OPTICS OF POLYCRYSTALLINE MINERALS

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1. INTRODUCTION

RECENTLY the writer had occasion to generalise the Raman-Nath theory for the case of optical diffraction in polycrystalline media. In seeking experimental confirmation for the theory he had to read the remarkable papers of Prof. Raman and his collaborators on polycrystalline minerals and gems. It was quite fascinating to find how by just allowing a pencil of light and by studying both the transmitted (or reflected) beam and the associated halo he was able to obtain a plethora of information about the nature of the polycrystalline media. It was also quite interesting to find that in each case the information derived from elementary optical observations had been confirmed by more complicated X-ray and other studies.

Prof. Raman's studies in this field are spread over four decades (1920–1960) and these may be classified into the following four categories :

(*i*) Isotropic crystallites in isotropic media (Christiansen's experiment).

(*ii*) Anisotropic crystallites in isotropic media (Christiansen's experiments, Opals, etc.).

(*iii*) Anisotropic crystallites in anisotropic media (Moonstones, Labradorites, etc.).

(*iv*) Anisotropic crystallites in aggregation, with no cementing media (Fibres, Agate, Alabaster, etc.).

Unfortunately space does not permit a detailed discussion of all these types. As an illustration one example from each group has been briefly presented below.

2. Prof. Raman's Investigations

(*a*) *Moonstones*

Moonstones are gems belonging to the class of feldspars with potash, calcium and soda feldspars as their main constituents. For all external appearances they look like single crystals. For instance the Ceylon moonstone which exhibits the famous Schiller effect appears to be a single crystal of monoclinic symmetry. In reality it has been shown to consist of triclinic soda feldspar segregating in monoclinic matrix of potash feldspar. The "Schiller effect" which endows the moonstone with its beauty may be described as follows. When white light falls normally on the (bc) plane of the Ceylon moonstone, it gets reflected as a bluish elliptic halo. The major axis of the ellipse is normal to the *c*-axis. The phenomenon is the same at any other angle of incidence, excepting that the halo appears at approximately the angle of reflection. The intensity and the size of the halo decrease very much when the crystal is tilted about the *b*-axis, while no great change is observed for a tilt about the *c*-axis. The elliptic halo is strongly polarized with its electric vector parallel to the *b*-axis. These beautiful features are also observed in other moonstones like the Korean moonstones, South Indian moonstones, etc. The Korean moonstones give two or four haloes instead of one, which make them all the more beautiful.

From scattering experiments Raman and Jayaraman (1950, 1953) were able to derive the following information. The particle size of the segregating soda feldspar must necessarily be small compared with the wavelength, as Rayleigh scattering dominates giving a beautiful blue hue to the halo. The ellipticity of the halo indicates that soda feldspar segregates are like fibrils with the fibrils extending along the *c*-axis. This is confirmed by the lattice matching between the two feldspars ($\Delta c = 0{\cdot}02$ Å while $\Delta a = 0{\cdot}31$ Å and $\Delta b = 0{\cdot}04$ Å). Further since the light with electric vector parallel to *b*-axis is scattered most strongly, difference in refractive indices between the two feldspars must be largest along the *b*-axis ; which is confirmed by the experimental observations that show $\Delta n_a = 0{\cdot}010$ while $\Delta n_b = 0{\cdot}015$ and $\Delta n_c = 0{\cdot}010$. The double and quadruple haloes in Korean moonstones arise due to twinning and double twinning.

(*b*) *Fibres*

Raman and Bhat (1954) have made a detailed study of the optics of fibres, both natural and synthetic. A narrow pencil of sunlight was focussed on to a screen (or a photographic plate) and the fibre was kept in the pencil of incident light so that a short length of it is completely bathed by the beam. A polarizer was placed in front of the fibre to polarize the incident light, while an analyser was kept behind the fibre to analyse the scattered light. The experimental results obtained by them are given briefly below :

(*i*) For all fibres studied (glass wool, silk, rayon, asbestos, cotton and wool) the centre of the pattern consists of a circular disc with streaks of light running in all directions, when observations are made with unpolarized light. Between crossed polaroids, the central disc vanishes for any setting of the fibre with respect to the vibration

directions of the polaroids. From this one concludes that the centre of the diffraction pattern is in the same state of polarization as the incident light.

(*ii*) Glass fibres give a diffraction pattern with streaks of light running transversely to the fibre being strictly confined to a plane normal to the fibre. Between crossed polaroids the whole pattern vanishes for any setting of the fibre. From this we conclude that the fibre consists of perfectly aligned glass cylinders. The whole diffraction pattern has the same state of polarization as the incident light.

(*iii*) Silk, rayon and asbestos give an exactly similar diffraction pattern excepting for their polarization characteristics. Only when the fibre is parallel to the vibration directions of the polarizer or the analyser does the diffraction pattern vanish. At an azimuth of 45° a maximum intensity is found. These fibres therefore consist of perfectly aligned anisotropic crystallites. It is also found out that the streaks of light have different colours and brightness for unpolarized light and between crossed polaroids.

