

# MAGNETIC ANISOTROPY AND PLEOCHROISM OF BIOTITE MICA.

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Received July 11, 1933.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.I.)

## 1. *Introduction.*

THE micas constitute a highly interesting class of minerals on account of their characteristic crystalline structure and optical properties. Most varieties contain iron to a greater or less extent, in the combined state as well as in the form of inclusions, and as a result they are generally paramagnetic.<sup>1</sup> Biotite is distinguished by the presence in it of comparatively large amounts of iron, and its characteristic optical property is a strong pleochroism in the visible region of light. Light vibrations parallel to the cleavage plane are strongly absorbed, whereas vibrations normal to the plane are more or less freely transmitted. It is also well known that pleochroism is most marked in varieties rich in iron. The present investigation was undertaken in the hope that a study of the paramagnetic anisotropy, susceptibility and pleochroism of biotites of known composition might lead to interesting results regarding the nature and origin of these properties, while serving to throw light on the probable connection between pleochroism and magnetic anisotropy in paramagnetic solids.

The magnetic anisotropy of a large number of varieties of mica has been studied by E. Wilson.<sup>2</sup> He examined both spotted as well as clear varieties and in all cases found that the paramagnetic susceptibility parallel to the cleavage plane was much greater than that perpendicular to it. The ratio  $\frac{\chi_{\parallel}}{\chi_{\perp}}$  was very much greater in the spotted varieties. It was not clearly stated to which group the specimens belonged. Presumably only muscovite was examined. It was tentatively suggested that the anisotropy might be due to either an orderly arrangement of the inclusions of magnetite present, or an actual difference in the behaviour of the mica itself in different directions relative to the crystallographic axes. No attempt was made, however, to decide between the two hypotheses. The position has now altered considerably. Clear inclusion-free specimens of mica containing iron which forms an integral part of the lattice (as in phlogopite and biotite) may well show a

genuine crystalline magnetic anisotropy. In the light of the X-ray crystallographic data now available<sup>3</sup> and recent developments in the theory of the magnetic anisotropy of paramagnetic solids due to Van Vleck and Penney and Schlapp,<sup>4</sup> a satisfactory interpretation of the magnetic data is now possible. In the present investigation the author has determined the susceptibility and magnetic anisotropy of three varieties of biotite and one each of muscovite and phlogopite. The ferrous and ferric iron contents of the specimens were determined by chemical analysis and the pleochroism of the specimens also estimated quantitatively.

## 2. *Crystal Structure and Chemical Constitution of the Micas.*

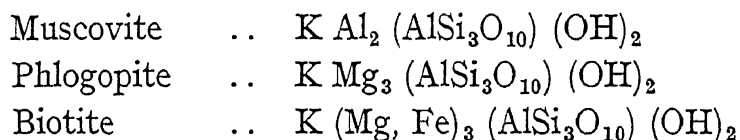
According to the recent theory developed by Van Vleck and Penney and Schlapp, the asymmetry of the strong crystalline electric fields acting on the paramagnetic ion is primarily responsible for magnetic anisotropy in paramagnetic solids. These electric fields are due to the environment of anions or dipole molecules which are grouped around the cation. The symmetry and nature of the grouping determines the character of the crystal fields and hence the magnetic anisotropy, in the case of any particular paramagnetic ion. A knowledge of the exact disposition of the atoms in the crystal lattice is thus necessary for the interpretation of the magnetic data in the light of theory.

The general scheme of the atomic structure of the micas was first elucidated by Pauling<sup>5</sup> and the full investigation in the case of muscovite has been made by Jackson and West.<sup>6</sup> It has been shown that all the micas are built more or less according to the same plan. The peculiar flaky structure and easy cleavage have been explained as being due to the formation of sheets of linked silicon-oxygen tetrahedra. A sheet is formed by linking the oxygen atoms at the corners of the tetrahedra so that they are all in the same plane and the result is a hexagonal network. Two such sheets placed with the vertices of the tetrahedra pointing inwards form a double sheet, the oxygen atoms at the vertices being cross-linked by aluminium atoms in muscovite, and magnesium and iron atoms in phlogopite and biotite. Hydroxyl groups are incorporated, linked to Al, Mg or Fe alone. We have thus a firmly bound double-sheet and the mica structure is a succession of such double-sheets interspaced alternately by sheets of potassium atoms. The iron atoms occupy positions of six co-ordination and are surrounded by an octahedral grouping of oxygen atoms and hydroxyl groups. X-ray evidence has shown that such a grouping is present in the hydrated sulphates and double-sulphates of iron, cobalt, nickel, etc., the water molecules in these salts constituting the octahedral environment. The crystalline electric

fields due to such an arrangement are presumably of a highly asymmetric character as has been pointed out by Krishnan recently.

