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The two species of fluorite

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Amongst the many interesting properties of the mineral fluorspar or fluorite is the luminescence which it exhibits under ultra-violet illumination. In many cases and especially with the larger specimens, the effect observed is indeed spectacular. The nature and origin of the phenomenon are thus problems of great scientific interest. In an earlier article (*Curr. Sci.* **31**, 361 (1962)), the present author gave a preliminary account of his investigations in this field. One of the significant discoveries recorded in that article is that when fluorite is cooled down to the temperature of liquid air, the spectrum of its luminescence undergoes a remarkable transformation. The diffuse band stretching from the violet end into the blue region of the spectrum seen at ordinary temperature is replaced by a sharply defined emission line or band centred at 4132 Å of which the spectral width is only a few Angstroms. This is accompanied by various subsidiary features which are noticeable in the part of the spectrum at greater wavelengths. Further studies have shown this behaviour to be entirely characteristic of fluorspar. The emission located at 4132 Å appears at the same position in all cases, irrespective of the place of origin of the mineral or the absolute intensity of its luminescence which indeed in some cases is enormously greater than in others.

The observations reported in the earlier article were made with naturally occurring fluorite specimens. It seemed to be of great importance to carry out similar studies with synthetically prepared fluorite of optical quality which is now commercially available. This material, as is well-known, is prepared from carefully purified CaF_2 by fusion and slow solidification. It is perfectly colourless and isotropic and its transparency extends into the far ultra-violet. Three specimens of such fluorite were available for the studies. One of them was a rectangular block 37 mm × 37 mm in area by 9 millimetres thick which was supplied by a well-known British firm. A piece 6 millimetres wide was sawn off from the block and employed for the study of the infra-red absorption spectra of plates of fluorite of various thicknesses. The results of this study will be reported in a separate communication. The second specimen was a polished window of synthetic fluorite 25 mm × 25 mm in area and 2 millimetres thick which was gifted to the author by Dr E K Plyler of the National Bureau of Standards at Washington. A third specimen was a smaller plate 1·7 millimetres thick which was sent by Professor R Mecke from his Institute at Freiburg. The infra-red transmission by the two plates was spectrophotometrically studied and did not

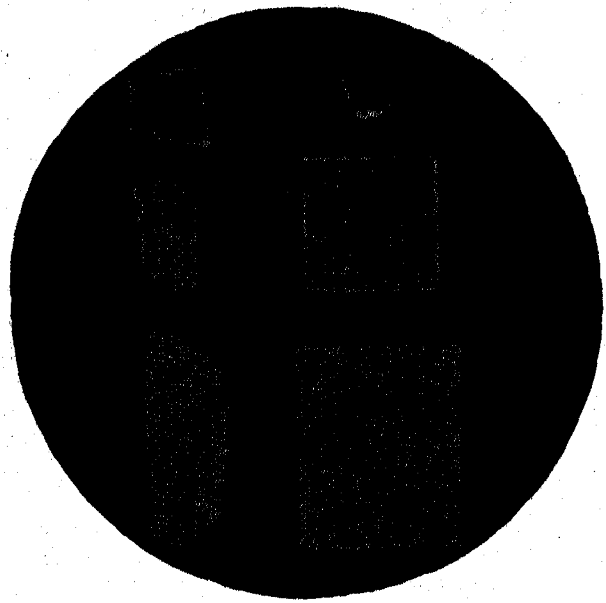

Figure 1. Six specimens of fluorite under ultra-violet illumination.

exhibit any noticeable differences as between themselves. The infra-red behaviour of the British specimen studied with thicknesses of 2 millimetres and one millimetre respectively was also similar to those of American and German manufacture.

Figure 1 is a photograph of six specimens of fluorite as seen under intense ultra-violet illumination. They were placed on a sheet of black paper and an appropriately chosen filter was placed before the lens of the camera to cut off the ultra-violet radiation scattered by the black paper or reflected at the surfaces of the specimens. The three specimens seen on the right-hand side of the picture are the synthetic crystals of German, American and British origin respectively. The three specimens seen on the left of the picture are pieces of natural fluorite whose thicknesses were about the same as that of the synthetic specimens set alongside of them and seen on the right-hand side of the photograph. It will be noticed that the two specimens (one natural and the other synthetic) at the top of the picture are non-luminescent. The two other pairs of specimens, on the other hand, exhibit a readily observable luminescence, of which the intensity is noticeably greater in the case of the natural fluorite.

It should be mentioned here that the spectrum of the luminescence of the synthetic fluorite supplied by the British firm has been studied with the material held at liquid air temperature. A very satisfactory spectrum has been recorded

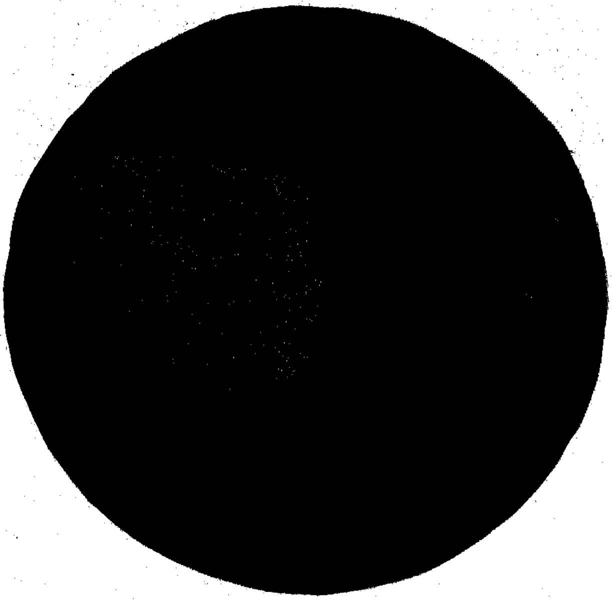

Figure 2. Luminescent and non-luminescent fluorspar.

