High-Pressure Spectral Studies of Mixed Valence Compounds of Antimony

(oxidation state)

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ABSTRACT In Cs$_2$Sb$_4$Cl$_6$ 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) → Sb(V) transfer near 18 and 27 kK (cm$^{-1}$). 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 (about 5 kK in 120 kbar), 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(II)–Sb(V) to Sb(V)–Sb(IV) at high pressure. Similar behavior is observed for Cs$_2$Sb$_{0.5}$Sn$_{0.5}$Cl$_6$ and (CH$_3$CH$_2$NH$_3$)$_2$Sb$_{0.5}$Sn$_{0.5}$Cl$_6$.

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 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.

$$E_{th} = h
\nu_{max} - \frac{1}{kT(2ln2)} \left(\frac{\Delta E}{\omega}\right)^2$$

where $h\nu_{max}$ is the energy of maximum absorption, $\Delta E$ is the peak half width, and $\omega$ and $\omega'$ 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 Fe$_3$O$_4$ 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 data on Cs$_2$SbCl$_6$, with some auxiliary data on Cs$_2$Sb$_{0.5}$Sn$_{0.5}$Cl$_6$ and (CH$_3$CH$_2$NH$_3$)$_2$Sb$_{0.5}$Sn$_{0.5}$Cl$_6$. These compounds have been studied extensively by Day and his colleagues (5, 6). Our method of synthesis 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 $5s^2 \rightarrow 5s^15p^1$ 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 MV$_1$ and MV$_2$. They shift rapidly to lower energy with increasing pressure. In Fig. 1 we exhibit the shift of the MV$_1$ peak in Cs$_2$SbCl$_6$ and also in Cs$_2$Sb$_{0.5}$Sn$_{0.5}$Cl$_6$. The shift is about 5 kK in 120 kbar with no significant difference between the two compounds. The MV$_2$ peak shifts at least as rapidly with increasing pressure. In Fig. 2 we exhibit the spectrum in the visible and ultraviolet (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

Fig. 1. Shift in frequency MV$_1$ peak as a function of pressure.

$\bullet$, Cs$_2$Sb$^{III}$-VCl$_6$; ○, Cs$_2$Sb$_{0.5}^{III}$-VSn$_{0.5}$Cl$_6$. 

Abbreviation: K, Kayser, = 1 cm$^{-1}$
The relative plotted but there is assigned
The crystal. The energy (about
cern any increased in area
creased (infrared) effect on

doubt that the electronic transition is feasible.
The Sb(III)–Sb(V) ground state to that of Sb(IV)–Sb(IV).
It is necessary to assume \( \mu = \left( \omega / \omega' \right)^2 = 1 \), 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 1 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(V) ground state at high pressure. It would, of course, be desirable to confirm this conclusion by high pressure magnetic susceptibility, electron spin resonance, or Mössbauer studies of antimony, when such techniques become available.

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<table>
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<th>Pressure (kbar)</th>
<th>( \nu_{\text{max}} ) (eV)</th>
<th>( \delta E_{1/2} ) (eV)</th>
<th>( 3.6 \left( \delta E_{1/2} \right)^2 )</th>
<th>( E_{\text{abs}} ) (eV)</th>
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<td>1.58</td>
<td>0.74</td>
<td>1.97</td>
<td>-0.39</td>
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TABLE 1. Thermal and optical transitions of MV1 in Cs2SbCl6

Fig. 2. Visible and UV spectra of Cs2SbCl6 at several pressures.

Fig. 3. Area (A) under the MV1 peak of Cs2SbCl6 relative to area at normal pressure \( (A_0) \), as a function of pressure.