Electronic structure of Cu$_{2-x}$S and related compounds

PAVEL LUKASHEV, WALTER R. L. LAMBRECHT, Case Western Reserve Univ., TAKAO KOTANI, MARK VAN SCHILFGAARDE, Arizona State Univ. — Chalcosite Cu$_2$S and digenite Cu$_{1.8}$S are possibly interesting semiconductors for photovoltaic applications. Their electronic structure is poorly understood because their crystal structure is complex. It consists of a close-packed lattice of S with mobile Cu occupying various types of interstitial sites with a statistical distribution depending on temperature. As a starting point for understanding these materials, we investigated the simpler antifluorite structure. Both local density approximation (LDA) and self-consistent quasiparticle GW calculations with the full-potential linearized muffin-tin orbital method give a semimetallic band structure with the Fermi level pinned at a degenerate Cu-$d$ band state at Γ. A random distortion of the Cu atoms from the perfect antifluorite positions inside each S cage is found to break the degeneracy of the $d$ state at Γ and thus opens up a small gap of about 0.1 eV in LDA. The experimental evidence for a semiconducting gap of about 1 eV is critically examined. To gain further insight into the Cu $d$ and $s$-band shifts beyond LDA, we considered other Cu compounds such as Cu$_2$O and CuBr. We compare their LDA and GW band structures and determined the effective masses and Kohn-Luttinger Hamiltonian parameters for CuBr.