LETTER

Internal Vibrational Structure Found in the Low Temperature Fluorescence of Silver Nitrite Crystals

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As briefly reported in the previous letter[1] pure silver nitrite crystals show the strongest fluorescence among the common silver salts. Moreover they are distinguished from other salts by the fact that they have a structure in the fluorescence spectra at the liquid oxygen temperature. The structure is somewhat diffuse, the stripes appearing on a broad emission band as a repetition of the nearly equi-distant darkness (Fig. 1). The structure

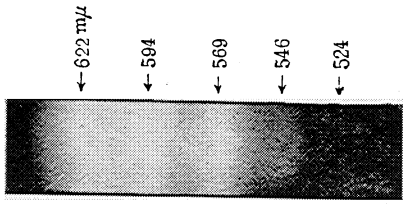

Fig. 1. Stripes of emission spectrum of solid $AgNO_2$.

vanishes at several ten degrees above the liquid oxygen temperature, although the fluorescence remains sufficiently strong. The structure is more distinct when the crystal is precipitated in the excess of nitrite ions. This suggests that the luminescence and its structure originate from some lattice defects. Upon examining the photometer curve it proved that the mean separation of the peaks in the structure is approximately 750 cm^{-1}. A comparison with the known Raman or infrared spectral data[2] concerning nitrites or nitrates makes us draw the conclusion that the structure is ascribed to the deformation vibration of NO_2 group. It seems very rare for an internal vibration with definite meaning to appear in the ordinary solid luminescence like this, because a silver nitrite crystal has no shielded electronic states which are characteristic of rare earths, uranyl salts or compounds containing π-electrons.

Almost the same luminescence characteristics are observed with $AgNO_3$ crystals containing a trace of NO_2^- or with $NaNO_2$ crystals containing a similar amount of Ag^+. A conclusion is reached, therefore, that the origin of the luminescence lies not in the whole lattice of $AgNO_2$, but in the localized bond between Ag and NO_2 group having a nature of an isolated molecule.

Silver nitrite possesses a considerable amount of the character of nitro-compound. This is easily predicted from the well-known fact, that the nitro-paraffins are formed together with the nitrite ester, when alkyl halides react with $AgNO_2$. In the state of a nitro-compound, silver is connected with the nitro-group by a perfectly covalent bond. So, the covalent nature is much more remarkable in the bond of $AgNO_2$ than in other silver salts. When the covalent part increases in the binding, a pair of anion and cation facing to the lattice defects bears the character of an isolated molecule. The interaction with the lattice vibrations is thus diminished, and it becomes possible to expect the appearance of the internal vibrational structure as well as the nonvanishing of the luminescence at higher temperatures. In fact, as shown below, silver nitrite has a higher vanishing temperature of fluorescence than any other salts tested. This agrees quite well with the nonappearance of the internal vibrations in the latter cases.

Salts	$AgNO_2$	AgCN	Ag_2SO_3	AgCl
Approx. vanishing Temp. °C	+90	−50	−90	−120

More detailed discussions may become possible, when the data concerning the temperatures of liquid hydrogen or helium are available, which, however are impossible in our laboratories.

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1) S. Makishima and T. Tomotsu, This Bulletin, **27**, 71 (1954).

2) A. Langseth and E. Walls, *Z. phys. Chem.* B **27**, 209 (1934), D. Williams, *J. Am. Chem. Soc.* **61**, 2987 (1939), E. A. Miller and C. H. Wilkins, *Anal. Chem.* **24**, 1253 (1952).