RECIPROCITY THEOREM IN COLLOID OPTICS.

(Case of Orientated Particles.)

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1. *Introduction.*

IT has been pointed out in a recent paper (Krishnan, 1938) in these *Proceedings* that the reciprocity relation

$$\rho_u = (1 + 1/\rho_h) / (1 + 1/\rho_v) \qquad (1)$$

is valid not for a single non-spherical particle with fixed orientation in space, but only for a colloidal solution containing a large number of particles, irrespective of their size, shape, structure and distribution, provided they have no preferred orientation in the plane containing the incident beam and the direction of observation. In the case of small ellipsoidal particles, Rayleigh's (1918) theory indicates that the two anisotropic components H_v and V_h are not equal for a single particle orientated in a specific way. But, if an averaging be carried out over all orientations of the particles in the horizontal plane which are similarly situated with respect to the vertical axis, it is easily verified from the expressions given by Rayleigh that the two quantities mentioned above become identical and hence the reciprocity relation (1) holds good. In the case of large non-spherical particles it can be shown (as indicated below) that the random orientation of the particles is a necessary condition for relation to (1) be satisfied.

For simplicity, let us suppose that the particles are in the form of rods. Let the horizontal plane X–Y be the plane of observation. Consider a small volume element of the colloidal solution which contains a large number of particles. If, in any horizontal section of the element of volume all the particles are orientated with their major axis parallel to the X-axis as shown in Fig. 1 *a*, the intensity and state of polarisation of the light scattered along the Y-axis for light incident along the X-axis will be quite different from the intensity and the state of polarisation of the light scattered along the X-axis for light incident along the Y-axis. This is because, in one case, the light is incident along the major axis of the particles and the scattered light is observed along the minor axis, while in the other case the light is incident

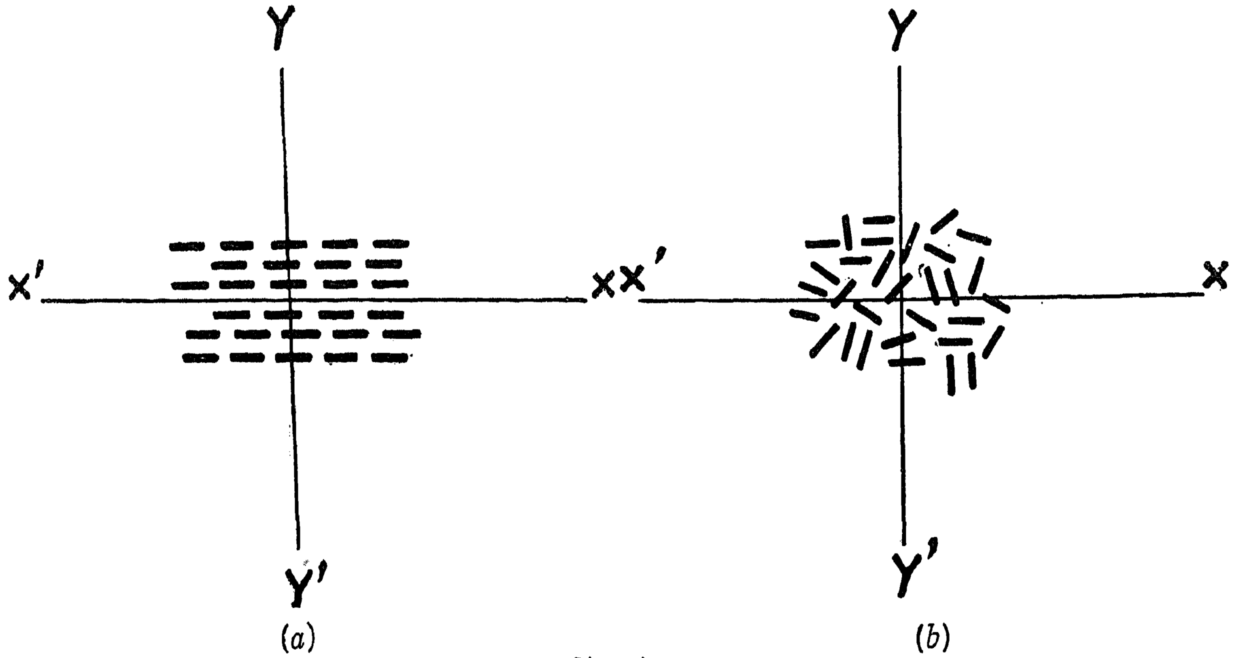

FIG. 1.

along the minor axis and the scattered light is observed along the major axis. Consequently, the two cases are entirely different, although the reciprocity principle as stated by Lord Rayleigh is applicable and the relations (22) and (23) given in the earlier paper (Krishnan, 1938) are valid. The relation (24) will not be valid since the depolarisation factors measured depend not only on the actual angle of scattering, but also on the relative orientations of the particles with respect to the incident and scattered beams, as in the case of a biaxial crystal. Consequently, the reciprocity relation (1) will cease to be valid.

