

## The dynamics of the fluorite structure and its infra-red behaviour—Part I. Introduction

SIR C V RAMAN

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Calcium fluoride ( $\text{CaF}_2$ ) crystallises in the cubic system and is found widely distributed in nature as the mineral known by the name of fluorspar or fluorite. This is a material of great economic importance which is much sought after, the world production at the present time being of the order of a million tons per annum. Fluorspar has many industrial applications, the major uses being as a flux in metallurgy and as the source for the manufacture of hydrofluoric acid and therefrom of a great number of organic and inorganic fluorine compounds. The mineral itself as found in nature exhibits several highly interesting properties. It crystallises beautifully, usually as cubes and also sometimes as octahedra. Indeed, fluorite specimens are some of the most attractive exhibits to be found in mineralogical museums, by reason of the large size of the individual crystals, their grouping together as interpenetration forms and as clusters adhering to the matrix from which they emerged, and also by reason of the varied colours which they present. The luminescence which fluorspar exhibits under the ultra-violet lamp adds further to the interest of the material as a subject for study and research.

The origin of the striking colours often exhibited by the mineral fluorite is a problem in itself. Closely related to this is the problem of explaining the enormous variations in the intensity of the luminescence exhibited by the natural material under ultra-violet illumination. Indeed, the correlation between the colour of the fluorspar and the intensity of its luminescence is in many cases so obvious that it could scarcely be doubted that the two properties are interrelated. Particularly significant is the fact that the variations in the colour and the luminescence often appear side by side in the same specimen as bands or layers running through the material. Noteworthy also is the remarkable constancy of the density and refractivity of fluorspar despite the variations in the colour displayed by it. All these features taken together make it extremely unlikely that the variations in colour and the intensity of the luminescence displayed by fluorspar are ascribable to variations in its chemical composition. Indeed, it does not appear that any such variations have been established by chemical analysis.

In the present memoir, we shall concern ourselves with the infra-red behaviour of colourless fluorite. Specimens of such fluorite are not altogether uncommon in the natural deposits of the mineral, and in former times were much sought after by reason of their usefulness in the optical industry where components of low refractive index or with a high degree of transparency in the ultra-violet were needed. At the present time, such needs are filled by synthetically prepared crystals of optical quality. The procedure by which such crystals are grown is well known, viz., by melting the carefully purified material in the platinum crucible and subsequent slow solidification as the result of which it emerges from the crucible as a cylindrical casting with one end conical. Castings as large as 150 millimetres in diameter and 125 millimetres tall, weighing over 8 kilograms have been successfully prepared by this technique, the apex angle of the cone being  $120^\circ$ . From the material thus obtained, the forms in which it is actually needed for optical purposes, viz., windows, prisms and lenses, are cut out and prepared by appropriate techniques.

Some of the physical properties of fluorite may be usefully recalled here. The refractivity of the material is very low, the index for yellow light is  $15^\circ\text{C}$  being 1.4339. The dispersion in the visible region of the spectrum is also small but improves as we proceed into the ultra-violet, the refractive index attaining the value 1.50 at the wavelength  $0.2\mu$ . The transparency of fluorite in layers of moderate thickness however extends further into ultra-violet being quite good at  $0.15\mu$  and sensible even at  $0.125\mu$ .

Prisms of synthetic fluorite are made use of for infra-red spectroscopy in the range of wavelengths between about  $4\mu$  and  $8\mu$ . At wavelengths smaller than  $4\mu$ , the dispersive power of the material is too small to give adequate resolution, while at wavelengths greater than  $8\mu$ , its absorptive power is so large as seriously to interfere with the usefulness of the material as a dispersing medium. It is worthy of remark the wavelength  $8\mu$  is far removed from the spectral region ( $\sim 30\mu$ ) in which the reflecting power of the surface of a fluorite crystal reaches high values.

Fluorite is practically insoluble in water. Its melting point is  $1360^\circ\text{C}$  being much higher than those of lithium and sodium fluorides. The strength of the binding between the metal and halogen atoms indicated by these facts is also shown by the elastic behaviour of the crystal. The bulk-modulus  $K = 8.78 \times 10^{11}$  erg/cm<sup>2</sup>, and the shear-modulus  $C_{44} = 3.58 \times 10^{11}$  erg/cm<sup>2</sup>. These may be usefully compared with the corresponding figures for lithium fluoride ( $K = 6.99$  and  $C_{44} = 6.35$ ) and for sodium fluoride ( $K = 4.85$  and  $C_{44} = 2.80$ ). It will be noticed that the bulk-modulus of fluorite is the highest of the three, while its shear-modulus is intermediate between those of the other two. Both moduli are however far greater than those of the other alkali halides having the rock-salt structure. The densities of LiF, NaF and CaF<sub>2</sub> are respectively 2.60, 2.79 and 3.18. The differences between them appear small in view of the enormous differences in the atomic weights of the three elements, Li, Na and Ca, viz., 6.9, 23 and 40 respectively. But they become intelligible when the differences in crystal spacing

are considered. For,  $\text{LiF}$ ,  $\text{NaF}$  and  $\text{CaF}_2$  these are respectively 4.01 Å, 4.62 Å and 5.45 Å respectively.

As is well known, the crystal structure of  $\text{CaF}_2$  presents a closer resemblance to that of diamond than to that of rock-salt.  $\text{CaF}_2$  also resembles diamond in having a very perfect octahedral cleavage. The calcium atoms in fluorite are located at the corners and at the face-centres of the unit cubes of its structure, while the fluorine atoms are located at the centres of the eight cubes into which the unit cube may be subdivided. Thus, each fluorine atom in the structure is surrounded by four calcium atoms to which it is held by bonds parallel to the tetrahedral axes of the structure. Each calcium atom is held similarly to eight fluorine atoms, the calcium atom and the two fluorine atoms on either side of it being in the same line. The locations of the metal and halogen atoms with respect to each other thus differ from what we find in the alkali halides. The fluorines and the calciums appear in distinct layers both in the cubic and in the octahedral planes of the structure. In the cubic planes, the chlorine atoms and the fluorine atoms appear in equidistant layers whose separation is one-fourth the edge-length of the unit cubes, the fluorine layers containing twice as many atoms as the calcium layers. In the octahedral layers, each calcium layer has two fluorine layers one on either side of it, at a distance equal to one-eighth of the length of the body-diagonal of the cube. The pattern of three layers thus constituted repeats itself at intervals of one-third of the length of the body-diagonal.

### Summary

The properties of fluorite, both as observed in the naturally occurring mineral and as exhibited by the synthetically prepared crystals, are briefly described and discussed.