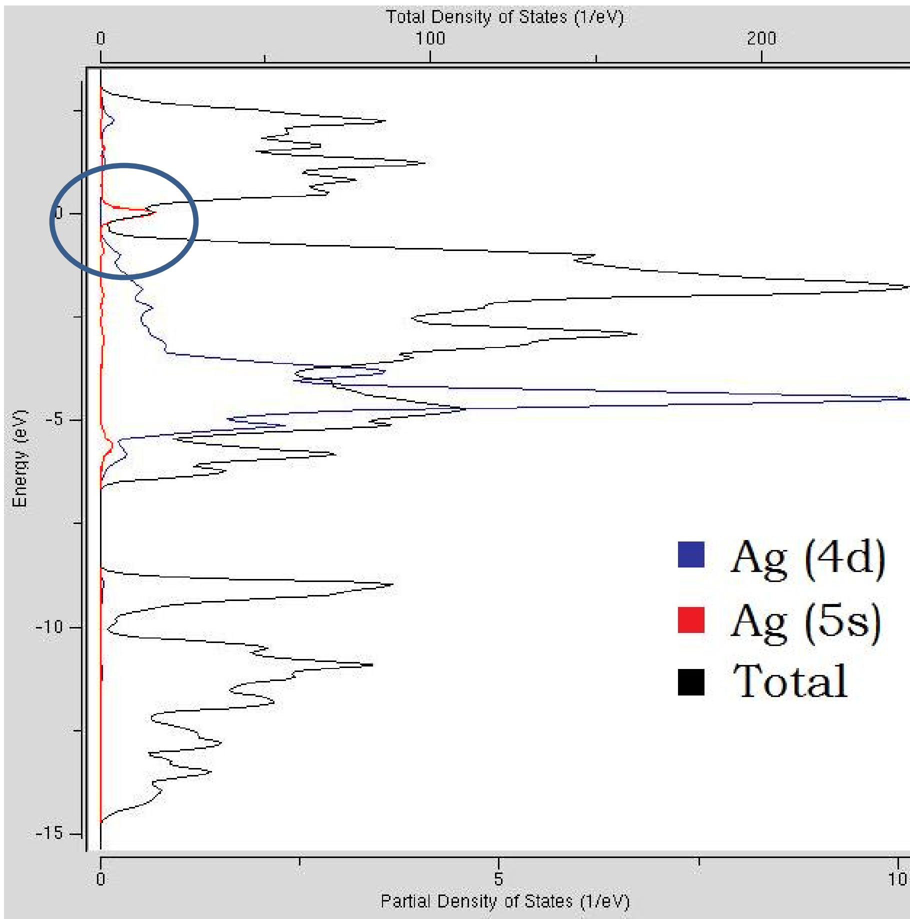
Electronic contributions to DOS.

