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### Title

ELECTRICAL CONDUCTIVITIES OF Fb/Xe AND Fb/SF<sup>+</sup> FILMS

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### Introduction

SF<sub>6</sub> has been of interest as a matrix material for trapping of metal atoms because of the possibility of electron transfer to form SF<sub>6</sub><sup>-</sup>. The reaction between SF<sub>6</sub> and alkali metals has been studied [1] and found to result in formation of alkali fluorides and sulfides. However, copper, silver, and gold atoms have been trapped in SF<sub>6</sub> matrices [1]. Gold gave good atomic spectra and has been studied also in SF<sub>6</sub>-Kr matrices. [2]

Pb has been trapped in SF<sub>6</sub> and Xe-SF<sub>6</sub> mixed matrices, but no discrete atomic spectra were observed. [3] When very high evaporation rates of Pb were used, molecular spectra of Pb<sub>2</sub> were observed. The IR spectrum, from 4000 to 600 cm<sup>-1</sup>, of these films shows only absorptions due to SF<sub>6</sub> vibrational modes. When SF<sub>6</sub> was trapped in Pb films which were thin enough to be transparent, again only absorptions of SF<sub>6</sub> appeared in the IR spectrum.

The lack of discrete atomic Pb spectra in matrices containing SF<sub>6</sub> could indicate (1) a chemical reaction similar to that observed with the alkali metals [1] or (2) an interaction of the charge-transfer type leading to Pb<sup>+</sup>SF<sub>6</sub><sup>-</sup>. If Pb<sup>+</sup> were formed, it would not be seen as its spectrum is in the vacuum UV region. As gaseous Ca<sup>+</sup> absorbs in the 4000 Å region, an attempt to observe a charge-transfer was made by trapping Ca in SF<sub>6</sub> but no discrete spectrum was observed [3] between 2200 and 6000 Å.

The present study of the conductivities of films of Pb trapped in SF<sub>6</sub> is an attempt to test for possible formation of Pb<sup>+</sup>SF<sub>6</sub><sup>-</sup>. Electrons transferred to SF<sub>6</sub> could be further transferred to the next SF<sub>6</sub> molecule

and thus given rise to a better conducting film than for a film of Pb in Xe where the Pb atoms would be in neutral form.

### Experimental

The matrix films were deposited at 20°K using cryo-tip model AC-21-110 built by Air Products and Chemicals, Inc. A chromel-constantan thermocouple wrapped on the cryo-tip was indium-soldered to the sapphire target. A Triplet model 630 voltmeter was used which could measure a minimum of 60 $\mu$ A. The resistance from the soldering spots on the target to the outside leads was 22  $\Omega$  and 16  $\Omega$  for the chromel and constantan wires, respectively. Other experimental details are given in reference 3.

### Results

a. Pb thin films: A pure Pb film was deposited at 20°K on the target until measurable conductance showed up. The film was then annealed at a higher temperature and cooled back to 20°K. On warming up again, the measured resistance vs temperature is shown in Table 1, and was reproducible on cooling down. The negative temperature coefficient of resistance is characteristic of thin metallic films which are known to have an island structure for which conduction involves/activated electronic emission or tunneling mechanisms for charge transfer between the islands. [4]

In all the later experiments of Pb in matrices, the total Pb amount deposited in the matrices were at least twice as much as that used in the pure Pb film. This was to assure that enough Pb was present in the matrix to offset the insulating effect of the matrix gas atoms or molecules.

b. Pb in Xe: Xe matrix containing 5 atomic per cent Pb was deposited rapidly at 20°K. The film showed a strong Pb<sub>2</sub> spectrum and no measurable conductance. On warming up at a rate of 10 deg. per 10 min., the film showed a weak conductance of  $2.5 \times 10^{-6} \Omega^{-1}$  at 79°K, where the film became brown and had lost the Pb<sub>2</sub> spectrum. The conductance decreased on cooling back, and became unmeasurable at 20°K. On warming up again, the conductance increased and became  $3 \times 10^{-5} \Omega^{-1}$  at 102°K.

A thinner Xe film containing 5% Pb was also deposited at 20°K. On warming at the same rate, the film showed very weak conductance of  $1.6 \times 10^{-6} \Omega^{-1}$  at 79°K. Again the film became brown at this temperature, and had lost the Pb<sub>2</sub> spectrum. On cooling back the conductance decreased and became unmeasurable at 20°K. When warming up again, the conductance was  $1 \times 10^{-8} \Omega^{-1}$  at 79°K and  $1 \times 10^{-6} \Omega^{-1}$  at 121°K.

c. Pb in SF<sub>6</sub> and Xe-SF<sub>6</sub> mixture: The Pb/SF<sub>6</sub> matrix film, deposited at 20°K showed a strong Pb<sub>2</sub> spectrum and no measurable conductance. The film was pale yellow colored. The Pb<sub>2</sub> spectrum disappeared between 90 and 100°K. At 110°K the film became grayish, and remained so at higher temperatures. At 120°K a very weak conductance of  $1 \times 10^{-8} \Omega^{-1}$  showed up. The conductance hardly increased at higher temperatures.

