

*The Low-temperature Luminescence  
Newly Found with a Number of  
Silver Salts*

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The low temperature luminescence of silver halides has been reported by several investigators<sup>1)</sup> and been criticised recently by F. Seitz<sup>2)</sup>. We have studied the luminescence of a number of common silver salts other than halides with a view to finding a more general relation between the luminescence and the photolytic discoloration of silver salts.

Insoluble silver salts were precipitated in the excess state of either anion or silver ion by mixing the solutions of silver nitrate and

various precipitants, each of A.R. grade. At first a small quantity of precipitates was formed in the solution of both reagents by adding a small portion of the one to the other. Then the precipitates were filtered off, and finally the filtrates were mixed. The action of actinic light was carefully avoided throughout the procedures of preparation and measurements.

The luminescence was examined at room and liquid air temperature in a Dewar vessel furnished with two quartz windows under the excitation of 365 m $\mu$  of a mercury vapor lamp. The emission spectra consist of a single broad band at liquid air temperature in most cases. The luminescent characteristics are given below:

sulfite Ag<sub>2</sub>SO<sub>3</sub> (orange, strong), sulfate Ag<sub>2</sub>SO<sub>4</sub> (orange, medium), pyrophosphate Ag<sub>4</sub>P<sub>2</sub>O<sub>7</sub> (orange, medium), oxalate Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (orange, medium; white purple\*, weak\*), carbonate Ag<sub>2</sub>CO<sub>3</sub> (red, medium), molybdate Ag<sub>2</sub>MoO<sub>4</sub>\* (red, weak; red\*, weak\*), tungstate Ag<sub>2</sub>WO<sub>4</sub> (red, very weak), nitrite

1) W. Meidinger, *Phys. Z.*, **40**, 517 (1939); **41**, 277 (1940)  
G. C. Farnell, P. C. Burton and R. Hamalla, *Phil. Mag.*  
**41**, 157, 545 (1950).

2) F. Seitz, *Rev. Mod. Phys.*, **23**, 349 (1951).

$\text{AgNO}_2^*$  (greenish yellow, very strong; yellow\*, medium\*), sulfocyanide  $\text{AgCNS}$  (green, strong), cyanide  $\text{AgCN}$  (blue, medium), perchlorate  $\text{AgClO}_4$  (yellow, weak), mercuri-iodide  $\text{Ag}_2\text{HgI}_4^*$  (green, strong; red\*, weak\*).

Fluoride, nitrate, ferrocyanide, ferricyanide and phosphate are not luminescent at both room and liquid air temperatures, the last one, however, fluorescing probably infrared. The salts with asterisk are luminescent at room temperature, whose luminescence characteristics are also marked with asterisks.

Evidences were obtained that these fluorescences are not ascribed to the print-out silver. On the contrary, the fluorescences depend sometimes on whether the salt is of silver or of anion body. So, for instance, the emission color changes from silver body to anion body as follows:  $\text{AgCNS}$  (green  $\rightarrow$  orange),  $\text{AgCN}$  (blue  $\rightarrow$  yellowish orange),  $\text{Ag}_2\text{SO}_4$  (orange  $\rightarrow$  white purple). This indicates an intimate connection of lumines-

cence with lattice defects. The same light as excites the luminescence leads to the blackening of the salts at higher temperature, but not at liquid air temperature. The blackening is generally less remarkable in the salts of an anion body. The authors concluded that silver salts can be luminescent in their pure state by the reverse process of photolytic absorption, in which, however, some lattice defects are undoubtedly involved. The mechanism suggested by F. Seitz, namely the transition  $d^9s \rightarrow d^{10}$  within the silver ion, seems to be invalid, for similar emission spectra (orange-red) appear in some cases (as in  $\text{Ag}_2\text{SO}_3$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_4\text{P}_2\text{O}_7$ ), whereas spectra are quite different with one another in other cases (as in  $\text{AgNO}_2$ ,  $\text{Ag}_2\text{HgI}_4$ ,  $\text{AgCN}$  etc.). Spectroscopic and other details are to be published in later reports.

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