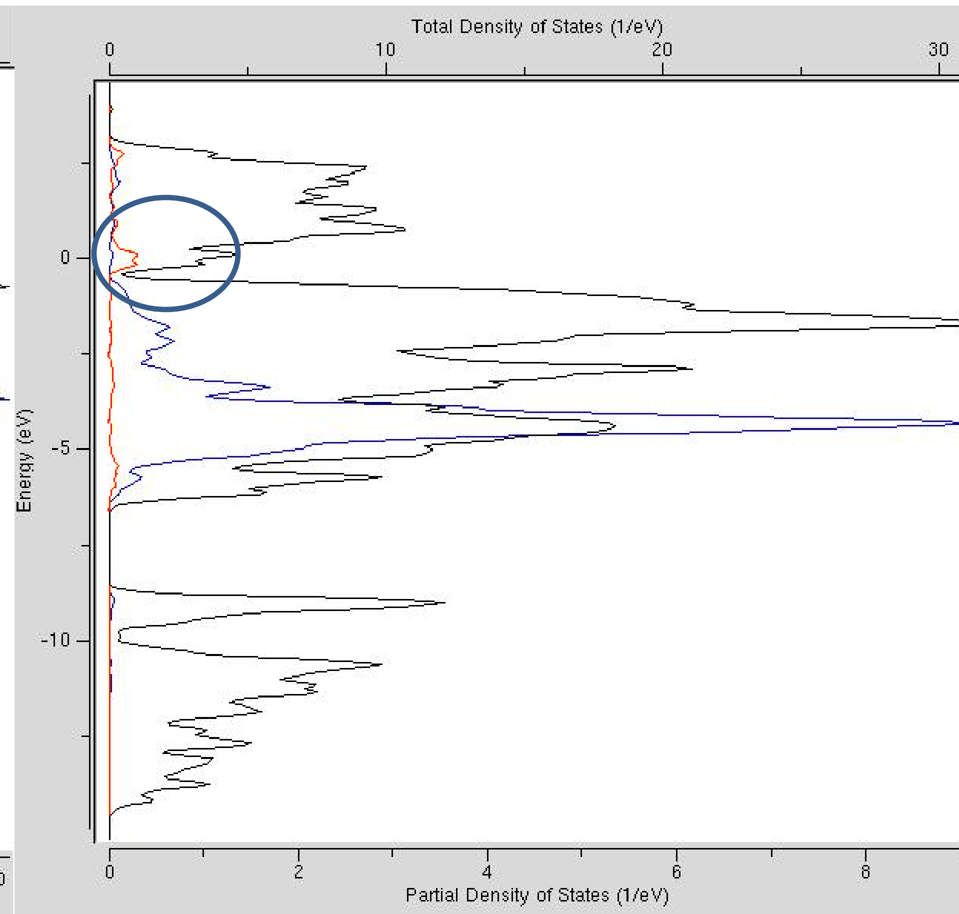


Electronic contributions to DOS.

25 % filled (Ag)

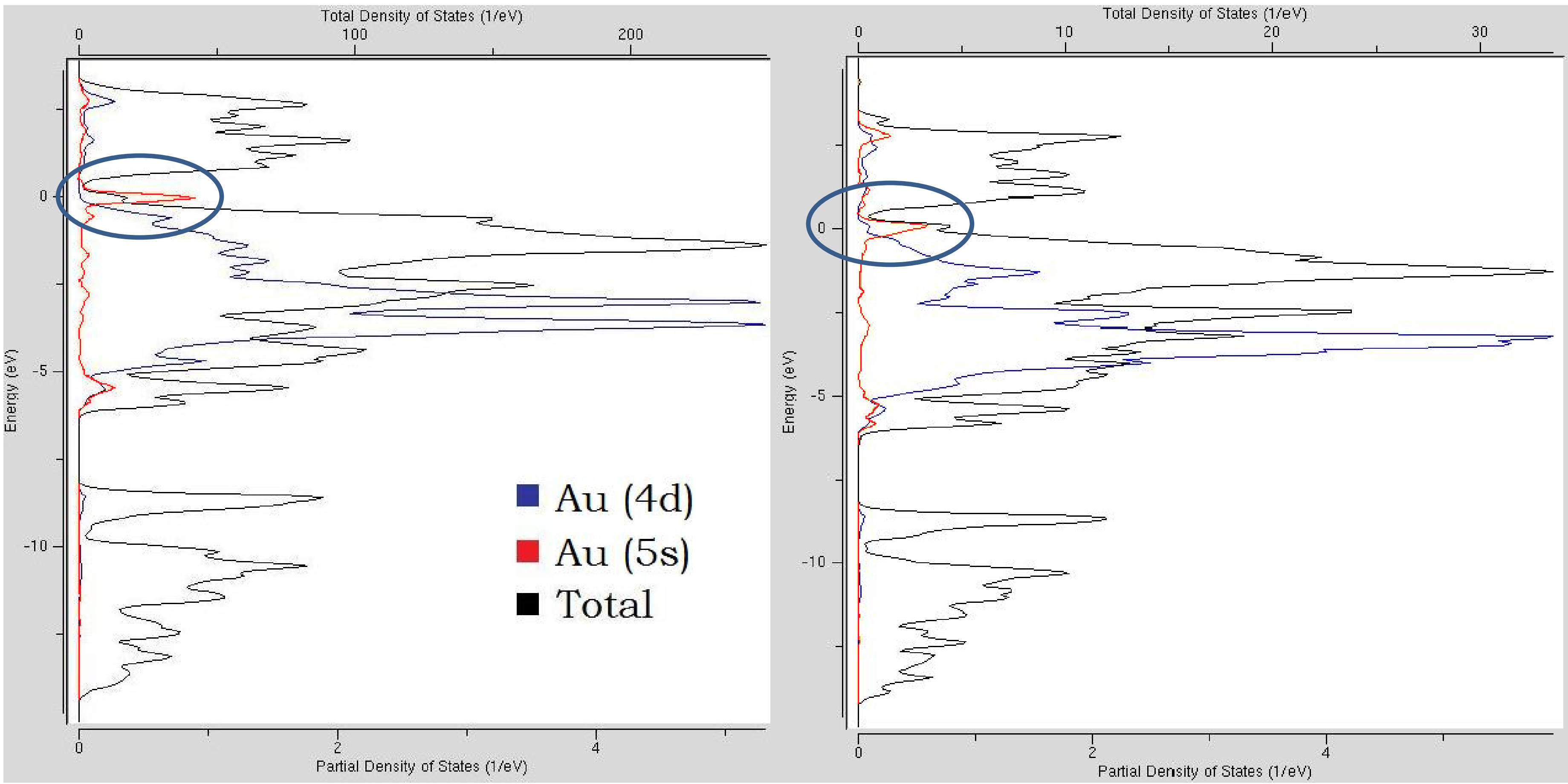
100 % filled (Ag)



