MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES.

I. Mother of Pearl.

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1. Introduction.

The recent investigations of K. S. Krishnan and his collaborators[1] have shown that in magne-crystallic action we have a powerful method of determining molecular orientations in crystals. When magnetically anisotropic molecules or ions are arranged regularly as they are in a crystal, the crystal also will show anisotropy, the magnitude of which will depend upon the orientation of the molecules in the crystal lattice. A correlation of the anisotropy of the crystal with that of the individual molecules enables the orientations of the latter to be calculated. The approximate molecular orientations in the naphthalene crystal were first determined by S. Bhagavantam[2] by this method. Recently, accurate determinations of anisotropy for a large number of para- and dia-magnetic crystals, both organic and inorganic, have been made by Krishnan and his collaborators, and in some favourable cases such as biphenyl and dibenzyl, the orientations of the molecules have been determined with precision.

Just as a crystal is an aggregate of ions or molecules regularly arranged, there are naturally occurring substances which are known to be aggregates of minute crystals in a more or less regular arrangement. If the individual crystals are anisotropic, we should expect the substance also to show anisotropy, and we can employ Krishnan's method for determining the crystal orientations. One such substance is the nacre of iridescent shells. The magnetic properties of nacre have not been investigated quantitatively, although Nacken[3] and others[4] have observed its anisotropy in connection with the study of the differences between real and "culture" pearls. The latter contain a small spherical inner core of mother-of-pearl and as a consequence take up a definite orientation in a magnetic field unlike real pearls, which do not show any preferred orientation. The object of the present investigation is chiefly to determine the anisotropy of nacre quantitatively with a view to

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gain some knowledge of its structure and thereby supplement what is already known from X-ray and optical studies.

2. *Structure of Nacre.*

It is well known that mother-of-pearl consists of minute crystals of aragonite arranged in thin layers and honey-combed in between an organic cementing medium called conchyolin.[5] Aragonite is diamagnetic, and its magnetic properties are known both as regards its absolute susceptibilities along the three axes (Voigt and Kinoshita)[6] and magnetic anisotropy (Krishnan)[7].

By examination under the polarising microscope, W. J. Schmidt[8] has shown that the aragonite crystals are orientated in nacre with the c-axes normal to the elementary laminæ. Recently, from a study of the diffusion haloes of nacre, Sir C. V. Raman[9] has drawn attention to the structural differences in the shells of the three main classes of molluscs. These differences have been verified by Dr. S. Ramaswamy[10] by X-ray analysis. He has found that while the c-axes of the crystals are orientated normal to the laminæ in all the shells, the orientations of the a and b axes are different in the various shells, viz., a random orientation in *Turbo* and *Trochus* and a preferred orientation in *Margaratifera vulgaris* and *Mytilus viridis*. Evidence of twinning has been found in *Nautilus pompilius*, the twins being arranged symmetrically with respect to the lines of growth. In a more recent paper[11] a preferred orientation has been found by the same author in the case of *Haliotis* also with however a very large error in orientation.

3. *Determination of the Anisotropy of Nacre.*

This was done by means of the method of oscillations developed by Krishnan.[12] If χ_1 and χ_2 are algebraically the maximum and minimum values of the susceptibility along two perpendicular directions in the plane of oscillation of a body suspended by means of a quartz fibre in a uniform magnetic field, it will orientate itself with the χ_1 axis in the field direction. If the torsion head is turned so that the torsion of the fibre is zero at this position, and if T_1 and T are the periods of oscillation in and outside the field respectively, we have,

$$\chi_1 - \chi_2 = \frac{1}{m} \; \frac{c}{H^2} \cdot \frac{T^2 - T_1{}^2}{T_1{}^2}$$

$\chi_1 - \chi_2$ = Specific anisotropy in the plane of oscillation.

c = Modulus of torsion of the fibre.

m = Mass of the body.

H = Field strength in Gauss.

Some preliminary experiments showed that all the shells examined are diamagnetic, the direction of maximum diamagnetic susceptibility being normal to the plane of the laminæ. This direction then is one of the principal magnetic axes in nacre. The other two axes lie in the laminar plane and could be easily located by observing the orientation in the field.