(*iv*) Cotton and wool, on the other hand, give a diffraction pattern with light streaks not only in a plane transverse to the fibre but also about it. It is impossible to extinguish the pattern between crossed polaroids for any setting of the fibre, though it shows a minimum of intensity when the fibre is parallel to the vibration directions of the analyser or the polarizer, It is therefore to be concluded that these fibres consist of anisotropic crystallites imperfectly aligned along the fibre axis. It is also found that with the incident beam polarized at 45° to the polarizer or the analyser vibration directions, the diffraction pattern changes its colour when the analyser is turned from parallel to crossed setting; the colours being complementary.

Prof. Raman felt (Ramaseshan, private communication) that with a coherent source of light like the laser considerable amount of information about crystallite disposition and orientation may be obtained by a study of diffraction patterns of fibres.

(c) *Christiansen's Phenomenon*

This beautiful optical phenomenon may be described as follows. An optically isotropic (or anisotropic) solid is powdered and put into a flat sided cell which is then filled with a liquid whose refractive index may be altered either by varying the composition or by altering the temperature. Beautiful chromatic effects are observed in the transmitted beam when white light is incident on the cell. The cell becomes transparent for a restricted region of the spectrum at which the refractive indices of the solid and the liquid are nearly equal. The rest of the spectrum from the incident light is diffused out in various directions and appears as a halo surrounding the central direct beam.

Sethi (1920) and Raman and Bhat (1953, 1955) carried out detailed experimental investigations on this Christiansen's phenomenon with isotropic and anisotropic crystallites. [The special case of spherical particles was studied by Ramachandran (1943) and Raman and Ramaseshan (1949).] As said earlier the

emergent light consists of a direct transmitted beam and an associated diffusion halo. From their detailed studies Prof. Raman and his collaborators have come to the following conclusions about the direct as well as the diffused light.

Direct Light

(*i*) Intensity distribution in the spectrum has a Gaussian form. It exhibits a peak maximum of intensity in the spectral region where there is a good degree of agreement between the refractive indices of the crystallites and the liquid. This region of peak intensity can be shifted by varying the refractive index. The peak sharpness increases with decrease in the wavelength of region of optical matching.

(*ii*) Intensity falls as particle size increases. If the crystallites are anisotropic intensity diminution also depends on the crystallite birefringence.

(*iii*) In all the anisotropic crystallites studied the polarization state is the same as that of the incident beam, a result true also for isotropic crystallites.

Diffracted Light

(*i*) Diffusion halo has a colour complementary to that of the direct beam, in unpolarized light.

(*ii*) Angular spread is least for colours in the vicinity of the direct beam wavelength, while it increases progressively as the wavelength is altered on either side, more so towards the shorter wavelengths. Thus the colour of the halo depends on the direction of observation (in unpolarized light).

(*iii*) With anisotropic crystallites the halo shows a marked degree of polarization when the crystallites are fine. With isotropic particles the halo has the same polarization state as the incident light, thus getting extinguished between crossed polaroids.

(*iv*) In the case of magnesium fluoride the halo disappears between crossed polaroids. For barium sulphate extinction is less complete. In the case of calcium sulphate (gypsum) and α-quartz it is impossible to extinguish the halo between crossed polaroids.

(*v*) For weakly birefringent crystallites the brightness as well as the colour of the halo are different for the parallel and the perpendicular settings of the analyser, the colours being complementary. When the polaroids are parallel the halo has a colour complementary to that of the direct beam. When the polaroids are crossed the halo has the same colour as that of the direct beam (which itself is absent here).

(*vi*) Barium sulphate and lithium carbonate exhibit a dark cross between the vibration directions of the polaroids which are crossed.

3. Theoretical Analysis

Raman (1949) and Raman and Viswanathan (1955) have given a theoretical treatment of the nature of the direct beam ; using a simple model of crystallite orientation. They found the intensity diminution in the direct beam to be directly dependent on the crystallite size, to vary inversely as the square of the wavelength and to be also dependent on crystal birefringence. Recently a general treatment of the problem has been worked out (*see* Ramaseshan's article) wherein

we find apart from what Raman and Viswanathan got from their simple model, one more interesting fact, namely that the intensity diminution depends also on the polarization state of the incident beam.

Raman and Nath (1935) were the first to indicate a method of tackling problems of diffraction in an optically heterogeneous medium. An incident plane wavefront emerges from the medium as a corrugated wavefront with phase randomly varying over it. Raman and Nath successfully used this procedure for ultrasonic diffraction of light in liquids. Mueller (1938) extended this theory to ultrasonic diffraction of light in crystals. A completely plane polarized wavefront that is incident on the crystal through which an ultrasonic wave is travelling, emerges out as two wavefronts periodically corrugated to different extents and polarized in two orthogonal linear states. Diffraction patterns due to these two wavefronts are afterwards added in phase.