The chemical composition of the micas is variable within wide limits. Since the magnetic properties are determined by the iron content, as will be seen later, it is essential to know accurately the amount of iron present. In fact many properties of mica show a direct dependence on chemical composition. Kunitz<sup>7</sup> has made a detailed study, combining optical and density determinations with chemical analysis. He established three series of isomorphous replacements and showed that the change in optical properties within one series depended mainly on the iron content. Similar classifications have been made by Hallimond, Winchell and Jakobs, and recently Niggli<sup>8</sup> while discussing a recent paper by J. Holzner on the crystal structure of biotite, has summarised the evidence from reliable chemical analysis and has pointed out the variability of the three types, *i.e.*, the muscovite type, the lithia mica type and the phlogopite-biotite type. A consideration of the physical properties in relation to chemical constitution shows that we cannot speak of a continuous transition from one group to another. This is probably due to the fact that the properties depend on the structure also besides chemical composition, and differences among the three types exist although the general plan of their architecture is similar. G. Nagelschmidt<sup>9</sup> has recently found from an examination of the X-ray powder diagrams of eight different micas of known composition, density and optical properties, that they belong to at least two distinct types, the muscovite type and the phlogopite-biotite type. The lithia mica type could not, however, be distinguished.

The principles governing isomorphous substitution in the micas were established by the work of Mauguin<sup>10</sup> who measured the dimensions of the unit cell in varieties of known density and composition. Ideal formulæ have been assigned based on such measurements, as follows :



### 3. *Determination of Magnetic Anisotropy.*

The magnetic anisotropy has been measured by the torsional method developed by Krishnan.<sup>11</sup> If an anisotropic crystal is suspended with one of its axes vertical by means of a fine quartz fibre in a uniform magnetic field, the forces acting upon it will be (1) a couple due to anisotropy of shape which will tend to rotate the crystal such that its length is along the field and (2) couple due to the magnetic anisotropy which will tend to rotate the crystal such that the direction of algebraically maximum susceptibility in the

horizontal plane is parallel to the field. Let us assume that (1) is negligible compared with (2). Let  $\chi_{\max.}$  and  $\chi_{\min.}$  be the maximum and minimum susceptibilities in the plane. If initially the torsion head of the fibre is adjusted that  $\chi_{\max.}$  is parallel to the field direction no couple acts on the crystal when the field is put on. If now the torsion head is turned round, the crystal also turns round but to a smaller extent on account of the couple due to magnetic anisotropy which begins to act on it when it leaves the zero position. At a critical position when  $\chi_{\max.}$  and  $\chi_{\min.}$  are making  $45^\circ$  with the field direction, this couple is a maximum and with the smallest further rotation of the torsion head the crystal will quickly turn round. If  $\alpha_c$  is the angle through which the torsion head has been turned round, the specific anisotropy in the plane is given by the relation.

$$\chi_{\max.} - \chi_{\min.} = 2 \left( \alpha_c - \frac{\pi}{4} \right) \frac{c}{m H^2}$$