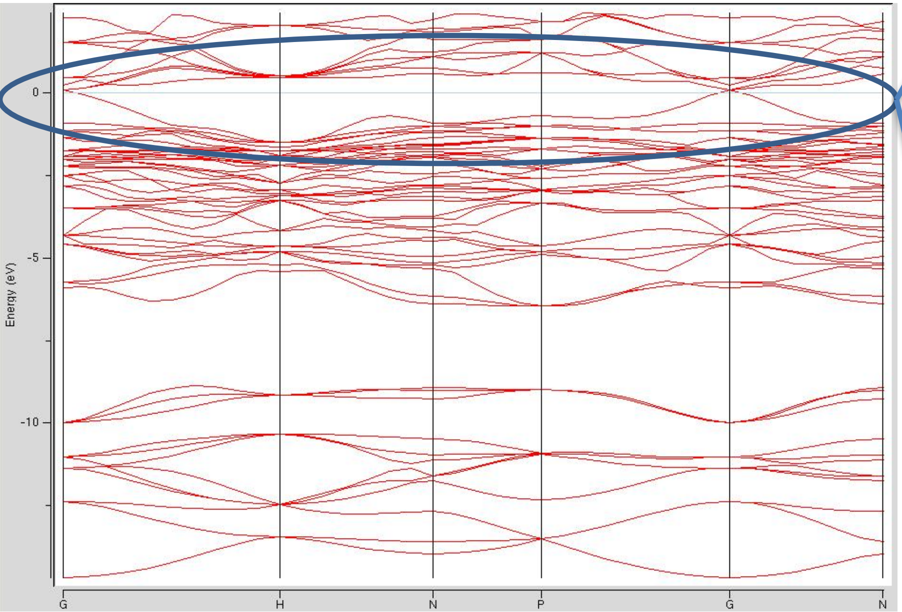


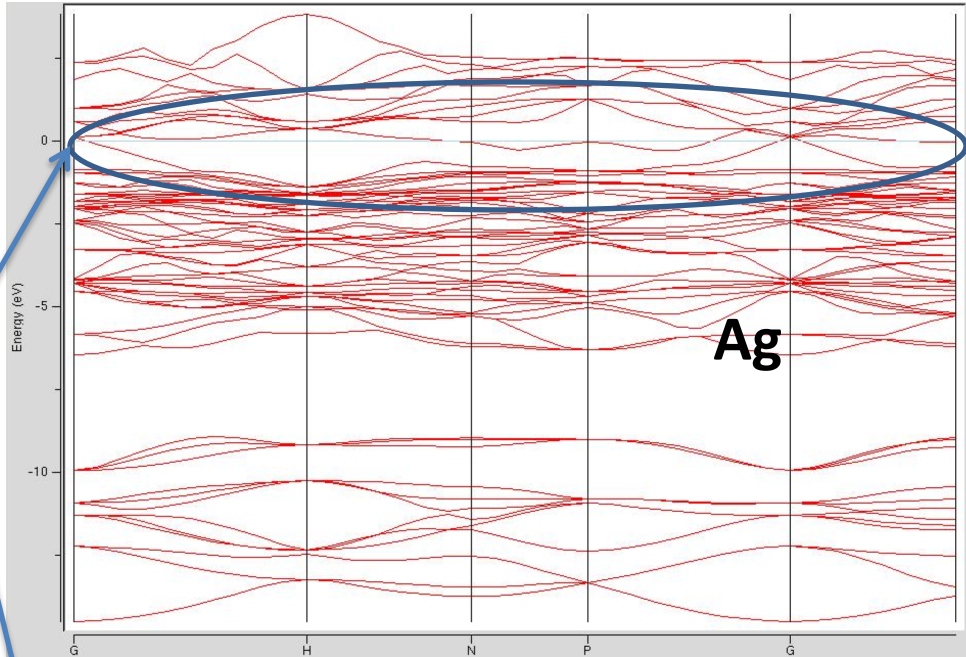
Electronic contributions to DOS.