For optical diffraction in polycrystals we can employ the same procedure [Ranganath and Ramaseshan (1972)]. When a completely polarized plane wavefront falls on a polycrystal of isotropic particles, the emergent wavefront is randomly corrugated with the amplitude and state of polarization remaining the same over the whole wavefront. However when the crystallites are birefringent the wavefront is not only corrugated randomly, but has also different state of polarization at different points. This wavefront can be split into two wavefronts, one in the same state of polarization as the incident light and the other in the orthogonal state. Though in reality the amplitude varies randomly over the two wavefronts we can replace them by an average amplitude. Let $\langle E_{\parallel}^{\circ} \rangle$ and $\langle E^{\circ}_{\perp} \rangle$ be the average amplitudes on the two wavefronts. Then the amplitudes due to the two wavefronts at a diffraction angle θ are given by

$$E_{\parallel} = \frac{R_{\parallel} \langle E_{\parallel}^{0} \rangle}{\sigma_{\parallel} \cos \theta} \exp \left\{ - \frac{R_{\parallel}^2 \tan^2 \theta}{8\sigma_{\parallel}^2} \right\} \quad (1)$$

and

$$E_{\perp} = \frac{R_{\perp} \langle E_{\perp}^{0} \rangle}{\sigma_{\perp} \cos \theta} \exp \left\{ - \frac{R_{\perp}^2 \tan^2 \theta}{8\sigma_{\perp}^2} \right\} \quad (2)$$

where R and σ are the correlation distance and the standard deviation on the wavefront. Hence β the azimuth of the net wave (obtained by adding $E_{\parallel}$ and $E_{\perp}$ in phase) with respect to that of the incident wave is given by

$$\tan \beta = (\tan \beta_0) \frac{\sigma_{\perp}/R_{\perp}}{\sigma_{\parallel}/R} \times \exp \left\{ - \frac{\tan^2 \theta}{8} \left[\frac{R_{\parallel}^2}{\sigma_{\parallel}^2} - \frac{R_{\perp}^2}{\sigma_{\perp}^2} \right] \right\} \quad (3)$$

β_0 is close to the azimuth of the incident beam ($\beta_0 = \pi/2$) and to a good approximation it can be equated to the azimuth of the incident beam.

Two interesting cases arise from (3). When $\sigma_{\parallel} > \sigma_{\perp}$; β will change from a value in the neighbourhood of β_0 to its orthogonal state as θ chages from 0 to $\pi/2$. When $\sigma_{\parallel} < \sigma_{\perp}$; β will remain at the same azimuth as the incident light when we go to any angle of diffraction. In either case at $\theta = 0$ diffracted light is in the same state of polarization as the incident light, a result amply supported by experiments. It can be shown by a careful analysis that $\beta = 0$ for the region of the spectrum where there is optical matching, while $\beta \approx \pi/2$ in the rest of the spectrum. This accounts for the change in colour as the analyser is turned from crossed to parallel setting. As the colour that is most freely transmitted is present to a very small extent in the halo, even the brightness changes as the setting of the analyser is changed. In the crossed setting the halo should have the same colour as that of the direct light, while

in the parallel setting both the halo and the direct beam appear but the two are of complementary colours.

The rate at which the azimuth changes depends upon

$$\psi = \left(\frac{R_{\parallel}^2}{\sigma_{\parallel}^2} - \frac{R_{\perp}^2}{\sigma_{\perp}^2}\right) \approx \frac{R^2}{(\overline{\delta n})^2\,\bar{\tau}} \qquad (4)$$

where $(\overline{\delta n})^2$ and $\bar{\tau}$ are the average crystallite birefringence and crystallite size. When $\bar{\tau}$ is small ψ will be large making the polarization effects conspicuous, a fact supported by experiments. Values of $(\overline{\delta n})^2$ for magnesium fluoride, barium sulphate, calcium sulphate and α-quartz are respectively 0·02, 0·009, 0·0005, 0·0006. Hence ψ is a minimum for magnesium fluoride while it is a maximum for calcium sulphate and α-quartz. Thus there is hardly any change in polarization in the case of magnesium fluoride which therefore gives a halo that can be extinguished between crossed polaroids. On the other hand, the change in polarization is large for α-quartz or calcium sulphate rendering it impossible to extinguish the halo between crossed polaroids. These are the very experimental observations of Raman and Bhat (1955).

In the case of oriented polycrystals like fibres of wool and cotton, we find maximum effects of birefringence (which itself is very small) for an incident light wave polarized at 45° to the fibre axis. Thus we expect polarization and chromatic effects to be conspicuous for this state of polarization. This has also been observed by Raman and Bhat (1954). Thus most of the observed facts can be explained by the theory presented here.

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