where  $c$  is the torsional constant of the fibre,  $H$  the field strength and  $m$  the mass of the crystal. The micas crystallise on the monoclinic system and there are three principal susceptibilities of which two lie in the symmetry plane and the third along the symmetry axis. We have to determine the quantities  $(\chi_1 - \chi_2)$ ,  $(\chi_1 - \chi_3)$  and the relative orientation of the axes of the magnetic ellipsoid with respect to the crystallographic axes.  $\chi_1$  and  $\chi_2$  are the principal susceptibilities in the  $b$  (010) plane,  $\chi_2$  being nearer the  $a$ -axis and  $\chi_3$  is the principal susceptibility in the direction of the  $b$ -axis. The mica specimen was suspended in the uniform magnetic field as follows:— (1) with the cleavage plane horizontal, (2) with the  $b$ -axis vertical and (3) with the  $b$ -axis horizontal and the cleavage plane vertical. We thus directly determine the quantities  $(\chi_3 - \chi_a)$ ,  $(\chi_1 - \chi_2)$  and  $(\chi_3 - \chi_N)$  where  $\chi_a$  is the susceptibility along the  $a$ -axis and  $\chi_N$  is that perpendicular to the cleavage plane. From (2) we can directly get the angle which the  $\chi_2$  axis makes with the  $a$ -axis. This angle can also be calculated from the known values of  $\chi_3 - \chi_N$  and  $\chi_3 - \chi_a$ , for,

$$\begin{aligned} \chi_3 - \chi_N &= \chi_3 - (\chi_2 \sin^2 \theta + \chi_1 \cos^2 \theta) \\ \chi_3 - \chi_a &= \chi_3 - (\chi_2 \cos^2 \theta + \chi_1 \sin^2 \theta). \end{aligned}$$

Solving the simultaneous equation we get both  $\theta$  and  $\chi_3 - \chi_1$ . In the case of the micas matters are very much simplified, since the  $\chi_2$  direction was found to coincide with the direction of the  $a$ -axis.

#### 4. *Experimental Precautions and Sampling of Specimens for the Anisotropy Measurements.*

A careful selection of specimens for the magnetic determinations is absolutely essential, since inclusions and stains in mica are the rule rather

than the exception. Another serious difficulty in the case of rock minerals is that not only is the composition variable for varieties obtained from different localities but it might differ over different parts of the same specimen. The minerals are seldom perfectly homogeneous. For instance, inclusions may be very prominent in some regions of the same 'book' of mica, whereas other parts are clear and transparent. Often these inclusions consist of magnetite in dendrite-like forms. The presence of even small quantities of magnetite may be sufficient to cause considerable anomalies in the results. Other inclusions are, generally, flattened crystals of garnet, tourmaline and quartz in thin plates found between the sheets.

The micas were obtained in the form of small plates and of these the best were selected. These were further examined under a high power microscope and the portions containing included particles rejected. Satisfactory samples practically free from inclusions could be obtained. Inclusions in biotite are often associated with pleochroic haloes and afforded another test for their absence or presence. Phlogopite often shows asterism and this has been attributed to symmetrically arranged inclusions of rutile or tourmaline. Plates showing asterism were therefore rejected. In all cases, however, minute traces of inclusions mostly of submicroscopic dimensions were probably present.

The optical characteristics of the specimens were also examined under the polarising microscope. With convergent polarised light the muscovite specimens gave the usual biaxial interference figure, whereas the phlogopite and the biotite samples were sensibly uniaxial. No evidence of twinning was found in the plates taken up for examination. The optical axial plane is perpendicular to the  $b$  (010) plane in muscovite and parallel to the  $b$  (010) in phlogopite and biotite.

Only freshly cleaved plates were employed. These were further cleaned with dilute sulphuric acid, distilled water and alcohol.

In the case of mica, which was available in the form of thin plates only, we cannot neglect the effect due to the anisotropy of shape of the specimen. For the paramagnetic susceptibility is fairly high, especially in the case of the biotites, and in some cases the magnetic anisotropy also is comparatively small. The possible errors on this account were eliminated by adopting the device of Krishnan of immersing the crystal in a liquid bath of the same mean susceptibility, for phlogopite and muscovite. An aqueous solution of manganese chloride was employed. For determining the anisotropy in the cleavage plane, which was found to be very feeble, discs of the material 5.5 mm. in diameter were prepared. In this case no correction for anisotropy of shape is necessary.

For the biotites the paramagnetic susceptibility was liquid-bath to be employed conveniently. Small plates 1 were cut out, cleaned with dilute acid and distilled water and the other to form a block  $10 \times 4 \times 4$  mm. using traces shellac for attaching them. Particular care was taken to crystallographic directions of the plates coincided when cut. The long edges were carefully rounded off so that a cylinder and 4 mm. diameter, was obtained. A silk thread was further the cylinder so that the pieces might not fall off. It was finally dilute sulphuric acid and distilled water. For determining anisotropy in the cleavage plane discs 5.5 mm. in diameter. Only the value of  $\chi_{\parallel} - \chi_{\perp}$  is given for biotite and phlog anisotropy in the cleavage plane was negligibly small.

