POLARISATION OF RAMAN SCATTERING AND OF FLUORESCENCE IN DIAMOND

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1. *Introduction*

It is well known that the principal vibration of the diamond lattice in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other manifests itself in the Raman spectrum as a sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ at room temperature. Observations of the state of polarisation of this line were made by Ramaswamy (1930) who reported it to be strongly polarised. Bhagavantam (1930) in the course of his study of the Raman effect in several diamonds however, observed the line to exhibit only imperfect polarisation. This difference between the two observers is not surprising in view of the numerous disturbing factors capable of influencing the experimentally recorded result. More recently, Nayar (1942) made a re-determination of the depolarisation ratio, using a small octahedral crystal and immersing it in benzene to reduce the disturbances arising from the refractions and internal reflections at the surfaces of the crystal. He found that when the incident light was unpolarised, the two components of the scattered beam were of equal intensity, giving a value of 1·0 for the depolarisation factor. This, as he pointed out, differs from the theoretical value of 2 predicted by Saxena (1940) on the basis of Placzek's theory for triply degenerate vibrations in cubic crystals. In view of these conflicting results reported by different observers and their divergence from the theoretical values, it was considered desirable to obtain more accurate polarisation data, taking the precautions necessary to eliminate the factors giving rise to errors, *viz.*, birefringence in the diamond, refractions at the surfaces of entry and emergence, internal reflections and finally the convergence error present in all depolarisation measurements. The first three of these were avoided by choosing for the investigation from Sir C. V. Raman's personal collection a diamond (N.C. 4) which had a symmetric and approximately octahedral form and smooth lustrous faces and was free from any internal flaws or inclusions. The diamond was also free from any noticeable birefringence. This was tested by passing a beam of polarised light through the crystal and determining the state of polarisation of the emergent beam. The disturbing effects of surface reflections and refractions were minimised by immersing the diamond in a high refractive index liquid, while convergence errors were reduced by using a small-aperture short-focus lens for condensing the light into the crystal. A careful study of the polarisation characters of the Raman line as well as of the fluorescense bands of diamond has been made in the present investigation, using incident unpolarised as well as polarised light for excitation.

2. *Experimental Technique*

The diamond was kept immersed in α-bromonaphthalene contained in a small Wood's tube just large enough to hold the crystal. The tube was provided with optically plane windows and was blackened throughout except for stops for the entrance and emergence of light, which besides cutting off parasitic light, served to confine the incident and scattered beam to mutually perpendicular directions. Light from a mercury pointolite arc was condensed by a small-aperture lens at the centre of the crystal through one of its octahedral faces, the scattered light being observed through another octahedral face approximately normal to the former. The scattered light was focussed on the slit of the spectrograph by a lens of small aperture. The convergence error in this arrangement was only 1%, the maximum semi-convergence angle being about 11°. A large aperture Ahrens Nicol interposed in the path of the incident light served as the polariser. A sodium nitrite filter isolated the 4358 radiation for exciting the Raman line effectively cutting off light of shorter wave-lengths which excite fluorescence, while during polarisation measurements of the fluorescence bands the filter was dispensed with. A quartz double-image prism of the Wollaston type properly oriented and placed just before the slit of the spectrograph split the beam into vertical and horizontal components. The spectra were photographed on Ilford Selochrome plates, the instrument used being a Hilger two-prism spectrograph having a dispersion of 28 A.U./mm. in the 4358 A.U. region.

3. *Polarisation Measurements of the Raman Line*

As usual in polarisation studies, three mutually perpendicular directions OX, OY and OZ in the crystal were chosen as reference axes; the direction of the incident beam was designated as along OX, the direction of the scattered beam as along OY while OZ was the direction mutually perpendicular to both. Since diamond is isotropic, it was possible to obtain only three different spectrograms of scattered light; *viz.*, with

(*a*) incident light unpolarised,
(*b*) incident light polarised with electric vector along OY,
(*c*) incident light polarised with electric vector along OZ.

Quantitative measurements of the depolarisation values for these three cases were made and are given in Table I along with the theoretical values predicted by Saxena for the triply degenerate vibrations in the cubic class.

TABLE I

$$\rho = \frac{E_x^2}{E_z^2}$$

Direction of the Incident Electric vector	Depolarisation	
	Experimental	Theoretical
Along OY	1·5	1
Along OZ	0·6	∞
Unpolarised Light	1·0	2

The depolarisation factor ρ was determined as usual by microphotometering the plates and obtaining the densities of the lines for the horizontal and vertical components. A set of intensity marks were obtained on the same photographic plate by the method of varying slit-widths, using as the source of illumination a small tungsten filament lamp fed from a battery at constant voltage. From the density-log intensity curve thus obtained for the wave-length of the Raman line, the intensity ratios of the horizontal to the vertical component were calculated. The ratios obtained in this way involve errors due to the spectrograph caused by oblique refraction and reflection at the prism surfaces which strengthen the horizontal component. This error, which is characteristic of the instrument used, was determined by allowing light from a tungsten lamp after it had passed through a double-image prism to fall on the slit of the spectrograph and photographing the spectra for a series of exposures. The ratio of the intensities of the vertical and horizontal components was determined microphotometrically as described above. This gave a value of 0·71 for the spectrographic correction. The values in Table I are corrected for the instrument error.

