

substance: chalcogenides of Co, Rh, Ir

property: crystal structure, chemical bond, general characterization

All the known cobalt chalcogenides are metallic. The pyrite phases that form with CoX_2 , RhX_2 or IrX_2 are metallic, but cation-defect pyrites $\text{Rh}_{2/3}\text{X}_2$ and $\text{Ir}_{2/3}\text{X}_2$ are semiconducting. These contain low-spin Rh(III) or Ir(III) in octahedral sites. - Similarly, the semiconducting phases RhX_2 and Ir_2X_2 have an orthorhombic structure in which half the chalcogenides belong the polyanion $(\text{X}_2)^{2-}$ units and the cations are octahedral, low-spin Rh(III) or Ir(III). An alternate structure that stabilizes low-spin, octahedral-site Ir(III) is found in IrS_2 and IrSe_2 ; they contain two types of anion units, $(\text{X}_2)^{2-}$ and X^{2-} . Finally, octahedral-site, low-spin Rh(III) and Ir(III) are found in the semiconductors Rh_2S_3 and isostructural Rh_2Se_3 and Rh_2S_3 [65H]. In all these semiconductors, the conduction band is formed from cationic d orbitals of e_g parentage as in FeS_2 . Any occupancy of this conduction band leads to metallic conductivity; RhSe_{2-x} is a superconductor with $T_c = 6 \text{ K}$ for $x = 0.02$ [55G].

References:

- 55G Geller, S., Cetlin, B. B.: Acta Crystallogr. 8 (1955) 272.
65H Hulliger, F.: J. Phys. Chem. Solids 26 (1965) 639.