The current through the electromagnet was adjusted by system of rheostats, and every time before the field was applied brought to a cyclic state by reversing the current several times of field over a large area was ensured by using flat pole-pieces cm. nearly.

The field strength was measured by means of a calibrated meter and a standard search coil made by the author consisting of No. 40 s.w.g. double silk-covered copper wire wound round turned cylinder of non-magnetic marble, the diameter of the 2.359 cm. Fields of the order of 1000–2000 oersteds were employed.

For mounting the crystal a thin glass fibre 1.5 cm. long like a pin was attached to the end of the quartz fibre with the mica pieces were fixed to the pin-head by traces of pure

The torsional constant of the fibre was determined by its end a glass cylinder 0.327 cm. diameter and mass 0.09 axis vertical and observing the period of oscillation, by the

The mean of several independent determinations is given

##### 5. Measurement of Absolute Susceptibilities.

The mean susceptibility of the micas in the form of powder mined by the Curie-Balance method. A torsion balance of the type was constructed by the author with a glass beam and glass for supporting the phial holding the substance, all made a schematic diagram of the balance is shown in Fig. 1. The magnetic field was obtained by keeping the pole-pieces (specially the author to go with an electromagnet made by Charles Son, Ashby de la Zouch) at an angle to each other. As is well

## Magnetic Anisotropy and Pleochroism of Biotite Mica

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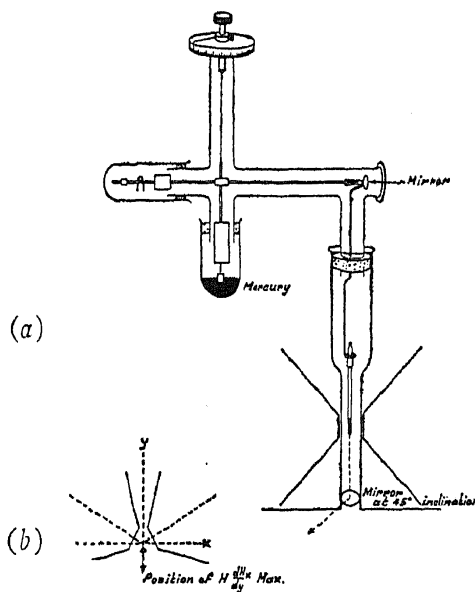


FIG. 1.

susceptibility is given by the formula

$$\chi = \frac{1}{m} \left\{ \chi' m' + (\chi'' m'' - \chi' m') \left( \frac{F_{x_2} - F_{x_1}}{F_{x_3} - F_{x_1}} \right) \right\},$$

where  $\chi$ ,  $m$  represent the susceptibility and mass of the specimen,  $\chi'$ ,  $m'$  the air and  $\chi''$ ,  $m''$  of the standard substance respectively, the  $m$  referring to equal volumes of the substances.

$F_{x_1}$  the force acting on the container alone measured by the torque on the torsion wire ;

$F_{x_2}$  the force acting on the phial + substance ; and

$F_{x_3}$  the force acting on the phial + standard substance.

All the usual precautions were taken, the most important being that the container is always brought back to the same position relative to the magnet when taking the measurements, and that the field is kept constant. The standard substances used was a solution of manganese chloride (33.8% Mn) the susceptibility of which was accurately determined by the Quincke U-tube method.

