

Structural and Electronic Properties of Copper Sulfides

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Chalcosite Cu_2S 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 antiferite 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 Gamma point. A random distortion of the Cu atoms from the perfect antiferite positions inside each S cage is found to break the degeneracy of the d state at Gamma point and thus opens up a small gap of about 0.1 eV in LDA. Supercell models were constructed for the cubic and hexagonal phases with the Cu positions determined by a weighted random number generator so as to obey the statistically observed distribution over different Wyckoff sites. The low temperature monoclinic phase, which can also be considered as a supercell of the hexagonally closed packed phase, was also studied. All these models gave negligibly small band gaps. Some simpler hexagonal model structures gave slightly larger band gap models but were found to be unstable. The optical absorption data all show a strong intraband absorption compatible with our nearly zero band gap in spite of previous assignments of these materials as having bandgaps of order 1 eV.