Proc. Indian Acad. Sci. A63 333-337 (1966)

# The new physiology of vision—Chapter XLIII. The colours of fluorspar

# SIR C V RAMAN

Received May 10, 1966

Fluorspar is outstanding amongst minerals for its varied displays of colour. Of particular interest are the nuances of colour, which vary from a very light to a deep yellow, from the palest to the darkest violet, from a very light green to a saturated greenish-blue. The colours of fluorspar and the fact that it crystallises beautifully forming cubes or octahedra either as individuals or as clusters or as interpenetrating aggregates result in making the museum specimens of the mineral very attractive objects.

The origin of the colours displayed by fluorspar is a problem of great scientific interest. It is evident that the problem does not stand by itself but is linked with other properties of the material and especially the luminescence which fluorspar displays. For, the emission of visible light as the result of irradiation by ultraviolet rays is possible only if the material is, in the first instance, capable of absorbing the incident radiation. The manifestations of colour and the luminescence are therefore connected phenomena and it is not surprising to find that the luminescence displayed by fluorspar varies enormously in brightness from specimen to specimen, and that there are also noticeable differences in the colour, in other words, of the spectral composition of the emitted radiation. It is also not surprising that these variations in the brilliancy and colour of the emission are correlated with the colour of the specimen as seen by daylight. It is worthy of note in this connection that colourless specimens of fluorspar as well as optical fluorite prepared by slow crystallisation from purified material also exhibit the blueviolet glow under an ultraviolet lamp. But such luminosity is, in general, feeble in comparison with the brilliant displays put up by some of the naturally occurring fluorspars.

The observed relationships between colour and luminescence suggest that both phenomena may have a common origin. Further, since the luminescence is exhibited also by the synthetically prepared crystals of fluorite, there are grounds for presuming that the phenomenon is a characteristic property of the material itself connected with its crystal structure, and is not due to the presence of extraneous impurities. This presumption is strengthened when we recall the fact, long known to mineralogists, that though fluorspar crystallises in the cubic

#### COLOURS OF FLUORSPAR

system and should therefore be optically isotropic, nevertheless plates of the substance viewed between crossed polaroids frequently display a feeble but readily observable birefringence. This manifests itself as a network of crisscrossing lines running parallel to the cubic planes of the crystal. This is a clear indication that the natural fluorspar has a lamellar structure, instead of the complete homogeneity characteristic of an ideal crystal. Miers, in his well-known treatise on mineralogy, remarks as follows: "No relation has been traced between the colour and composition of the mineral and there is no evidence that the birefringent lamellae are due to alternation of isomorphous compounds or to zones of varying composition."

The foregoing remarks are intended to provide the background for an understanding of the particular aspect of the subject with which we are concerned here, viz., the relation between the visually perceived colour of fluorspar and the spectral composition of the light which emerges from it after traversing a sufficient thickness of the material. What follows is essentially a factual report of the results of a study of the extensive collection of fluorpars which find a place in the museum of the author's research institute. This collection, acquired in the course of years, includes specimens from several different countries, including India. It received noteworthy additions when the discovery in the year 1962 of substantial fluorspar deposits at Amba Dongar in the Baroda District of Western India enabled the author to obtain numerous specimens from that area. Colourless and transparent specimens of fluorspar as well as specimens exhibiting a variety of colours are to be found in the museum.

Green fluorspar: Perhaps the most interesting exhibits in the collection are three specimens of Chinese art sculptured from green fluorspar. One of them is 6 cm in height and represents a human figure seated on a flat pedestal and holding a ball in each hand. The material is fairly clear and is of a bright green colour. The second is a larger piece about 16 cm high, which represents a mythical animal resembling a fish on the back of which is seated a human figure holding up a flag with both arms. The colour of the material is also green, but distinctly paler than the first specimen. The third work is a massive specimen about 25 cm  $\times$  25 cm  $\times$  15 cm in its dimensions. It represents a pastoral scene and is covered with elaborate carvings which need not here be described in detail. The colour of the specimen is mostly a bright green, but there are also some parts which are of a paler hue and some parts which are distinctly bluish in colour.