### 6. Determination of Ferrous and Ferric Iron in the Specimens.

The percentage of total iron and ferrous iron in the micas were determined by the following methods.<sup>12</sup>

*Total Iron.*—The sample was ground to a fine powder in an agate mortar and about 0.5 g. of the powder weighed in a platinum crucible and fused with fusion mixture (two parts of  $\text{Na}_2\text{CO}_3$  and one part of  $\text{K}_2\text{CO}_3$ ). The fused mass after cooling was dissolved in dilute HCl in a silica crucible. The solution was evaporated to dryness over a water-bath, redissolved in dilute HCl and

silica filtered off, washed on the filter and weighed after ignition. The filtrate was heated up to boiling point and a little concentrated nitric acid added followed by 20 g. of ammonium chloride. Ammonia was then slowly added to the boiling solution until all the aluminium and iron were precipitated as hydroxide and the solution became slightly alkaline. The precipitate was then filtered off, washed on the filter with a warm solution of ammonium nitrate and ignited in a platinum crucible and weighed. The ignited mass was then fused with sodium bisulphate and after cooling dissolved in dilute sulphuric acid. The solution was then run through a Jones' reductor (an improved form of which has been devised by the author and reported elsewhere) in an atmosphere of carbon dioxide and finally titrated against standard permanganate.

*Ferrous Iron.*—The accurate determination of ferrous iron in silicate rocks is a matter of considerable difficulty. The modified Pratt method recommended by Hillebrand was adopted. A weighed quantity of mica was carefully ground in an agate mortar under pure alcohol for about an hour. A thorough grinding is necessary since coarse particles take a very long time to get dissolved in HF. The ground mass was carefully washed down into a platinum crucible with air-free water and 10 c.c. of cold dilute sulphuric acid added. The crucible was supported over a water-bath and surrounded by an atmosphere of  $\text{CO}_2$  by the arrangement shown in Fig. 2. 6 c.c. of

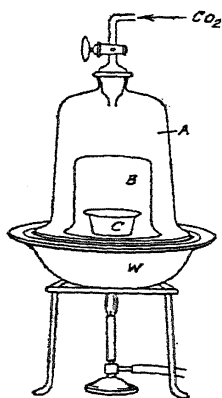


FIG. 2.

A.—Bell-jar; B.—Beaker; C.—Platinum crucible; W.—Water-bath.

40% hydrofluoric acid (Kahlbaum's analytical reagent) were quickly introduced into the crucible which was then covered with the lid and the water-bath heated, carbon dioxide being passed all the time. The reaction was allowed to go on for 3 hours. Meanwhile a solution containing 50 g. of boric acid and 20 c.c. of sulphuric acid in 300 c.c. of air-free water was prepared and the crucible and contents, after the reaction was over,



were quickly transferred into the cold boric acid solution and titrated immediately against standard permanganate, until a pink colour lasting for a minute or two was obtained.

A blank experiment was performed under similar conditions with ferrous ammonium sulphate. About 0.5 g. was weighed and dissolved in 300 c.c. of dilute sulphuric acid and immediately titrated against permanganate. Another 0.5 g. was weighed in a platinum crucible and the ferrous iron determined by the modified Pratt method as described above, using 6 c.c. of HF. The necessary correction was found to be + 0.28 c.c. of permanganate.

7. *Measurement of the Pleochroism of the Micas.*

A comparative measure of the pleochroism of the micas was obtained by the following experimental arrangement based on the principle of Cornu's method for determining the percentage of polarised light (Fig. 3).

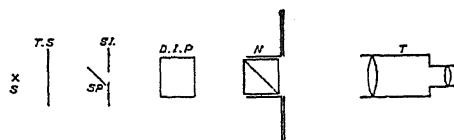


FIG. 3.

S.—Source of light; T.S.—Translucent Screen; Sp.—Specimen;  
Sl.—Rectangular slit; D.I.P.—Double-Image prism;  
N.—Nicol mounted on circular scale; T.—Telemicroscope.

The specimens were used in the form of thin plates, freshly cleaved, and of the same thickness 0.05 mm., selected from a very large number of cleaved plates. The mica plates were mounted behind the slit at an angle of 45° with the *b*-axes horizontal. The double-image prism was placed with the vibration directions vertical and horizontal, and the distance from the slit was adjusted until the two images, as seen through the telemicroscope, just touched one another. The horizontal vibrations are absorbed much more than the vertical and the images are of unequal intensity. By suitably rotating the nicol the intensities can be equalised. If  $2\theta$  is the angle between two positions of the nicol on either side of the vertical for which the intensities are equalised, then  $\frac{I_v}{I_H} = \tan^2\theta$ . A correction has to be introduced in the value of  $\theta$  to eliminate errors due to reflection, etc., at the faces of the plates. For this a blank experiment was performed with a glass microscope coverslip of nearly the same refractive index as the mica plates and the necessary correction applied to the value of  $\theta$ . The results are approximate only but afford a good comparative measure of the pleochroism of the micas.