If, on the other hand, the particles are distributed at random in the horizontal plane as in Fig. 1 *b*, the element of volume of the solution, taken as a whole, will be isotropic in the plane containing the incident and scattered beams. In consequence, the intensity and state of polarisation of the light scattered by the element of volume will depend only on the angle which the direction of observation makes with the incident beam, as in an ordinary fluid, and not on the actual direction of observation, as in a biaxial crystal. Therefore, relation (1) should hold good in this case.

The object of the present investigation is to study the effect of orientation of the particles on the reciprocity relation as well as on the intensity and state of polarisation of the scattered light. Fine graphite sol was chosen as the scattering substance. Magnetic fields were employed as the external orientating agency. The depolarisation factors ρ_u, ρ_v and ρ_h of the transversely scattered light were measured with white light for the following three cases, namely, (1) with the magnetic field perpendicular to the direction of observation and also to the direction of the incident beam, (2) with the magnetic field parallel to the direction of observation and (3) with the magnetic field, parallel to the direction of the incident beam.

2. *Results.*

Case 1.—Incident beam parallel to the X-axis, direction of observation parallel to the Y-axis and magnetic field parallel to the Z-axis. The last column in Table I gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h applying the reciprocity relation. In all the cases a satisfactory

TABLE I.

Strength of the magnetic field in gauss	ρ_h %	ρ_v %	ρ_u %	ρ_u calculated according to relation (1,
0	26·0	4·5	19·8	20·9
1120	13·2	2·7	25·9	22·5
4060	8·5	2·1	28·25	26·7
5730	5·3	1·7	33·3	33·6
6860	4·3	1·6	36·8	35
7620	3·8	1·4	36·8	37·6

agreement is obtained between the observed and calculated values, showing thereby that the reciprocity relation is valid for this case irrespective of the strength of the field. The disc-like graphite particles are orientated with their plane faces parallel to the magnetic field and are free to rotate about an axis parallel to the magnetic field and perpendicular to the plane of observation. Because of the free rotation of the particles, any direction in this plane is as important as any other and the factors ρ_u, ρ_v and ρ_h measured in this plane will depend only on the angle of scattering. Hence the reciprocity relation also holds good.

In this case, as the particles get orientated, ρ_h and ρ_v decrease, while ρ_u increases. The depolarisation factors are plotted against the field strength and the curves are reproduced in Figs. 2, 3 and 4. It is clear from the graphs that as soon as the field is put on, there is a sudden change in the values of ρ_u, ρ_v and ρ_h. The depolarisation factors attain a steady value for a field strength equal to about 7000 gauss showing thereby that all the particles are orientated. Any further increase in the field strength does not appreciably affect the depolarisation factors.

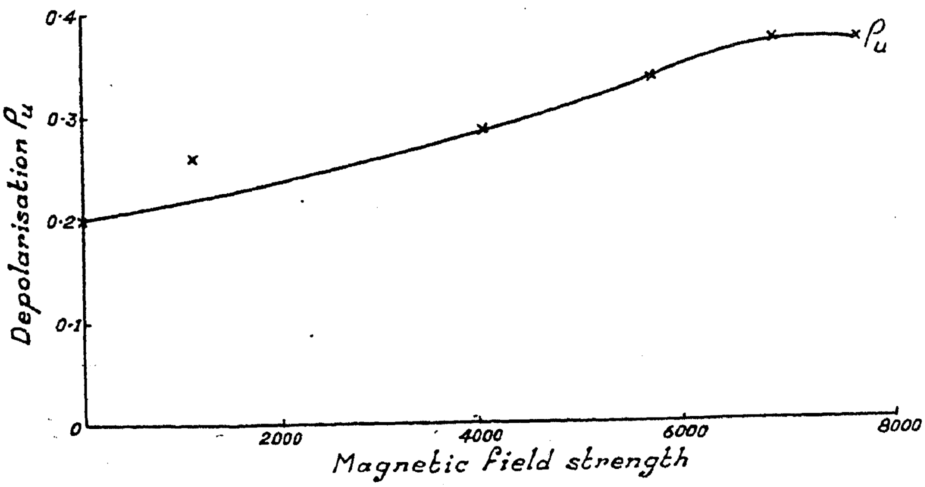

FIG. 2.

