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High Pressure Studies of Mixed Valence

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Compounds of Antimony

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Abstract

In $\operatorname{Cs}_2\operatorname{SbCl}_6$ 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 $\operatorname{Cs}_2\operatorname{Sb}_{0.3}\operatorname{Sn}_{0.7}\operatorname{Cl}_6$ and $(\operatorname{CH}_3\operatorname{CH}_2\operatorname{NH}_3)_2$ Sb_{0.5}Sn_{0.5}Cl₆.

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

A basic effect of pressure is to shift the energy of one type of electronic orbital with respect to another. Under a variety of circumstances there may be an excited state which lies not too far in energy above the ground state. The relative shift with pressure may be sufficient to provide a new ground state for the system or greatly to modify the characteristics of the ground state by change in configuration interaction^(1,2). These electronic transitions involve the thermal transfer of electrons between orbitals. The usual technique for measuring the difference in energy between orbitals is by optical absorption. The energy required for thermal and optical processes is, in general, different due to a number of factors. These include: (1) the Franck-Condon principle, (2) differences in selection rules, (3) relaxation of the Born-Oppenheimer condition (configuration interaction), and (4) the possibility that different configuration coordinates may be involved in the two processes.

Nevertheless an approximate relationship between the thermal and optical energy for a given process has been developed (1,3) based primarily on the Franck-Condon effect, but which can be extended to include multiple configuration coordinates.

$$E_{th} = hv_{max} - \frac{1}{kT(2\ln 2)} (\delta E_{1/2})^2 (\frac{\omega}{\omega})^2$$
(1)

where $h\nu_{max}$ is the energy of maximum absorption, $\delta E_{1/2}$ is the peak half width and ω and ω' are force constants for the ground and excited state potential wells. The analysis is approximate but it has been shown^(1,3)

to give the right order of magnitude for the pressure for initiation of electronic transitions.

Mixed valence compounds, in which an ion exists in two valence states at different sites in a crystal, have been widely investigated. Robin and Day⁽⁴⁾ have provided an analytical review and classification of these compounds according to the degree of interaction between sites of different valence. In Class I there is little or no interaction between sites. In Class II there exist optical excitations which transfer an electron between sites but there is very little if any thermal transfer. There may also be optical excitations localized on a given site for Class II compounds. Class III compounds involve relatively free transfer of electrons among sites, as in Fe₃0₄ or certain tungsten bronzes. Class II compounds would seem to provide a particularly fruitful field for possible electronic transitions.

In this paper we present high pressure optical studies on Cs_2SbCl_6 with some auxiliary data on $Cs_2Sb_{0.3}Sn_{0.7}Cl_6$ and $(CH_3CH_2NH_3)_2 Sb_{0.5}Sn_{0.5}Cl_6$. These compounds have been studied extensively by Day and his colleagues ^(5,6). The method of synthesis used was taken from their papers. Analyses indicated that all elements were present in very close to the theoretical amounts. The high pressure optical techniques have been previously described ^(7,8).

The spectrum at one atmosphere includes a peak near 31 kK assigned (4) to a $5s^2 \rightarrow 5s^1 5p^1$ excitation on Sb(III) and one near 37 kK assigned⁽⁴⁾ to an excitation on Sb(V) mixed with the fundamental absorption edge of the crystal. In addition there are mixed valence peaks near 18 and 27 kK. We label these MV1 and MV2. They shift rapidly to lower energy with increasing pressure. In Fig. 1 we exhibit the shift of the MV_1 peak in Cs₂SbCl₆ and also in Cs₂Sb_{0.3}Sn_{0.7}Cl₆. The shift is ~5 kK in 120 kilobars with no significant difference between the two compounds. The MV2 peak shifts at least as rapidly with increasing pressure. In Fig. 2 we exhibit the spectrum in the visible and UV at several pressures. There are a number of features to be observed. The MV_2 peak shifts to lower energy and fades in intensity with pressure. The peak at ~31 kK assigned to Sb(III) also shifts to lower energy (~2.3 kK) and loses intensity. It is hard to discern any appreciable effect on the peak located near 37 kK and assigned to Sb(V) mixed with the absorption edge of the crystal. The spectrum was resolved into Gaussian peaks and the relative area of the MV₂ peak as a function of pressure is plotted in Fig. 3. These results must be taken as an estimate, but there is no doubt about the decrease in area. The MV, peak also decreased in area, but its position was measured using a different (IR) photomultiplier tube so that it was difficult to obtain a fiducial point to calculate areas. It decreased in area by over a factor of two with no appreciable change in half width.

In Fig. 2 we note at high pressure an apparent new peak in the spectrum near 33-34 kK. It seems reasonable to assign this to Sb(IV). The $Cs_2Sb_{0.3}Sn_{0.7}Cl_6$ and $(CH_3CH_2NH_3)_2 Sb_{0.5}Sn_{0.5}Cl_6$ give qualitatively similar high pressure visible and UV spectra. All changes were reversible upon release of pressure.

Equation (1) can be applied to MV_1 to estimate the relative stability of the Sb(III)-Sb(V) ground state to that of Sb(IV)-Sb(IV). It is necessary to assume $R = (\omega/\omega')^2 = 1$, but in a variety of systems it appears that the deviation from 1 is always less than 10%. Configuration interaction would doubtless modify the quantitative nature of the results, but it is clear from Table I that the electronic transition is feasible.

The various pieces of evidence put together are rather convincing that the mixed valence Sb(III)-Sb(V) compound transforms to an Sb(IV)-Sb(IV) ground state at high pressure.

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TABLE I

THERMAL VS. OPTICAL TRANSITIONS OF MV1

Pressure (kbar)	hv _{max} (eV)	$\delta E_{1/2}(eV)$	3.6(8E _{1/2}) ²	$E_{th}(eV)$
0.8	2.17	0.74	1.97	0.20
20	1.98	0.74	1.97	0.01
60	1.77	0.74	1.97	-0.20
120	1.58	0.74	1.97	-0.39
				7

Cs₂SbCl₆

Figure Captions

Fig.	1	Shift of MV_1 peak vs. Pressure - Cs_2SbCl_6 and $Cs_2Sb_{0.3}Sn_{0.7}Cl_6$.
Fig.	2	Visible and UV Spectra at Several Pressures - Cs ₂ SbCl ₆ .
Fig.	3	Estimated Area Under the MV, Peak vs. Pressure - Cs, SbCl,







Figure 2



Figure 3