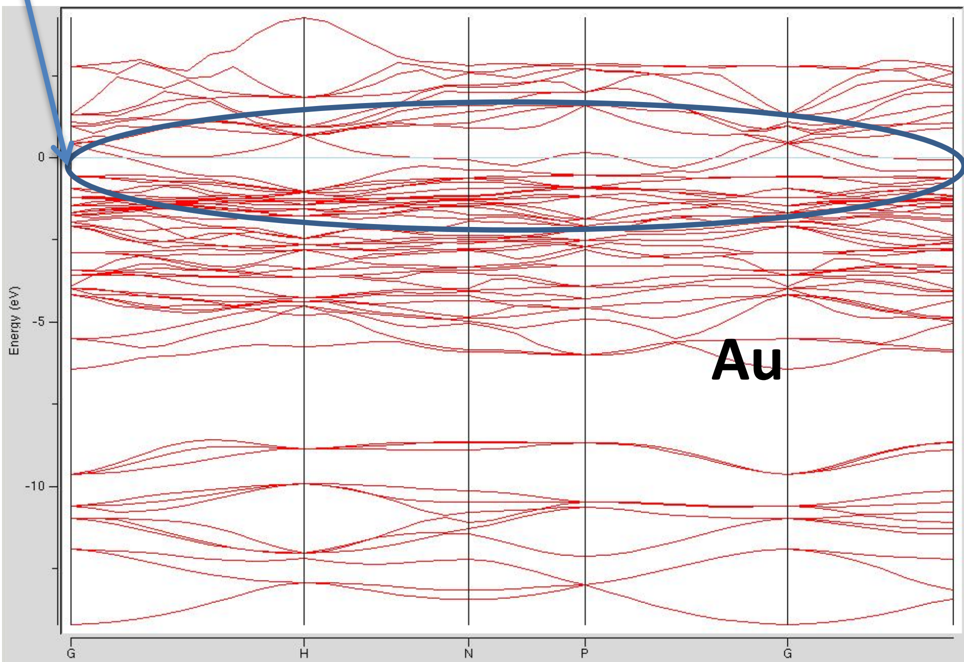
25 % filled (Au) | 100 % filled (Au)



Band structure calculations.