Examination of the first specimen which transmits light of a bright green colour shows that this colour has its origin in the practically complete extinction of the yellow region in the spectrum in the wavelength range from 570 to 590 m $\mu$  while the green from 500 to 560 m $\mu$  remains in practically full strength. The blue sector of the spectrum is much weakened but is not totally extinguished. On the other hand, the red sector from 600 m $\mu$  to the end of the spectrum, though in diminished intensity, continues to be conspicuously visible.

## C V RAMAN: FLORAL COLOURS AND VISUAL PERCEPTION

The foregoing statement describes in the main what is noticeable also with the numerous other specimens in the collection exhibiting a green colour. The only qualification necessary is that the extinction of the yellow sector of the spectrum becomes less complete when the green colour exhibited by the fluorspar is less saturated. We may mention, as an example, a crystal of octahedral form in the collection which exhibits a pale green hue. The spectrum of the light which has traversed the crystal through a pair of opposing faces and an absorption path of 4 cm shows the weakening of the yellow sector in a striking fashion, but it is by no means in the nature of a complete extinction. The blue sector is also reduced in its intensity but continues to be visible, while the green and red sectors both remain conspicuous, the former being definitely the brighter of the two.

The purple octahedron: A crystal of octahedral form with an edge-length of 1.5 cm and with lustrous faces is one of the items of special interest in the collection. Seen by transmitted light, it resembles amethystine quartz, though the colour is not very deep. The spectrum of the light transmitted through a pair of opposing faces showed the blue, green and red sectors with the same brightness relatively to each other as normally, but the regions between 560 and 600 m $\mu$  which is the yellow sector is much weakened so much so that the presence of this colour in the spectrum is scarcely recognisable.

Two massive pieces of almost colourless fluorspar in the collection exhibit large areas in which the light which has filtered through exhibits a purplish hue. In both cases, the spectroscope reveals that in this area, there is a weakening or nearly complete extinction of the yellow sector, while the other regions of the spectrum retain their normal relative intensities.

The blue octahedron: Another interesting item in the collection is a perfect octahedron of edge-length 1.5 cm which is quite clear and transparent and has lustrous faces, and which when placed on a white sheet of paper appears of a skyblue colour. Spectroscopic examination shows that the light which has traversed the crystal through a pair of opposing faces shows an extinction of the yellow sector, while a distinct weakening of the red sector relatively to the green and the blue sectors is also noticeable.

The yellow octahedron: This crystal which is octahedral in form with an edgelength of 2 cm has lustrous faces but exhibits internal defects which prevents a free transmission between its opposing faces. It is definitely yellow in colour. The light which filters through it when examined spectroscopically shows a practically complete extinction of the blue sector, and remarkably enough also of the yellow sector in the spectrum, while the green and red sectors come through freely. Thus, we infer that the yellow colour exhibited by the crystal is a "synthetic yellow" resulting from a superposition of the red and green parts of the spectrum passing through it.

432

### COLOURS OF FLUORSPAR

Fluorspar of optical quality: Included in the collection are two specimens which are extremely clear, in other words, free from all observable cloudiness within the volume of the crystal. One of the pieces is pyramidal in shape, 10 cm long and 7 cm broad at the base, allowing a clear optical path through it of that length. The other piece is smaller, but permits of light passing through it freely in two directions, the path lengths being 4 cm and 3 cm respectively. The interesting feature in both cases is that the transmitted light along these optical paths is of a very pale yellow colour. The spectroscope reveals that this is due to an extinction of the violet end of the spectrum beyond  $430 \text{ m}\mu$  and a distinct weakening upto  $460 \text{ m}\mu$ . At greater wavelengths, there is perfect transparency.

Some remarks concerning luminescence: We may usefully here record some notes regarding the behaviour under the ultraviolet lamp of the various individual specimens referred to above.

The three Chinese works of art of green fluorspar all showed a blue-violet glow of considerable intensity. The octahedron of a pale green hue showed a violet-coloured luminescence of much smaller intensity.

The purple and blue octahedra both exhibit a feeble luminescence of a violet colour as also the massive specimens which allow light of a purplish light to filter through.

The two very clear pieces of fluorspar also exhibit luminescence, that of the smaller specimen being particularly brilliant. This suggests that the pale yellow colour exhibited by these specimens is due to the absorption at the violet end of the spectrum associated with luminescence.

The most remarkable case of all is the yellow fluorspar which exhibits a bright luminescence exhibiting a colour similar to that of the specimen itself.