

## The luminescence of fluorspar

SIR C V RAMAN

Calcium fluoride ( $\text{CaF}_2$ ) appears widely distributed in nature in the form of the mineral known as fluorspar or fluorite. In the year 1529, the usefulness of fluorspar as a flux in metallurgical processes was recognised, and after a lapse of four centuries this application of the material continues to be one of its most important uses, especially in the metallurgy of steel. Fluorspar is the only common mineral containing a large proportion of the element fluorine and it is therefore employed for the production of hydrofluoric acid by treatment with sulphuric acid, and therefrom also the production of the many organic and inorganic compounds of fluorine which find application in the arts and industries. Fluorspar is also used in the ceramic industries as an opacifier in the production of enamels and of glass. There are also other miscellaneous uses. It will be readily understood that in these circumstances, fluorspar is a much sought-after mineral. Indeed, at the present time, the world production of this material is over a million tons per annum.

Many countries possess workable deposits of fluorspar amongst which may be mentioned particularly the United States of America, the USSR, Great Britain, Germany, Spain and so forth. Until the present time, the deposits of fluorspar known in India were few and of small productivity. The recent discovery at Amba Dongar in the Baroda District of substantial deposits of fluorspar is therefore an event of more than ordinary interest and importance. The announcement which appeared in the Press greatly interested the author and led him immediately to contact the Geological Survey of India. Through the kindness of the officers of the Survey, he was enabled to obtain an ample supply of this fresh material. This served as an encouragement to the author to undertake a fact-finding investigation aimed at discovering the nature and origin of the luminescence exhibited by fluorspar, a phenomenon with which he had long been familiar and which had interested him for many years.

Fluorite, it should be mentioned, is a material of importance to the physicist for other reasons. It has a low refractive index and a low dispersive power in the visible region of the spectrum,  $\mu$  being equal to 1.432 and 1.440 respectively at its red and violet ends. It has also a very low aqueous solubility. The melting point of  $\text{CaF}_2$  is  $1360^\circ\text{C}$ , and synthetic optical crystals of as large a size as 150 millimetres in diameter and 125 millimetres in length have been successfully prepared by the well-known method of melting, casting and annealing in cylindrical platinum

containers. The material thus fabricated is transparent throughout the spectral range from 0.125 microns to 9 microns. It finds uses as windows and prisms in ultra-violet, visible and infra-red spectroscopy, in telescope and microscope optical systems, apochromatic lenses and camera objectives.

Fluorite as found in nature displays some remarkable peculiarities of behaviour. It crystallises beautifully, the simple cube being the form most commonly found, though octahedra and other forms are also known. It also exhibits a perfect octahedral cleavage. Surprisingly enough, however, colourless crystals are rather rare; in the majority of cases, the mineral exhibits colours which both in respect of hue and saturation exhibit a great range of variation. By reason of the beautiful crystallisation and of the attractive colours displayed, fluorite specimens are spectacular exhibits in a museum. Some fifty such exhibits from different countries and from India are included in the author's collection. They are representative of the forms and colours exhibited by the mineral. Included in it are several single crystals which are transparent and colourless, as also single crystals in the form of octahedra and cubo-octahedra exhibiting nuances of colour; also clusters of cubes or octahedra attached to the matrix from which they crystallised out, aggregates of various kinds and also massive lumps. All colours ranging from yellow through green and blue to violet and purple are represented in the collection.

Another remarkable optical anomaly exhibited by the natural fluorite was long ago noticed and remarked upon by mineralogists. This is the fact that though it is a cubic crystal and hence should be optically isotropic, it very commonly exhibits a weak birefringence. This usually appears in the form of bands parallel to the cubic planes when a section is viewed between crossed nicols. A lamellar structure parallel to the faces of the cube is thus indicated for the material.

Still another property of fluorite as exhibited by some richly tinted specimens is the appearance of colours as seen by reflection at the surface of the crystal which are different from those seen by transmission through it. It is this phenomenon which led to the name "fluorescence" being given to effects of the same nature exhibited by other materials as well.