The corrected values of  $\tan^2\theta$  are given in Table III.

8. *Results.*

The results are presented in the tables shown below.

TABLE I. *Specific Magnetic Anisotropy of Phlogopite and Biotite.*  
*C.G.S. E.M. Units. Temperature 25° C.*

Specimen	Anisotropy $\chi_{\parallel} - \chi_{\perp}$ $\times 10^6$	Remarks
Phlogopite .. ..	1.38	The magnetic anisotropy in the cleavage plane was negligibly small in all cases and, therefore, only the values of $\chi_{\parallel} - \chi_{\perp}$ are given
Biotite (Canada) ..	6.25	
„ (Ural Mts.) ..	10.3	
„ (Bihar) .. ..	12.4	

*Specific Magnetic Anisotropy of Muscovite.*

Mode of Suspension	Orientation	Anisotropy $\Delta\chi \times 10^6$	Remarks
Cleavage plane horizontal	<i>b</i> -Axis perpendicular to the field	$\chi_2 - \chi_3 = 0.11$	The $\chi_2$ direction coincides with the <i>a</i> -axis
<i>b</i> -Axis vertical	Cleavage plane parallel to the field	$\chi_2 - \chi_1 = 0.70$	
<i>b</i> -Axis horizontal and cleavage plane vertical	Do.	$\chi_3 - \chi_1 = 0.61$	

TABLE II. *Mean Susceptibility of the Micas at 25° C.*

Specimen	$\bar{\chi} \times 10^6$
Muscovite .. ..	8.01
Phlogopite .. ..	7.85
Biotite (Canada) ..	30.8
„ (Ural Mts.) ..	40.6
„ (Bihar) .. ..	43.8

TABLE III.  
Pleochroism of the Micas.

Specimens of thickness 0.05 mm.	$\text{Tan}^2 \theta = \frac{I_V}{I_H}$
Muscovite .. ..	1.03
Phlogopite .. ..	1.09
Biotite (Canada) ..	1.58
,, (Ural Mts.) ..	1.89
,, (Bihar) .. ..	1.97

TABLE IV.  
C.G.S. E.M. Units. Temperature 25° C.

Specimen, Description (Colour of the Biotites refers to very thin plates)	Mean Susceptibility $\chi \times 10^6$	Magnetic Anisotropy $\chi_{\parallel} - \chi_{\perp} \times 10^6$	$\chi_{\parallel} \times 10^6$	$\chi_{\perp} \times 10^6$	Total Iron %	Ferrous Iron %	Ferric Iron %	Magnetic Anisotropy referred to a g. ion of $\text{Fe}^{++} \times 10^6$
Muscovite .. Clear. Tinge of green	8.01	0.65	8.23	7.58	3.93	1.79	2.14	
Phlogopite .. Brownish yellow Submetallic lustre	7.85	1.38	8.31	6.93	4.34	3.18	1.06	2420
Biotite (Canada) .. Dark greenish brown	30.8	6.25	32.9	26.6	15.2	13.1	2.12	2670
Biotite (Ural Mts.) Dark brown	40.6	10.3	44.0	33.7	21.8	19.6	2.22	2930
Biotite (Bihar) .. Dark reddish brown	43.8	12.4	47.8	35.4	23.1	22.2	0.9	3120

## 9. Discussion of Results.

Both the susceptibility and the magnetic anisotropy are seen to depend upon the amount of iron present. The biotites exhibit a fairly large magnetic anisotropy and the paramagnetic susceptibility is also correspondingly high. The values for muscovite and phlogopite are comparatively small. In the case of the biotites the mean susceptibility is seen to increase with the percentage of iron almost linearly (Fig. 4).