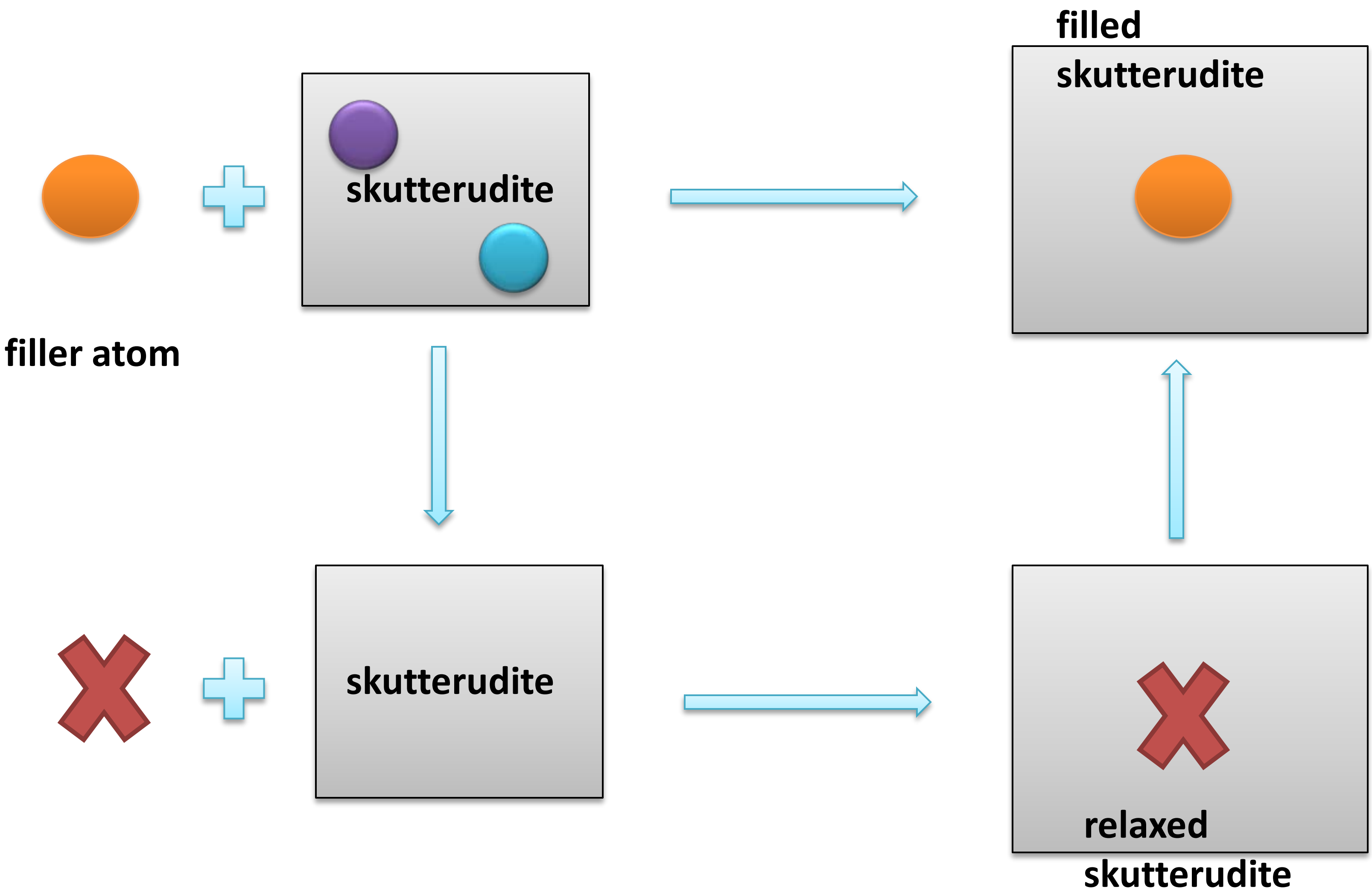




Transition to negligible (<.05 eV) band gap.

Increased population around the fermi level.

Energy calculations.



Energy calculations.

- Filled skutterudite is always more (As, Sb, P) stable in energy, for all filling fractions.

- The only barrier to filling fraction should be the need for charge compensation (achieved with doping).

Theoretical methods for calculating σ, S.

"dark" electrical conductivity can be calculated from first principles

$$\sigma_{\alpha\beta}(T,E_F)=\frac{1}{\Omega}\int\sigma_{\alpha\beta}(\varepsilon)\left[\frac{\partial f_{E_F}(T;\varepsilon)}{\partial\varepsilon}\right]d\varepsilon$$

energy dependent σ can be determined from

$$\sigma_{\alpha\beta}(\varepsilon)=\frac{1}{N}\sum_{i,k}\sigma_{\alpha\beta}(i,k)\frac{\delta(\varepsilon-\varepsilon_{i,k})}{d\varepsilon}$$

$$\boxed{\sigma_{\alpha\beta}(i,k)=e^2\tau_{i,k}\upsilon_\alpha(i,k)\upsilon_\beta(i,k)}$$

Equations obtained from Madsen, GKH. J. AM. CHEM. SOC. 2006, 128, 12140-12146

Theoretical methods for calculating σ, S.

Seebeck coefficient (S) and electronic contribution to thermal conductivity (κ_e) are related to the electrical conductivity through:

$$\nu_{\alpha\beta}(T,\mu) = \frac{1}{eT\Omega}\int \sigma_{\alpha\beta}(\varepsilon)(\varepsilon-\mu)\left[\frac{\partial f_{\mu}(T;\varepsilon)}{\partial\varepsilon}\right]d\varepsilon$$

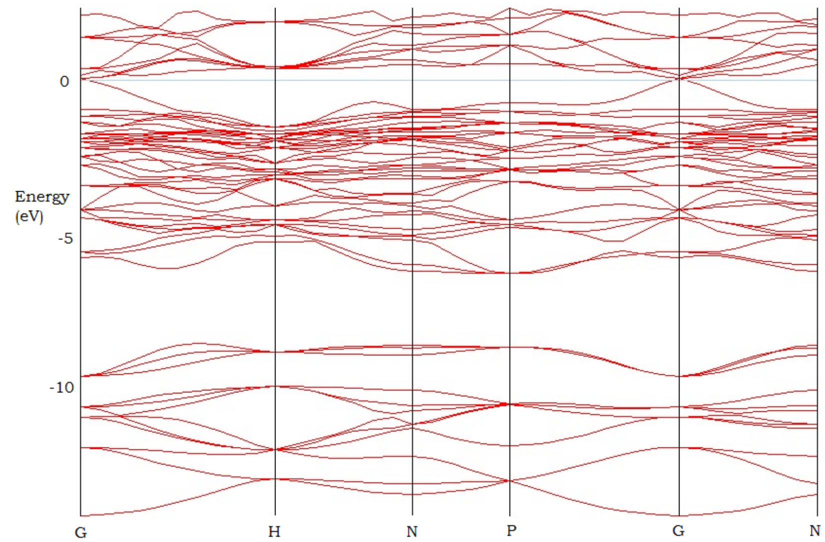
$$S = \sigma^{-1}\nu$$

$$\kappa_e = \sigma L_0 T$$

Determining the group velocities.