The present communication is a first report on the facts which have emerged from a study of the material at the author's disposal. With such an extensive collection of material, even the simplest observations when made on a comparative basis serve to reveal the broad features of the case and to indicate the lines on which a more detailed and comprehensive investigation should proceed. We may, therefore, begin with the simplest of all the methods of study, viz., the visual observation of the luminescence as exhibited by the various specimens. For this purpose, the most convenient way of examining the specimens is to view them in a darkened room under ultra-violet illumination. This is provided by a mercury arc of small size completely enclosed in a bulb of black glass which transmits the near ultra-violet radiation of the arc freely but cuts out all visible light except at the extreme red end of the spectrum. The luminosity of the

specimen under ultra-violet excitation can then be readily observed. The red light escaping through the black-glass envelope of the lamp makes itself evident to the observer by reason of the reflection or diffusion of the light by the specimen. But this is readily recognised by its colour, and its disturbing effect may be greatly reduced by giving the surfaces of the specimen a smooth polish. By using specimens in the form of polished plates, the effect may even be completely eliminated. With a set of three lamps held together and backed by aluminium reflectors, the intensity of the ultra-violet excitation is notably enhanced. It is then possible to detect even the weakest luminescence.

The spectacular character of the effects exhibited by fluorspar under ultra-violet irradiation is illustrated in figure 1 which is a photograph of one of the specimens in the author's collection as thus seen. The largest dimension of the piece is some 20 centimetres. It is a close aggregate of cubic crystals of various sizes adhering to the matrix from which they were formed. The surface of the crystals is mostly covered by a thin deposit of quartz, and the specimen has therefore a very unattractive appearance in ordinary circumstances. But under the ultra-violet lamp, the superficial deposits are invisible and the entire specimen glows with a resplendent blue. This is the characteristic colour of the luminescence of fluorspar which is much the same for all the specimens which exhibit the phenomenon, though the intensity of the glow varies enormously from specimen to specimen, and in a few cases the glow appears of a darker hue.

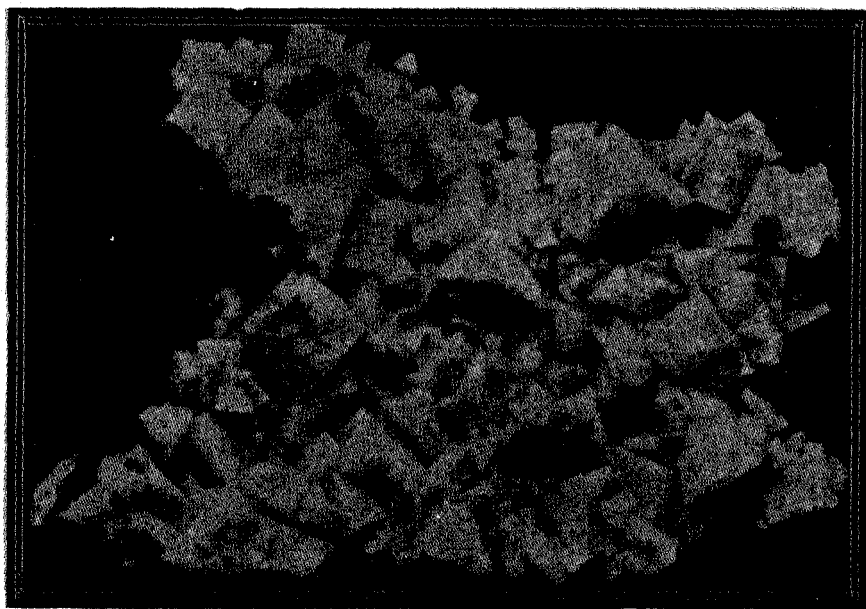


Figure 1. Luminescence of fluorspar.

A remarkable feature exhibited by the crystal aggregates from Amba Dongar is that the luminescence is manifested in strata running roughly parallel to the external faces of the aggregate, a luminescent layer being located between layers on either side which are non-luminescent. The luminescent layer can be distinguished even in daylight from the non-luminescent layers on either side by its appearance and transparency, the luminescent layer being more transparent and colour-free than the non-luminescent ones.