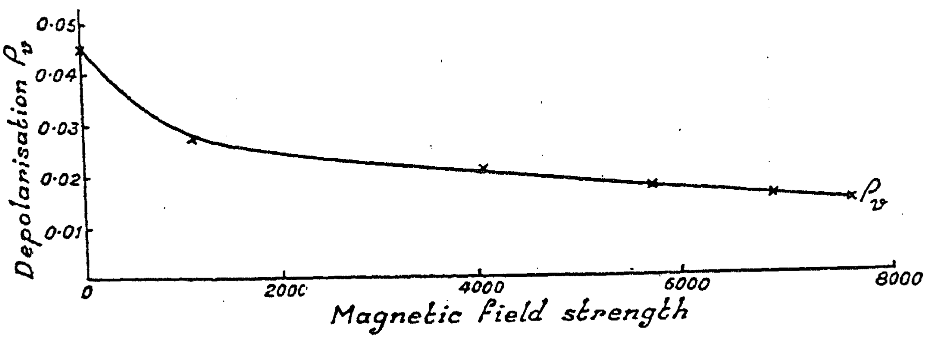

FIG. 3.

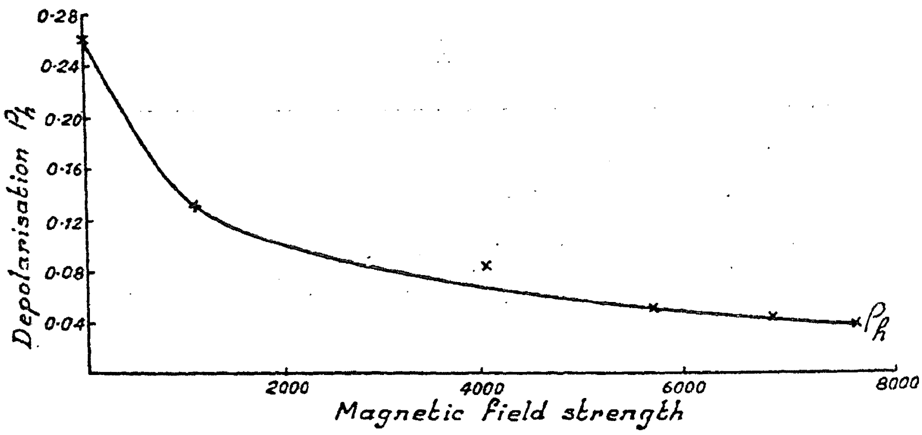

FIG. 4.

Another interesting observation was made when the field was put on. Out of the four components, $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$ which could be seen by the double double-image prism method, as the field was put on, not only were the two middle components equal to each other, but the intensity of each of these also remained sensibly unaffected. The intensity of the two outer components, on the other hand, brightened up when the field was put on. This shows that the anisotropic scattering which is represented by the components $\overline{H}_v$ and $\overline{V}_h$ is not influenced by the orientation of the particles in the manner stated above. There is an apparent increase in the volume scattering. It is well known that the light scattered from a rod the axis of which is parallel to the incident electric vector or from a disc with a diameter in the same position, is considerably stronger than the light emitted by a particle with any other azimuth. This seems to be true in respect of the volume scattering and not noticeably for the anisotropic scattering.

Case 2.—Incident beam parallel to the X-axis, direction of observation parallel to the Y-axis and the magnetic field parallel to the Y-axis. The depolarisation factors ρ_u, ρ_v and ρ_h measured for this case are given in Table II.

TABLE II.