Energy-dependent equation

$$\upsilon_k = \frac{1}{\hbar}\frac{\partial \varepsilon_k}{\partial k}$$

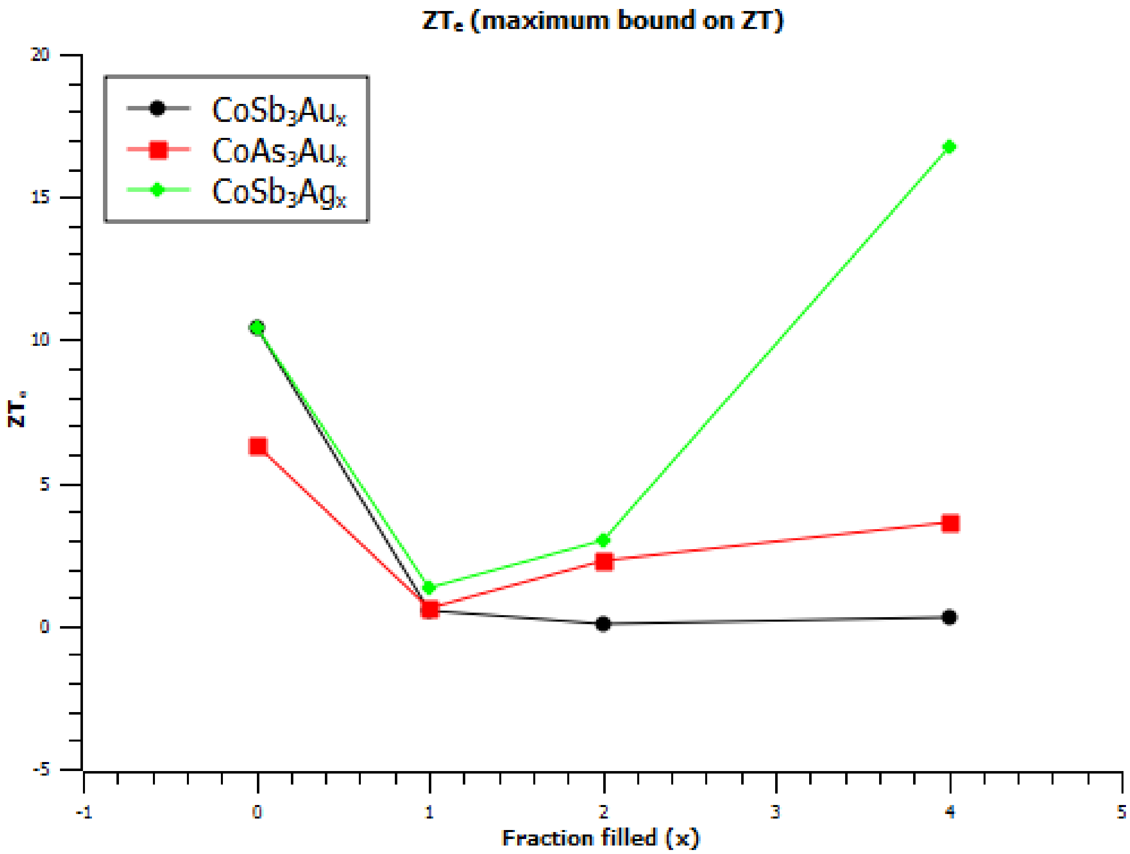


Expansion in terms of wave functions and momentum operator

$$\upsilon_k = \frac{1}{m}\langle \psi | \hat{p} | \psi \rangle$$