The following precautions were taken :—

(1) The specimens selected were seen to be as white as possible and free from discolourations. By chemical test it was found that none of the pieces contained even traces of iron.

(2) The pieces of nacre were carefully cleaned before use.

(3) The elementary laminæ are usually inclined at a small angle to the shell surface. The shell faces were ground until they were parallel to the laminæ in the pieces used.

Experimental Details.—Fine quartz fibres drawn in the flame were employed. The pieces were mounted on the suspension as described in Krishnan's paper.

The field was tested for homogeneity and the strength determined by means of the Ballistic Galvanometer, in the usual way. Some preliminary experiments were made with a single crystal of calcite for which the anisotropy values are known, with satisfactory results.

The modulus of torsion c of the fibre was determined by observing the period of oscillation of a small rectangular plate of glass suspended at its end of which the moment of inertia about the axis of suspension can be calculated from the dimensions.

The arrangement shown in Fig. 1 was employed for observing the orientation of the shell in the field.

The piece of shell is illuminated from below by means of a powerful lamp and condensing lens. The image reflected at the glass plate G kept inclined at an angle of 45° is viewed through the short focus telescope T. The telescope is provided with a circular brass scale by means of which its angular rotations can be measured. The orientations of the shell can be easily determined by rotating the telescope suitably such that the cross-fibre coincides with any position of the image of the shell.

The angle of inclination of the elementary laminæ to the shell surface can be determined magnetically, since the orientation of the laminar plane is found to be always along the field in the case of all the shells. This angle has also been measured optically by Sir C. V. Raman.[13] The values of the angle found by the optical and the magnetic methods agreed satisfactorily.

H .. Torsion Head
P .. Shell Piece
G .. Glass plate
L .. Condensing Lens
I .. Lamp
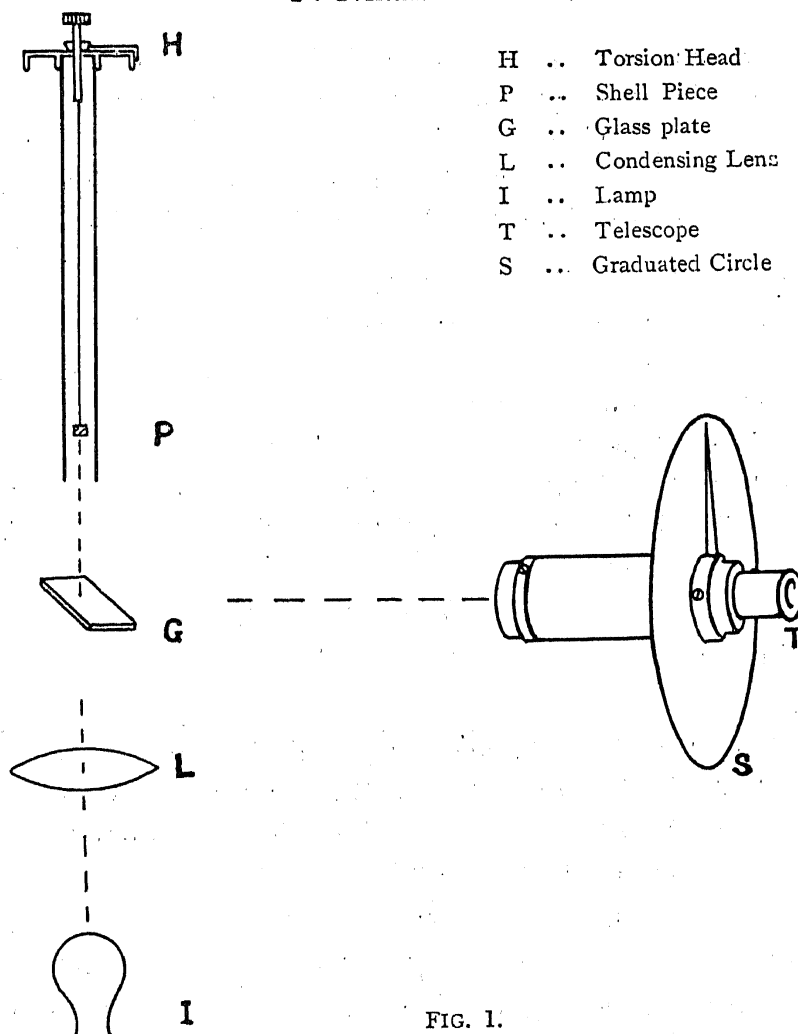T .. Telescope
S .. Graduated Circle

FIG. 1.

