

1974

C00-1198-999

High Pressure Studies of Mixed Valence

Compounds of Antimony*

by

V. C. K. Chiu and H. G. Drickamer

School of Chemical Sciences

and

Materials Research Laboratory

University of Illinois, Urbana, Illinois 61801

Abstract

In Cs_2SbCl_6 and related compounds antimony appears as Sb(III) and Sb(V) in alternate halide octahedra. The optical spectrum contains "mixed valence" peaks assigned to Sb(III) \rightarrow Sb(V) transfer near 18 and 27 kK. In addition there is a peak near 31 kK assigned to an internal transition on Sb(III) and one near 37 kK assigned to Sb(V), mixed with the absorption edge of the crystal. The mixed valence peaks shift strongly to lower energy with pressure (~ 5 kK in 120 kilobars), and decrease rapidly in integrated intensity, as does the Sb(III) peak near 31 kK. A new peak appears near 33-34 kK, tentatively assigned to Sb(IV). The ground state apparently transforms from Sb(III)-Sb(V) to Sb(IV)-Sb(IV) at high pressure. Similar behavior is observed for $\text{Cs}_2\text{Sb}_{0.3}\text{Sn}_{0.7}\text{Cl}_6$ and $(\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{Sb}_{0.5}\text{Sn}_{0.5}\text{Cl}_6$.

* This work was supported in part by the U. S. Atomic Energy Commission under Contract AT(11-1)-1198.