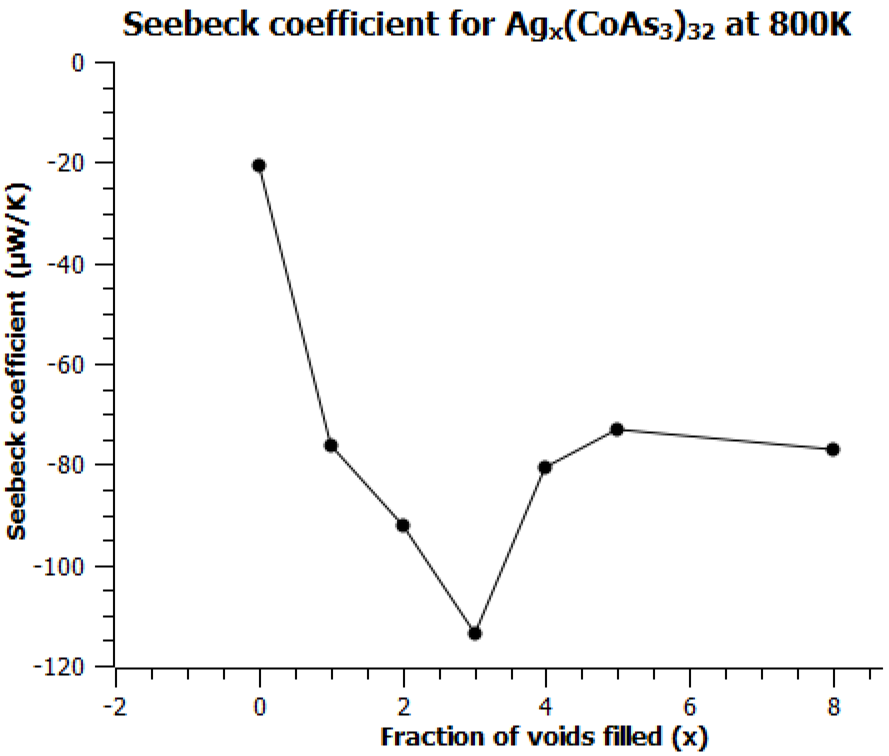
Equation from: Scheidemantel, Ambrosch-Draxl, et al. *Physical Review B* 68, 125210 (2003)

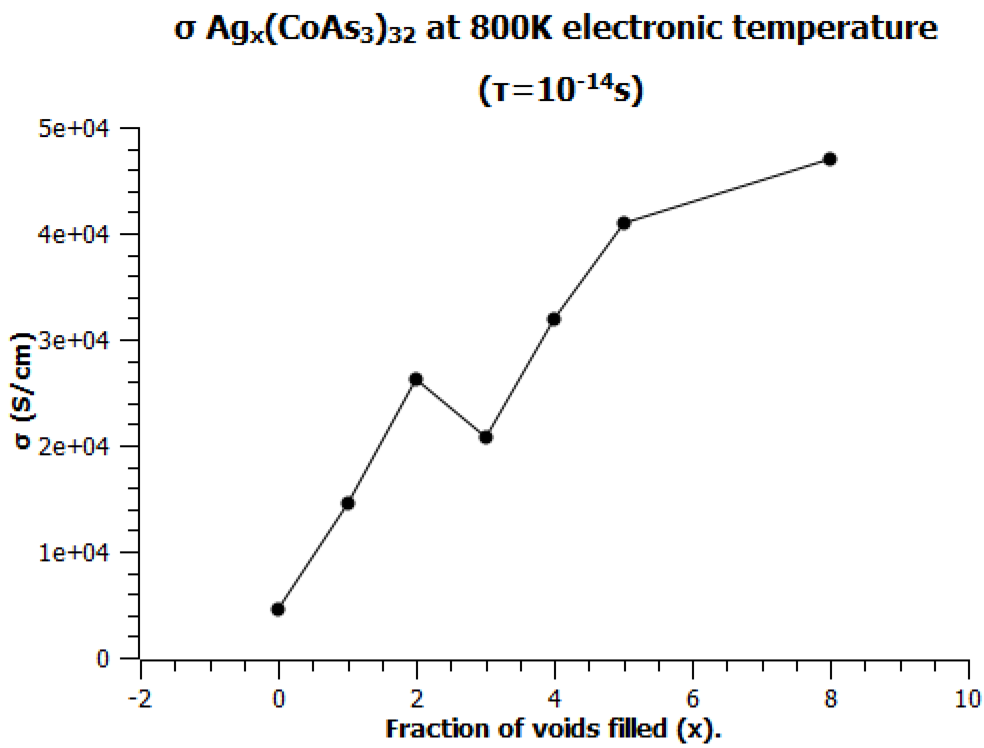
Quick sweep to test effects of Ag, Au.



