Light-induced metastability in the wide-gap ZnO and CuGaSe$_2$
caused by anion vacancies

STEPHAN LANY, National Renewable Energy Laboratory, Golden, CO 80401, ALEX ZUNGER, National Renewable Energy Laboratory, Golden, CO 80401 — First-principles electronic structure calculations [1] show that anion vacancies in II-VI and chalcopyrite I-III-VI$_2$ semiconductors are a class of intrinsic defects that can produce metastable behavior and persistent photoconductivity (PPC), arising from a pronounced coupling between electronic and structural degrees of freedom. In ZnO, $V^0_O$ has a deep localized donor state in the gap, while $V^{2+}_O$ has a shallow level near the CBM. Illumination excites $V^0_O$ to $V^+_{O}+e$ and to $V^{2+}_O+2e$, and this transition is accompanied by large lattice relaxation. The latter state is metastable and acts as a shallow donor, leading to persistent electron photoconductivity (n-type PPC), which persists until it is thermally activated into the deep $V^0_O$. Comparing the behavior of the anion vacancy in the wide-gap chalcopyrite CuGaSe$_2$ to that in ZnO, we find an interesting asymmetry: $V_{Se}$ produces persistent hole photoconductivity in p-CuGaSe$_2$, constituting the unusual case where a donor-like defect creates p-type PPC.