4. *Theoretical Derivation of the Polarisation Characteristics of the Raman Line*

Tables of selection rules for the different types of oscillations in crystals belonging to the seven classes of symmetry have been given by Placzek (1934, 1938). On the basis of these, Saxena (1940) has calculated the polarisation ratios and the total intensities of Raman lines in terms of the tensor components in the transverse and longitudinal scattering. He has shown that Raman lines in crystals may be considered as due to the deformations of the optical polarisability ellipsoid of the solid produced by the internal oscillations and that the deformations can be expressed in terms of the six components of the change of polarisability tensor. The equation for the deformed ellipsoid is given by

$$(\mathrm{A}+\epsilon_{xx})\,x^2+(\mathrm{B}+\epsilon_{yy})\,y^2+(\mathrm{C}+\epsilon_{zz})\,z^2+\epsilon_{xy}\cdot xy+\epsilon_{xy}\cdot yz+\epsilon_{xz}\cdot xz=1$$

where A, B and C are the lengths of the principal axes of the polarisability ellipsoid and $\epsilon_{ii}=(\epsilon_{xx},\ \epsilon_{yy},\ \epsilon_{zz})$ $\epsilon_{ik}=(\epsilon_{xy},\ \epsilon_{yz},\ \epsilon_{zx})$ are the six components of the change of polarisability tensor. It is possible to evaluate these tensor components by illuminating the crystal along a fixed direction, say OX, and observing the scattered light along OY, and calculating the induced moments in the scattered radiation. The components of the scattered radiation lie along the x and z directions and the induced moments in these directions are given by

$$\Delta \mathrm{M}_x=\epsilon_{xx}\cdot \mathrm{E}_x+\epsilon_{xy}\cdot \mathrm{E}_y+\epsilon_{xz}\cdot \mathrm{E}_z$$
$$\Delta \mathrm{M}_z=\epsilon_{zx}\cdot \mathrm{E}_x+\epsilon_{zy}\cdot \mathrm{E}_y+\epsilon_{zz}\cdot \mathrm{E}_z$$

Since the depolarisation ratio ρ is given by

$$\rho=\frac{(\Delta \mathrm{M}_x)^2}{(\Delta \mathrm{M}_z)^2}$$

it will be seen that for an incident electric vector along OY

$$\rho_{\mathrm{OY}}=\frac{(\epsilon_{xy})^2}{(\epsilon_{yz})^2}$$

and for an incident electric vector along OZ

$$\rho_{\mathrm{OZ}}=\frac{(\epsilon_{xz})^2}{(\epsilon_{zz})^2}$$

while for incident unpolarised light

$$\rho_{\mathrm{unp.}}=\frac{(\epsilon_{xy})^2+(\epsilon_{xz})^2}{(\epsilon_{yz})^2+(\epsilon_{zz})^2}.$$

The principal vibration of the diamond lattice falls under the triply degenerate class for which the selection rules given by Placzek are

$$\epsilon_{xx}=\epsilon_{yy}=\epsilon_{zz}=0$$
$$\epsilon_{xz}=\epsilon_{yz}=\epsilon_{xy}\neq 0$$

Thus we find that $\rho_{\mathrm{OY}}=1$, $\rho_{\mathrm{OZ}}=\infty$ and $\rho_{\mathrm{unp.}}=2$.

It will be seen from Table I that while the results for incident unpolarised light agree with those obtained by Nayar (in spite of the small error introduced in his results by the crystal birefringence), they agree in no case with the theoretical values obtained on the basis of the selection rules given by Placzek. This discrepancy between the theoretical and the experimental values indicates the necessity for a reconsideration of the theoretical ideas, on the basis of which the selection rules have been derived.

5. Polarisation of the Fluorescence Bands of Diamond

Table II gives the values for the depolarisation ratio ρ for the fluorescence bands of the 4152 system for the 3 cases mentioned above, corrected for the instrumental error.

TABLE II

$$\rho = \frac{E_x^2}{E_z^2}$$

Incident light unpolarised	1·0
Incident light polarised with electric vector along OY	0·8
Incident light polarised with electric vector along OZ	0·2

Ramaswamy had previously observed that with incident unpolarised light the fluorescence bands were depolarised. It will be observed from the table that the two components of the fluorescent beam are of equal intensity for incident unpolarised light, while the bands appear partially polarised with the incident electric vector along OY and strongly polarised with the incident electric vector along OZ. No obvious difference was noticed in the polarisation characters of the main band at 4156 A.U. and the subsidiary bands at longer wave-lengths.

In conclusion, the auther wishes to express her grateful thanks to Professor Sir C. V. Raman for his helpful interest and encouragement in this work.

6. Summary

The depolarisation values for the principal Raman line in diamond have been determined using a natural crystal and taking the necessary precautions to eliminate errors due to the birefringence of diamond and to refractions and internal reflections in the crystal. The results obtained for the three different cases, *viz.*, with the incident light unpolarised and polarised with the electric vector along the OY and OZ axes, are found to differ notably from the theoretical values predicted by Saxena on the basis of the selection rules given by Placzek.

The polarisation of the fluorescence bands of the 4152 system has also been studied. It is found that with incident unpolarised light the bands appear depolarised while they appear polarised in the other two cases.

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