Strength of the magnetic field in gauss	ρ_h %	ρ_v %	ρ_u %	ρ_u calculated according to relation (1)
0	26·0	4·5	19·8	20·9
1120	41·0	8·6	21·7	27·2
4060	47·2	12·4	20·5	34·4
5730	53·7	15·0	22·8	37·3
6860	53·7	16·3	23·8	39·6
7620	53·7	16·3	25·4	40·0

The last column in Table II gives the values of ρ_u calculated from the observed values of ρ_v and ρ_h applying the reciprocity relation (1). It will be seen that the calculated values do not agree with the observed values except for the case when the field strength is zero. When the observations were made with the double-image prism method, it was found that the two middle components became unequal in intensity as soon as the field was put on. The second component $\overline{H}_v$ was brighter than the third component $\overline{V}_h$. In this case, the disc-like particles of graphite get themselves orientated with their plane faces parallel to the direction of observation and consequently the reciprocity relation ceases to be valid.

Unlike in the previous case, the depolarisation factors ρ_u, ρ_v and ρ_h, all of them increase as the particles get themselves orientated as indicated above. There is an apparent increase in the optical anisotropy. It is further observed that the effect of orientation of the particles with their plane faces parallel to the direction of observation, is to weaken the components $\overline{V}_v$ and $\overline{H}_h$ and to increase the intensity of the component $\overline{H}_v$. The component V_h is sensibly unaffected.

Case 3.—Incident beam parallel to X-axis, observation along the Y-axis and the magnetic field parallel to the X-axis. The depolarisation factors are given in Table III.

TABLE III.

Strength of the magnetic field in gauss	ρ_h %	ρ_v %	ρ_u %	ρ_u calculated according to relation (1)
0	26·0	4·5	19·8	20·9
1120	75·5	4·5	17·0	10·0
4060	134·2	4·5	12·5	7·5
5730	219·8	4·0	9·9	5·6
6860	300·0	3·7	8·2	4·7
7620	300·0	3·7	8·2	4·7

In this case also, it is found that the reciprocity relation does not hold good. This is quite in accordance with the theoretical considerations. On applying the magnetic field the values of ρ_u and ρ_v decrease, while that of ρ_h increases. The fall in the value of ρ_v is less pronounced than that of ρ_u. As the particles get progressively orientated the factor ρ_h exceeds 100% showing thereby that the vertical component is brighter than the horizontal component when the incident beam is polarised with vibrations horizontal. In this case also, the effect of orientation of the particles with their plane faces parallel to the direction of the incident beam is to increase the intensity of $\overline{V}_h$ and to weaken the components $\overline{V}_v$ and $\overline{H}_v$. The component $\overline{H}_h$. remains sensibly unaffected.

3. *Conclusion.*

It is clear from what has been said above that the reciprocity relation is valid for the case of orientated non-spherical particles only if they are free to rotate about an axis perpendicular to the plane containing the incident beam and the direction of observation, or if, in the aggregate, they have random distribution in this plane. The same considerations can be extended to the case of crystals also. For a uniaxial crystal the reciprocity relation will be true if the plane containing the incident beam and the direction of observation is perpendicular to the optic axis of the crystal. For a biaxial crystal it will not be true for any plane of observation.

The changes produced in the intensities of the component $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$ and also in the values of ρ_u, ρ_v and ρ_h, by the orientation of the particles are rather complicated. It is, however, premature to draw any conclusion from the results obtained from a study of the light-scattering in one particular sol. A comparative study of the depolarisation factors ρ_u, ρ_v and ρ_h and also the intensities of the four components $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$ has to be made in a large number of colloidal solutions containing particles of varying size and shape, when they are subjected to the action of external agency such as magnetic or electric fields or streaming flow. This will be taken up soon.

In conclusion, the author takes this opportunity to express his respectful thanks to Professor Sir C. V. Raman under whose guidance the present investigation was carried out.

4. *Summary.*

The effect of orientation of the particles on the reciprocity relation as well as on the intensity and state of polarisation of the scattered light has been studied for the case of graphite sol. Magnetic fields were employed as the external orientating agency. The depolarisation factors ρ_u, ρ_v and ρ_h of the transversely scattered light have been measured with the magnetic field (1) perpendicular to the incident beam and the direction of observation, (2) parallel to the direction of observation and (3) parallel to the direction of the incident beam. The values of ρ_u, ρ_v and ρ_h are found to satisfy the reciprocity relation only when the magnetic field is perpendicular to both the incident and the scattered beams. In the other two cases the reciprocity relation is not satisfied. Marked changes are observed in the intensities of the components $\overline{V}_v$, $\overline{H}_v$, $\overline{V}_h$ and $\overline{H}_h$ and also in the values of ρ_u, ρ_v and ρ_h.

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Rayleigh, *Phil. Mag.*, 1918, 35, 377.