That fluor spar can crystallise in two distinct forms which are respectively luminescent and non-luminescent is demonstrated in a very striking fashion by the single crystals from Amba Dongar of which many are in the author's possession. The surprising fact emerges that part of the volume of the same crystal may be luminescent and the other part may be non-luminescent, the boundary between the two parts being a sharply defined plane. Irregular lumps which do not exhibit well-defined crystal faces may be ground down into the form of plates and their two faces then polished. It is then found that part of the area of the plate may be luminescent and the other part non-luminescent, the boundaries between them being sharply defined. A great number of section-plates of this kind showing these features have been prepared in the course of the investigation.

The most perfect specimens of fluorite in the author's collection exhibit the usual blue luminescence. This is weak, but readily observable. On the other hand, there are numerous single crystals, both large and small, in the collection in which the effect is unobservable and which therefore must be designated as belonging to the non-luminescent class of fluorite. The question arises whether the artificially prepared fluorite of optical quality would or would not exhibit luminescence. This question can only be answered by actual study of such material. Three specimens were available for examination, which were obtained respectively from Great Britain, USA and Germany. The British and American specimens were found to be blue-luminescent, though only weakly so and to an extent comparable with natural fluorite of the best quality. On the other hand, the product from Germany showed not a trace of the phenomenon.

The most important questions regarding the luminescence of fluorite which need to be answered are firstly, why does it appear in the region of the spectrum where it is observed, and secondly, why it does vary so enormously in its intensity from specimen to specimen? Highly instructive in regard to both of these issues is the result of a spectroscopic study of the luminescence. Visually observed, the spectrum appears as a continuous band extending from the violet into the blue and perhaps a little beyond. This is confirmed by a photographic record of the spectrum. A remarkable change in the character of the emission however appears when the specimen is held continuously at the temperature of liquid air during the exposure. This change is exhibited by the spectrographs reproduced as figure 2. The two spectra (a), (b) appearing at the top of the picture were recorded with different exposures with the specimen held at room temperature, while the three spectra below (c), (d) and (e) were likewise recorded but with the specimen cooled

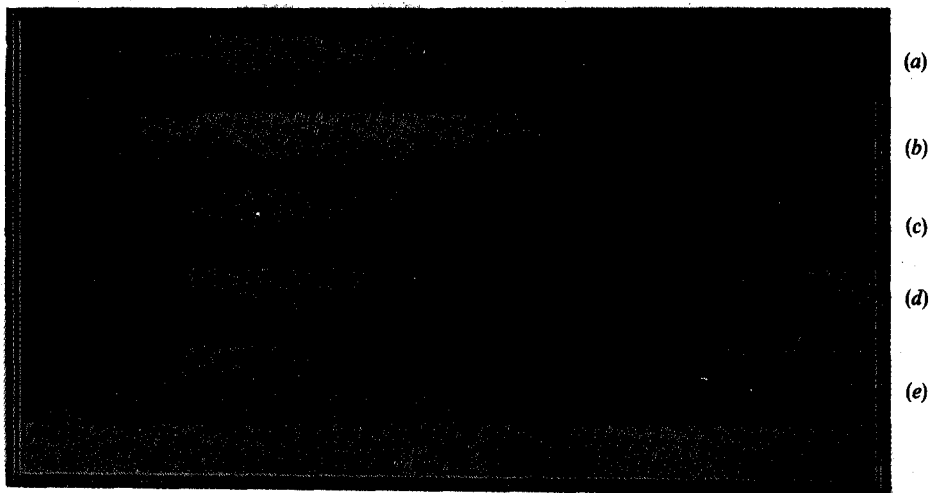


Figure 2. Luminescence spectra of fluorite. (a), (b) Room temperature; (c), (d), (e) liquid air temperature.

down to liquid air temperature. The heavily-exposed spectrum at the foot of the record is that of the mercury arc after removal of the black glass filter held in front of it for exciting and photographing the luminescence spectrum. It will be noticed that the lowering of the temperature of the luminescent fluorite has resulted in the continuum extending to the violet end of the spectrum being replaced by a sharply defined emission located at  $4125 \text{ \AA}$ , followed by a set of imperfectly resolved bands extending into the blue; further, an emission appears in the region of longer wavelengths which is not recorded when the specimen is at room temperature.