4. Measurement of Absolute Susceptibility.

This was done by Rabi's[14] null method, the liquid used being a saturated solution of potassium iodide. The piece of shell was suspended by means of a torsionless silk fibre about 60 cms. long, with one of its magnetic axes vertical. It orientated itself in the field with the axis of maximum diamagnetic susceptibility normal to the field. The measurements give the susceptibility along that axis which is parallel to the field.

The concentration of the potassium iodide solution was determined by titration against a standard solution of silver nitrate using eosin as indicator. From the measured values of the concentration used, the density of the solution, and the density of the shell, we can deduce the susceptibility of the shell making use of well-known relations.

5. Results.

The shells investigated were M. margaratifera, Turbo, Haliotis, Mytilus viridis and Nautilus pompilius. Table I gives the observed values of the anisotropy. Krishnan's values for aragonite are also included for comparison.

TABLE I.

Unit: 10^{-8} of a C.G.S. Electromagnetic Unit. $\chi_1' > \chi_2' > \chi_3'$ algebraically.

Class	Shell	Mode of Suspension	Orientation	Specific Anisotropy		Remarks
				Observed	Calculated	
Gastropod	*Turbo* sp.	(A) Laminar plane horizontal	..	$\chi_1'-\chi_2'=0,05$	0,07	Orientation in the laminar plane, indefinite
		(B) Plane vertical and χ_1' axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=5,6_0$		
		(C) Plane vertical and χ_2' axis vertical	„	$\chi_1'-\chi_3'=5,6_7$		
„	*Haliotis* sp.	(A)	..	$\chi_1'-\chi_2'=0,07$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=6,0$		
		(C)	„	$\chi_1'-\chi_3'=6,1$		
Bivalve	*M. Margaratifera*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0,21$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=5,6$		
		(C)	„	$\chi_1'-\chi_3'=5,7$		
Bivalve	*Mytilus viridis*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0,16$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=5,7$		
		(C)	„	$\chi_1'-\chi_3'=5,8$		
Cephalopod	*Nautilus pompilius*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0,5$	0,3	Comparatively large anisotropy in the laminar plane
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=6,1$		
		(C)	„	$\chi_1'-\chi_3'=6,4$		

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TABLE II.

Anisotropy of Aragonite (Krishnan).

Unit: 10^{-8} *of a C.G.S. Electromagnetic Unit.*

Mode of Suspension	Orientation	Specific Anisotropy
a-axis vertical	b-axis along the field	$4 \cdot 2$ $X_b - X_c = 4 \cdot 2$
b ,, ,,	a ,, ,,	$4 \cdot 0$ $X_a - X_c = 4 \cdot 0$
c ,, ,,	b ,, ,,	$0 \cdot 13$

TABLE III.

Absolute Susceptibility of the Shells.

Shell	Susceptibility in a direction normal to the laminar plane
Turbo	$-0,39 \ 10^{-6}$
Haliotis	$0,38$,,
M. margaratifera	$0,39$,,
Mytilus viridis	$0,39$,,
Nautilus pompilius	$0,36$,,

TABLE IV.

Density of the Shells.

Shell	D in Gm/cm³
Turbo	2,77
Haliotis	2,73
M. margaratifera	2,78
Mytilus viridis	2,80
Nautilus pompilius	2,62

Density of
Aragonite .. $2 \cdot 92$

For the sake of brevity, the magnetic axes are denoted as the χ_1', χ_2' and χ_3' axes. The χ_3' axis is normal to the elementary laminæ. $\chi_1' - \chi_2'$, $\chi_2' - \chi_3'$ and $\chi_1' - \chi_3'$ are respectively the anisotropies in the respective planes. If two of these are determined, the third can also be easily obtained from these. As a check, the third was also independently determined.

The values of anisotropy differed by about 10% for the pieces taken from different parts of the same shell. The stated values represent only an average.

