Notes on the Luminescence of Glass and Fluorite

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(Received April 1, 1932)

In the first part of this paper a simple method for showing the relation between the absorption of light and the resulting luminescence in glass is described. The second part contains some observations on the luminescence of clear and colored fluorites and of quartz in the extreme ultraviolet. In the case of clear colorless fluorite light on the short wave-length side of the absorption limit at $\lambda1230$ is responsible for luminescence in the visible and also in the ultraviolet. This ultraviolet luminescence seems to consist of two parts. In the first place, there is a rather strong, broad band extending from the neighborhood of $\lambda2450$ to $\lambda3810$. Secondly, in the second there are sharp lines at $\lambda3812$, $\lambda3144$ and $\lambda3133$.

IT IS a commonplace in physics that absorption is necessary to the emission of light by luminescent substances. The following experiment affords a simple means of demonstrating this fact.

The only apparatus required is a small quartz spectrograph and a condensed spark between metal terminals. A piece of microscope cover glass about 0.1 mm thick is placed inside the plate-holder in contact with the photographic plate. A second piece of the same glass may be placed in front of the slit when required.

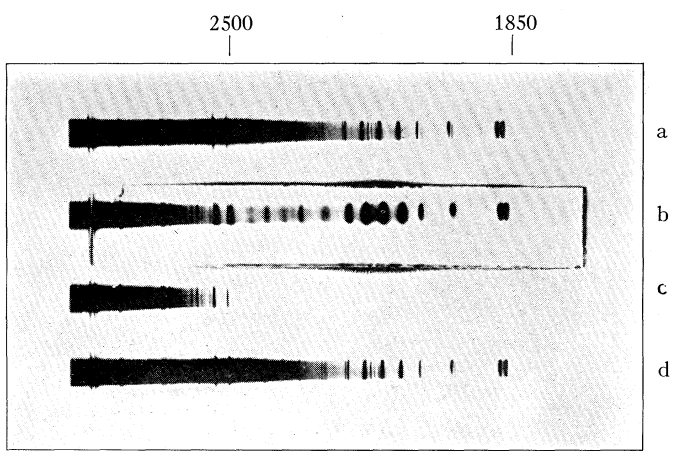


Fig. 1.

Fig. 1. illustrates the nature and results of the experiment; (a) Is the spark spectrum of aluminium and zinc. (b) Is this same spectrum taken through the strip of glass in contact with the plate. (c) Shows the result of placing a bit of cover glass in front of the slit. With a "Seed 23" plate the time of exposure was thirty seconds in each case.

If attention is fixed on (b) it is obvious that the spectrum lines are transmitted through the glass up to the limit set by absorption; in this region they are quite sharp. On the violet side of this point the broader impressions on the photographic plate are due to the luminescence of the glass. A broad line corresponds to each sharp line in the spark spectrum; the effect continues throughout the length of the plate to the aluminum pair at λ1862–54.

This simple experiment demonstrates that the luminescent light is due to the part of the spectrum which lies within the absorption band of the glass.

The same effect is shown by clear colorless fluorite. All the specimens of this quality which have been used were from Zell in Baden. When tested in a vacuum spectroscope they were all found to be of excellent transparency down to the limit of the Schumann region near λ1230. A given specimen was placed in contact with the photographic plate, usually a "Seed 23", sensitized with Nujol and this plate in turn was introduced into a vacuum spectroscope. A hydrogen tube served as source. In the resulting spectrum the lines on the long wave-length side of λ1230 were transmitted through the fluorite, but on the other side of the absorption limit each spectrum line gave rise to luminescence in the fluorite which was recorded on the photographic plate in a number of broad lines.

It is well to note that the effect with glass differs from that with fluorite in one particular. For while with the former substances every strong line in the spectrum excites luminescence throughout the spectral range of the quartz spectrograph, with fluorite the action is confined to a rather limited region from about λ1230 to the neighborhood of λ990. Beyond this point strong spectral lines excite no luminescence. This fact has been checked by substituting a continuous and a disruptive discharge in helium and a hot spark, for the hydrogen tube source.

