Lower band gap energy of stibnite (Sb2S3) induced by orbital overlap of Sb 5s2 inert pair electrons

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The crystal structure of stibnite (Sb2S3, Pnma, a = 11.314(2), b = 3.837(2), c = 11.234(3) A, V = 487.7(3) A3 at 293 K) was refined in situ at 230, 173, and 128 K. It is a major characteristic of the structure that the Sb-S secondary bonds enclosing Sb 5s2 inert lone pair electrons at 293 K are significantly shorter than the corresponding sum of the Sb and S van der Waals radii. Concerning the temperature dependence, although both the polyhedral volume and the cation eccentricity of the two SbS7 polyhedra exhibit continuous contractions with decreasing temperature, the sphericity values remain constant, indicating the isotropic shrinkage. Consequently the geometries of Sb 5s2 inert lone pair electrons and ligand atoms remain unchanged at low temperatures. This is because the crystal structure of stibnite at low temperature induces contraction with attractive interactions, which is called the orbital overlap between Sb 5s2 inert lone pair electrons and ligand orbitals to maintain the coordination environment. In this case, Sb 5s2 lone pair electrons are not inert, but active. Such orbital overlaps of inert lone electron pairs can provide an reasonable explanation for shorter secondary bonds and lower band gap energy of the binary compounds containing heavy elements such as Sb, Te, Pb, and Bi, which are key factors in tracing the origins of color, luster and semiconductivity of their minerals or compounds.