It will be seen that the anisotropies of the shells corresponding to the modes of suspension B and C are higher than should be expected from aragonite alone. This suggested that the conchyolin itself might have an anisotropy which adds itself to that of the aragonite crystals. An attempt was made to observe this anisotropy directly, by isolating the conchyolin. The aragonite was carefully dissolved off by dilute hydrochloric acid. The gas evolved had to be squeezed out from time to time since its accumulation prevented further action. This, however, could not be done without disturbing the conchyolin layers. One could not be sure, therefore, whether conchyolin retained its structure after its separation. This element of uncertainty, which is unavoidable, is a serious drawback of the method.

It was a matter of difficulty to prepare the conchyolin from *Nautilus pompilius* since it easily broke up and lost its structure. *Haliotis*, however, gave more satisfactory specimens.

The results obtained were inconclusive, for whereas two specimens showed slight anisotropy, others were only feebly so.

Conchyolin was found to be diamagnetic.

6. *Discussion.*

The anisotropy of nacre definitely indicates that the *c*-axes of aragonite crystals are orientated normal to the elementary laminæ in the case of all the shells. This is in accord with the results of X-ray and optical investigations.

The high values of the anisotropy for the (B) and (C) modes of suspension show that there is an additional anisotropy over and above that due to the aragonite crystals. The only way of explaining this seems to be to attribute anisotropy to conchyolin itself, although no conclusive results could be obtained by direct experiments on the separated conchyolin, owing to experimental uncertainties. If we assume that conchyolin is anisotropic, we at once arrive at two significant conclusions; firstly, that the molecules are anisotropic themselves, and secondly, that they are arranged more or less regularly in a quasi-crystalline structure. Conchyolin belongs to the class of sklero-proteins

and its empirical formula is $C_{30}H_{48}N_9O_{11}$. The structural formula is not known. The indirectly observed rather considerable anisotropy would indicate the presence of aromatic groups in the molecule, these being arranged with their planes parallel to the laminar planes.

It is difficult to draw definite conclusions as regards the orientations of the a and b axes of the aragonite crystals on account of the fact that the c-axis is one of approximate magnetic symmetry and that there are a few complications such as :—

(1) Slight differences in the curvatures of the elementary laminæ in different directions. The error caused by this was eliminated as far as possible by choosing very small pieces for experiment.

(2) The difficulty in mounting the piece with the laminar plane exactly horizontal. A spurious anisotropy of a small order can be caused by this.

(3) Natural irregularities in the elementary laminæ such as small pits and elevations.

We can however tentatively arrive at the following conclusions :—

In *Turbo* and *Haliotis*, the a and b axes are oriented more or less at random, since the anisotropy is very small in the laminar plane. This is in general agreement with the X-ray analysis by Dr. Ramaswamy. The preferred orientation of the a and b axes which he has found for *Haliotis* cannot, however, be detected by the magnetic method, since, owing to the very large error in orientation reported, the anisotropy will be negligibly small.

In *M. margaratifera* and *Mytilus viridis*, a preferred orientation is probably present, with the a-axis approximately along the line of growth. In the case of *Nautilus pompilius*, however, the anisotropy is comparatively large. Two explanations are possible ; it is either due to the conchyolin which is present in comparatively large quantity, or to a preferred tilting of the c-axes of the aragonite crystals in the direction of the line of growth, in the specimens examined.

The absolute diamagnetic susceptibility of the shells appears to be lower than that of aragonite in all cases, *Nautilus pompilius* having the lowest value.

The present investigation shows that the determination of the magnetic anisotropy of many natural substances is likely to throw some light on their constitution and structure. Further work in this direction is being undertaken.

In conclusion, I thank Sir C. V. Raman, Kt., F.R.S., N.L., who suggested the problem and under whose guidance the work was carried out.

Summary.

The magnetic anisotropies of the nacre of *Turbo, Haliotis,* M. *margaratifera, Mytilus viridis* and *Nautilus pompilius,* respectively, have been determined. The observations indicated that the *c*-axes of the aragonite crystals are in every case normal to the elementary laminæ. A random orientation of the *a* and *b* axes in *Turbo* and *Haliotis,* and a preferred orientation, with the *a*-axes approximately along the line of growth for M. *margaratifera* and *Mytilus viridis,* are tentatively suggested. A quasi-crystalline structure for conchyolin is suspected. The absolute susceptibilities of the shells have also been determined.

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