The emission at  $4125 \text{ \AA}$  has been recorded with several different specimens and it is clearly a characteristic feature of the luminescence of fluorspar. That it appears only when the crystal is cooled down to low temperature is a readily understood feature. Such a sharpening of the emission spectra at low temperatures is known in other cases, as for example, the luminescence of the uranyl salts. We are, therefore, justified in inferring that the luminescence of fluorspar is an inherent property of the crystals which show the phenomenon and that it indicates the presence of specific electronic levels between which a transition can occur in their cases.

Comparative study of the luminescence of numerous specimens of fluorite shows very clearly that the intensity of luminescence is correlated with the appearance of visible colour in the specimens. In particular, it is noticed that fluorite exhibiting lighter shades of green emits a luminescence of extraordinary intensity, but that on the other hand, the strength of the luminescence is less when the colour of the fluorite is of a deeper green. These facts indicate that visible

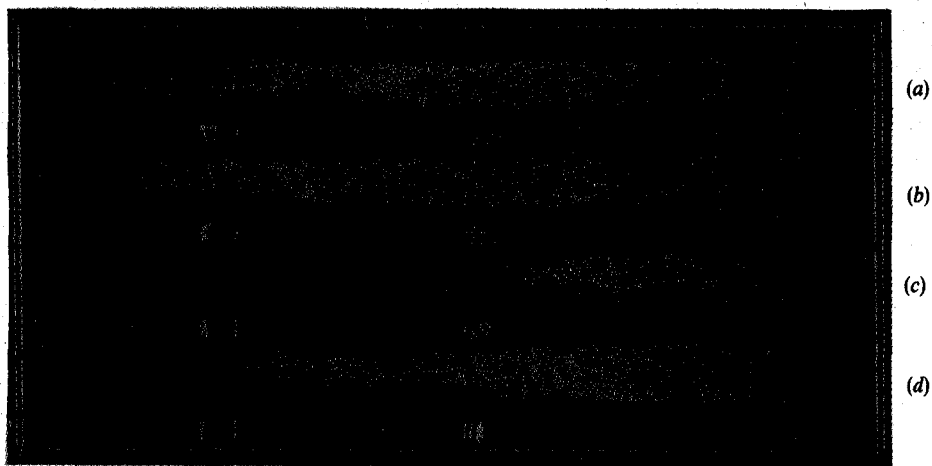


Figure 3. Absorption spectra of green fluorite. (a), (b) Room temperature; (c), (d) liquid air temperature.

colour in fluorite arises from the possibility of inner electronic transitions, which if they occur in one direction result in luminescence and if in the opposite direction result in absorption and the manifestation of visible colour by the specimen.

Accepting the foregoing view of the origin of the colours observed in natural fluorite, we should expect to find that their absorption spectra should, as in the case of the emission spectra, resolve themselves into well-defined bands when the material is cooled down to liquid air temperatures. That this is actually the case is shown by the spectra reproduced in figure 3. They were obtained with a piece of fluor spar exhibiting a bright green colour and which also showed a strong luminescence. The two spectra at the top of the picture record the light of a tungsten filament lamp after transmission through the piece of fluor spar when the latter is held at room temperature. The two lower spectra represent the effect of cooling down the specimen in the temperature of liquid air on the transmission. The appearance of specific absorption bands is very clearly seen in the latter two spectra. The mercury arc spectrum has been recorded in the plate to indicate the positions where the bands appear.

The appearance of weak birefringence patterns in natural fluorite is a feature of great interest calling for an explanation. The present investigation has revealed that this is a field of investigation which is not unrelated to the explanations of the luminescence and of the colours exhibited by natural fluorite. Amongst the facts which indicate such a connection is that a marked difference is noticeable between the appearance of the luminescent and non-luminescent areas in a section-

plate of fluorite when it is viewed between crossed polaroids. In several cases, also, it has been noticed that the luminescence resolves itself into a set of parallel laminae in positions adjacent to or coincident with the lamellae visible in birefringence. The further unravelling of these relationships can, however, well await the results of a more detailed and elaborate investigation of the whole subject.