One is reminded of some results of Gudden and Pohl[1] on the electric conductivity produced in solids by the action of light. These investigators found that the group of wave-lengths which was responsible for the observed result was situated within the optical absorption band of the solid in question, but was limited to a region near the long wave-length side of this band. The luminescence of clear fluorite seems to obey the same general rule. This relation may prove true even for glass if the spectral area is extended into the extreme ultraviolet.

The position in the spectrum of the ultraviolet light excited in clear fluorite by radiations in the extreme ultraviolet was determined in the following manner.

A discharge tube of the internal capillary type was used closed at the end opposite the capillary by a plate of clear, colorless Zell fluorite some 2 mm thick. Matters were so arranged that a number of screens of different materials could be interposed in turn between the end of this capillary and the fluorite window. The essential feature of the device by which this was accomplished consisted in a windlass-like arrangement operated from outside by means of a stopcock. The screens were of course entirely within the discharge

[1] Gudden and Pohl, Phys. Zeits. **23**, 419 (1922).

tube, their distance from the internal capillary being about 14 millimeters, and from the window about 4 millimeters. The discharge tube was filled with hydrogen at a pressure of a few millimeters. The luminescence was studied by means of the small quartz spectrograph already mentioned arranged to view the fluorite window edge on. The first experiment was made with the light from the end of the capillary falling directly on the flurite window. With a "Seed 23" plate an exposure of one half hour showed a broad band extending from λ2450 to λ3810 with a maximum near λ2900 and also certain fairly sharp lines at λ3812, λ3144 and λ3133. To make sure that these radiations were really due to the luminescence of fluorite, another series of exposures were made on the same plate. In the first a piece of cover glass was interposed between the capillary and the window; in the second, a screen of fused quartz was interposed and in the third a piece of fluorite transparent to the Schumann region was employed. In the first two cases, the band just mentioned was absent, in the last case the band was very feeble but the lines were relatively strong. Now experiment had shown that the cover glass transmitted to λ2500, while the quartz and fluorite cut off the spectrum near λ1525 and λ 1230 respectively. The glass was therefore fairly transparent to the region occupied by the band in question while both the quartz and fluorite were very transparent to this region. All the screens were opaque to light of shorter wave-length than λ1230.

Since the band was very feeble even when fluorite was used as a screen, we may conclude that it is chiefly excited by light of shorter wave-length than λ1230. Since the lines did not appear when quartz was used and as they were present when fluorite was employed as a screen, it seems probable that these radiations are partly due to light lying between the absorption limit of the specimen of fused quartz at λ1525 and that of fluorite at λ1230.

In this connection it is interesting to recall that Winkelmann and Straubel[2] have shown that fluorite, excited by x-rays, gives out a luminescent radiation in the form of a band extending from near λ2330 to λ3960 with a maximum near λ2800.

Line spectra in the luminescent light from fluorite were observed by H. W. Morse[3] many years ago. He worked almost entirely with colored specimens. Curiously enough he found that the character and position of the lines depended not only on the particular specimen of the mineral employed but also upon the character of the exciting source; an observation rather at variance with the results of some later experimenters.

The work of Urbain[4] on the presence of rare earths in fluorite is well known. It is probable that the lines which I have observed in the luminescent spectrum of clear, colorless specimens of this mineral are due to traces of these rare earths. On the other hand it is just possible that the presence of these lines has a more fundamental meaning.

Lau and Reichenheim[5] have found that the visible phosphorescence of

[2] Winkelmann and Straubel, Wied. Ann. **59,** 339 (1896).

[3] H. W. Morse, Astrophys. J. **21,** 83 (1905); Proc. Am. Acad. XLI, 590 (1906).

[4] Urbain, Ann. de Chem. et de Physique **18,** 222 and 289 (1909).