A thick film of Pb/SF<sub>6</sub> containing 5% Pb was also deposited at 77°K. The film showed no Pb<sub>2</sub> spectrum, but was transparent, like the films deposited at 20°K. At 77°K it showed no measurable conductivity, but started to show conductivity at 120°K, and increased to  $1.5 \times 10^{-4} \Omega^{-1}$  at 199°K and  $1 \times 10^{-3} \Omega^{-1}$  at 215°K. At 215°K the film left on the target was exposed to SF<sub>6</sub> gas. No effect on the measured conductance was seen.

Pb was also trapped at 20°K in a 77% Xe-23% SF<sub>6</sub> matrix to a concentration of 5%. At 20°K this film showed no conductance. It became grayish at 83°K, and showed no conductance even at 197°K.

#### Discussion

The Pb/Xe film conductivity experiments showed that no conductance could be measured in the temperature region where the discrete Pb<sub>2</sub> spectrum was observed. By the time the matrix film started to conduct, both Pb and Pb<sub>2</sub> spectra had been lost. This indicated that, within the experimental measurability, no electron jump from one isolated Pb to the next was observed.

In the Pb/SF<sub>6</sub> film deposited at 20°K, a large portion of Pb atoms from the vapor was expected to be trapped in the isolated form. As was mentioned, the absence of atomic Pb spectrum implied that Pb atoms could either form a charge transfer complex with SF<sub>6</sub>, or react with SF<sub>6</sub> to give fluorides and sulfides. The fact that much lower conductance was measured for Pb/SF<sub>6</sub> film would favor the reaction possibility.

Pb in the Xe-SF<sub>6</sub> mixed matrix deposited at 20°K showed no measurable conductance up to 220°K and was in agreement with the above discussion.

When Pb/SF<sub>6</sub> film was deposited at 77°K, a much higher conductance was observed at higher temperatures. This was expected from the above discussion, because at 77°K the isolation of Pb in SF<sub>6</sub> was very poor, even for the Pb<sub>2</sub> molecules whose spectrum was absent in this film. Pb existed in this film in the form of small aggregates which were expected to be inert to SF<sub>6</sub>

molecules, like the  $Pb_2$  molecules. [3] After  $SF_6$  gas was evaporated at higher temperatures, these Pb aggregates connected to form a rather intact Pb film which was responsible for the high conductance observed.

### Conclusions

Combining the earlier spectroscopic studies [3] and the present conductivity work, we conclude:

(1) The presence of  $SF_6$  molecules between Pb atoms, molecules, or aggregates does not enhance conductivity by way of a mechanism involving  $SF_6^-$ .

(2)  $Pb_2$  molecules and higher aggregates of Pb are inert to  $SF_6$  in the matrices. This is shown by the presence of  $Pb_2$  spectrum as well as the much higher conductivity of the Pb/ $SF_6$  film deposited at 77°K than those deposited at 20°K.

(3) The fact that the IR spectrum of  $SF_6$  deposited with excess Pb showed only  $SF_6$  vibrational modes is in agreement with (2). The valence electrons of Pb atoms are delocalized into the molecular orbitals of Pb neighbors around the trapped  $SF_6$  molecules and are no longer free to be transferred to  $SF_6$  for complex ion formation or chemical reaction.

(4) The absence of discrete atomic Pb spectra and poorer conductivity in films of Pb in  $SF_6$  compared to films of Pb in Xe might be taken to indicate a chemical reaction between Pb atoms and  $SF_6$ . On the other hand, Ag and Cu also did not give discrete atomic spectra in  $SF_6$  matrices, [2] but Timms [5] has reported that he could cocondense the metal vapors with



SF<sub>6</sub> at liquid nitrogen temperatures and recover the SF<sub>6</sub> quantitatively with pure metal left behind. The nature of the interaction of SF<sub>6</sub> that destroys the discrete atomic features remains in question. However, if it is an interaction that produces SF<sub>6</sub><sup>-</sup>, the charge is not transferred from one SF<sub>6</sub> molecule to another to provide ready electronic conduction through the matrix. [6]

1. BREWER L., CHANG C-A. and KING B.A., Inorg.Chem. 9, 814 (1970), and references therein.
2. BREWER L. and KING B.A., J. Chem. Phys. 53, 3981 (1970).
3. CHANG C-A., Ph.D. Thesis, UCRL-19662 (1970) and paper in preparation.
4. NEUGEBAUER C.A. and WILSON R.H., In Basic Problems in Thin Film Physics (Edited by R. Niedermayer and H. Mayer), Vandenhoeck & Ruprecht, Göttingen (1966), pp. 579-590.
5. TIMMS P., private communication, April 1969.
6. This work was performed under the auspices of the U.S. Atomic Energy Commission.

TABLE 1.

Resistance vs temperature for the pure Pb film after annealing

| T°K | Resistance $\Omega$ |
|-----|---------------------|
| 20  | $1.1 \times 10^5$   |
| 30  | $9.8 \times 10^4$   |
| 40  | $9.2 \times 10^4$   |
| 50  | $8.7 \times 10^4$   |
| 60  | $8.3 \times 10^4$   |
| 67  | $2.3 \times 10^4$   |
| 70  | $2.3 \times 10^4$   |
| 77  | $2.2 \times 10^4$   |
| 104 | $1.9 \times 10^4$   |

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