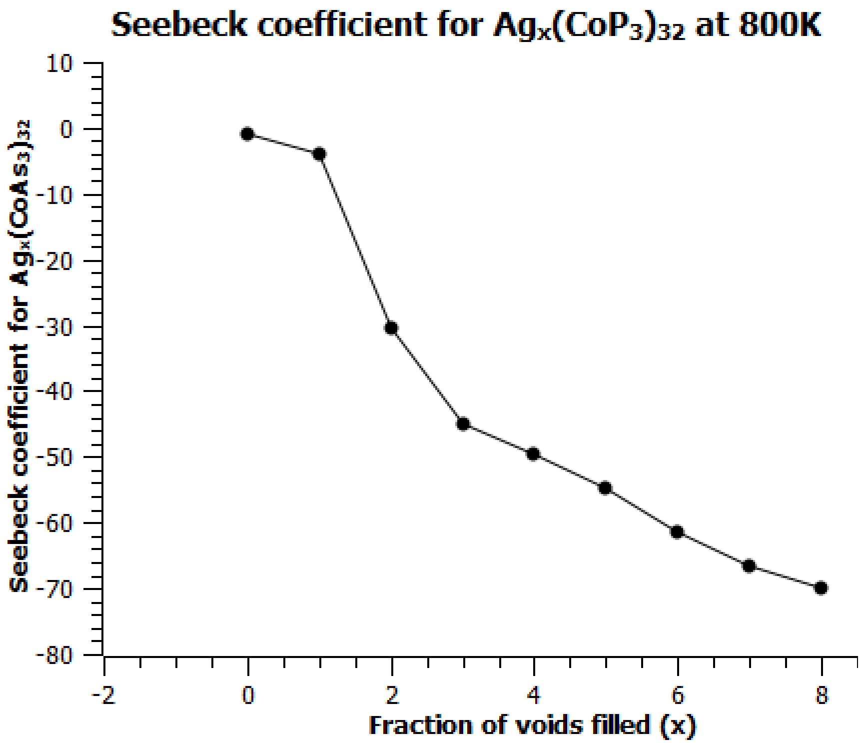
$$ZT_e = \frac{S^2\sigma}{\kappa_e}$$

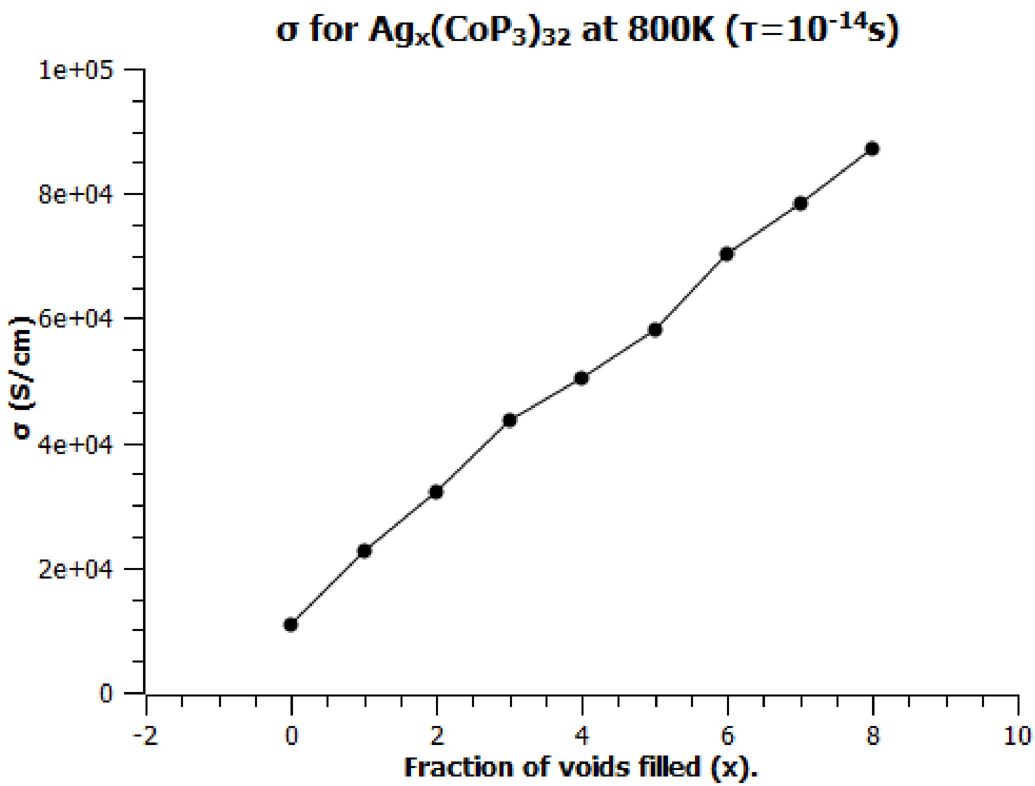
Electronic properties at 800K: $CoAs_3$.





Electronic properties at 800K: CoP_3.





Summary and Future Work

- A significant improvement in electrical properties is observed for Ag-filling of CoP_3, and possibly for $CoAs_3$ as well, but not for $CoSb_3$.
- Au does not seem to have the same effect.
- We suspect this may have to do with hybridization of s- electrons in Ag but not in Au.
- Our calculations find slightly n-type $CoAs_3$ and CoP_3 which is contradicted by experimental findings.
- A method that corrects this error (such as hybrid functionals or the GW method in VASP) will be used to determine if this can improve prediction of band gap and thus, electronic properties.

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