[5] Lau and Reichenheim, Ann. d. Physik **12,** 69 (1932).

colorless fluorite is strongly excited by light near the short wave-length limit of the Schumann region. I have checked this observation for Zell fluorite. Visible phosphorescence is also excited in this mineral but to a much feebler degree by light from a condensed spark between aluminium terminals in air. Since the effect is cut off by cover glass but is only slightly weakened by quartz, and since the phosphorescence occurs even when the spark is distant several centimeters from the fluorite, it would seem that the wave-lengths of the stimulating light must lie between the limit of transparency of cover glass and that of two or three centimeters of air, i.e., between λ2500 and say λ1800. As far as I am aware no strong absorption of fluorite has been discovered in this region. The action then is probably due to light only slightly absorbed over a wide range of wave-lengths.

One specimen of fluorite from Derbyshire described as white and investigated by Nichols and Merrill,[6] had a slight but well-marked absorption near λ4240 and was luminescent in the visible. The material however may well have been of very different composition from that which I have investigated.

One fact is important to remember. The brightness of the phosphorescence excited by the spark in air is no indication of the transparency of the particular specimen of fluorite in the extreme ultraviolet. This fact was demonstrated by testing the transparency of a number of pieces of clear, colorless fluorite with a vacuum spectroscope and then observing the brightness of the luminescence from the same pieces when excited by the light from an aluminum-zinc spark. A number of specimens all cut from crystals coming from the same source, namely from Zell in Baden, showed nearly the same transparency in the extreme ultraviolet but exhibited great differences in the intensity of their visible luminescence.

The phenomenon exhibited by fluorite of poor transparency are somewhat different from those just described. A piece of clear and apparently colorless fluorite when examined in the vacuum spectroscope showed very marked absorption between λ1600 and λ1300, but in this region no luminescence appeared to be excited. Total absorption occurred beyond λ1250. Beyond this region the specimen behaved much like the excellent Zell mineral, that is to say, strong lines in the hydrogen spectrum near the absorption limit produced luminescence. In this case therefore absorption is a necessary but not a sufficient condition for luminescence.

Three specimens of colored fluorite were next examined. In nearly all cases a strong absorption began near λ1700. On the short wave-length side of this limit and near it, luminescence was excited. Then followed a region of complete absorption without luminescence or with only the faintest trace, extending to near λ1250, and then a region in which each strong spectral line gave rise to secondary radiation very much as in the case of the colorless fluorite just described.

It seems likely therefore that in the case of these colored fluorites two regions of absorption exist one beginning near λ1700 the other near λ1250. Near both these regions luminescence is excited.

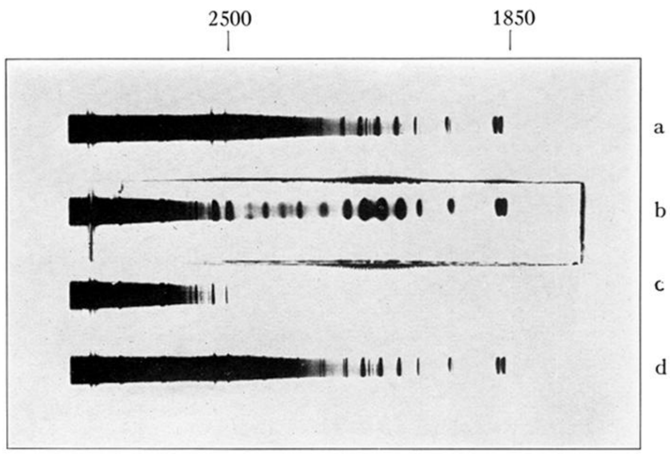
[6] Nichols and Merritt, Phys. Rev. [1] **19,** 31 (1904).

A number of specimens of crystalline quartz were also examined. The limit of absorption was in the neighborhood of λ1500. Only very feeble luminescence seemed to be excited; in fact it is doubtful if the phenomenon exists at all.

With fused quartz the case is different. Absorption begins strongly near λ1525; luminescence is excited but only for a very limited region close to the edge of this absorption band.[7]

I am much indebted to Mr. H. W. Leighton who has carried out much of the experimental work described in this paper.

[7] Compare Webb and Messenger, Phys. Rev. **34,** 1463 (1929).



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