with it, exhibiting the well-defined feature at 4132 Å accompanied by other details in the region of greater wavelengths. Figure 1 may in the circumstances be regarded as a demonstration of two results of fundamental importance. In the first place, it is clear that luminescence is a characteristic property of fluorite. Secondly, there are two species of fluorite, (either natural or synthetic), of which one exhibits luminescence and the other does not. The difference between the two species is not a difference in degree, but an absolute difference in the sense of luminescence being either present or being totally absent. The total absence of luminescence in one species and its visible presence in the other specimens becomes most clearly evident when the specimens of the two species are set side by side under ultra-violet illumination of the greatest obtainable intensity and against the darkest possible background and are compared visually. Such a comparison made photographically instead of visually is exhibited in figure 2. The specimen of fluorspar on the left is one of the numerous examples of the mineral finding a place in the museum of the Raman Research Institute. It is a block of colourless fluorite which is an aggregate of cubic crystals, and was selected for the comparison by reason of the fact that the luminescence which it exhibits is of extremely low intensity. The specimen on the right is a large transparent single crystal in the shape of a cubo-octahedron with well-defined faces. Under the ultra-violet lamp, it is scarcely visible. Indeed it is only seen in the

Figure 3. Luminescent layer in Amba Dongar fluorite.

photograph by reason of the reflection at its faces of the illumination from the neighbouring luminescent sample.

Why one species of fluorite exhibits luminescence and the other does not is a problem in itself. Much useful light is thrown on this question by the author's studies of the material from the newly discovered deposit of fluorite at Amba Dongar near Chota Udaipur in the Baroda District. Through the kindness of the officers of the Geological Survey of India, a considerable quantity of this material has been made available to the author for his studies. Much of it is in the form of fairly thick blocks which are close aggregates of cubic crystals. The crystal forms are visible on one external face of each block, while the other face shows evidence of the mother rock from which the fluorspar crystallised.

Placing a block under the ultra-violet lamp, it is immediately evident that the material is not all of the luminescent variety. This becomes most clearly evident when the edge of the block is viewed under ultra-violet illumination. The feature then noticed is that a layer of luminescent material which is more or less exactly parallel to the external faces of the block is sandwiched between two layers of non-luminescent fluorspar, while the external face of the block showing the individual crystals usually exhibits an observable luminescence. The former feature is illustrated in figure 3 which shows *the edge of one block*, the upper face of the block seen in profile being only dimly visible in the picture. The luminescent

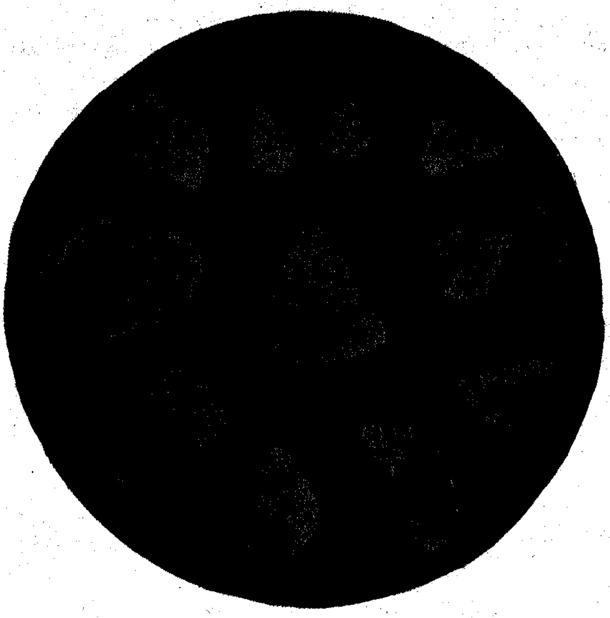

Figure 4. Single crystals of fluorite exhibiting luminescent and non-luminescent sections.

layer is clearly seen in the photograph, while the non-luminescent layers on either side of it are only seen by reason of the light from the luminescent layer which penetrates both above and below and is reflected or scattered within those layers. It should be mentioned that the luminescent layer can easily be distinguished in ordinary daylight from the non-luminescent ones above and below it, by reason of its being clearer and more transparent.

A considerable part of the Amba Dongar fluorite as it came into the hands of the author consisted of small individual fragments and individual crystals which had evidently broken off from the bulk of the mineral during its excavation from the site. Many of the fragments were found to be totally non-luminescent, while others showed luminescence which in most cases did not extend over the whole volume of the fragment. The reason for this becomes clear when such pieces were shaped by grinding and polishing into flat plates with optically good faces. A collection of such plates as photographed under ultra-violet illumination is illustrated in figure 4. The luminescent and non-luminescent areas appear side by side in the same individual crystal, the surfaces of separation being nearly always sharply defined planes.

The facts of observation set forth above indicate that whether fluorspar exhibits luminescence or does not is determined by the ultimate structure or texture of the crystal which is determined by the temperature and other conditions under which the crystallisation took place. That the difference in the two species arises from the presence or absence of extraneous impurities is a hypothesis which can be scarcely regarded as tenable in the light of the overwhelming factual evidence to the contrary.