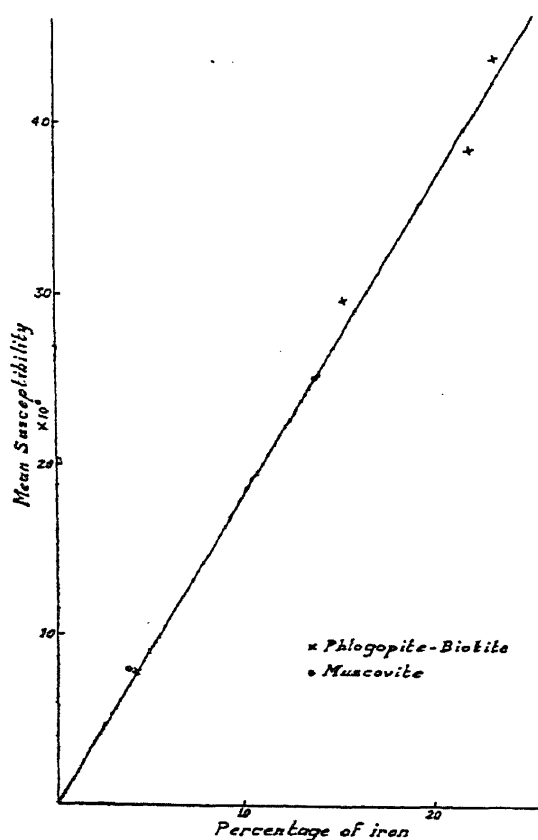


FIG. 4.

The total susceptibility of mica may be considered to consist of three parts, namely (1) that due to the ferrous iron, (2) that due to the ferric iron and (3) the contribution due to the other atoms. The first two are evidently paramagnetic terms while the last is diamagnetic. When the percentage of iron is large, as obtains in the case of the biotites, the diamagnetic term will be negligibly small as compared with the paramagnetic terms. But it will be considerable in muscovite and phlogopite which contain only about 4% of iron.

It will be of interest to calculate in a rough way the approximate Bohr magneton values for the biotites. The susceptibility of the biotites is amenable to theoretical considerations for the following reasons: (1) The percentage of iron is very high and we may neglect the diamagnetic term in the susceptibility; (2) Most of the

iron is present in the ferrous state ; (3) The disturbing effects due to possible minute traces of inclusions can be safely ignored. (In fact, the biotite samples were particularly free from defects.) Considering only the total iron present, the effective Bohr magneton value is obtained according to the formula  $P_{B \text{ eff}} = 2.84 \sqrt{\chi_M T}$

	$P_{B \text{ eff}}$
Biotite (Canada)	= 5.2
„ (Ural Mts.)	= 5.0
„ (Bihar)	= 5.0

The values are seen to be much lower than the theoretical values to be expected in the case of the free paramagnetic ion just as in the case of other solid salts of iron. They are found to approach the spin only value of  $Fe^{++}$ , which is equal to 4.92 Bohr magnetons. The significance of this fact in the light of Van Vleck's theory of the quenching of the orbital moments by the crystalline electric fields in paramagnetic solids will be discussed later.

It is important to consider the effect of microscopic and submicroscopic inclusions on the magnetic anisotropy, especially in the case of muscovite which, according to the ideal formula  $KAl_2 (AlSi_3O_{10}) (OH)_2$ , cannot take in ferrous iron in the positions of six co-ordination replacing the aluminium atoms. We have to see if the magnetic anisotropy of muscovite is merely due to symmetrically arranged inclusions or if it can be of crystalline origin as in biotite, at least in part. If according to the ideal formula, the ferrous iron cannot form an integral part of the lattice, then apparently we are led to conclude that only the inclusions, microscopic or submicroscopic, are responsible for the anisotropy. But chemical analysis shows that very often the amount of ferrous iron present is much larger than can be accounted for by any of the common inclusions. For instance, in the muscovite sample examined by the author which contained inclusions of magnetite, the percentage of  $FeO$  is much larger than should be expected. The ferrous iron, therefore, is most probably present in the mica lattice itself in the positions of six co-ordination. The iron atoms should be present in groups to satisfy the rules of co-ordination and as such they really constitute a discontinuity in the lattice. We may regard them as being of the nature of inclusions of extremely small dimensions. This view gains support from the fact that biotite inclusions in muscovite are often met with and from what we know of the crystal structure of the micas a biotite inclusion can really be regarded as a discontinuity of the above character occurring over an extended region, magnesium also being present along with the iron in the positions of six co-ordination. Thus the anisotropy measurements throw an interesting side-light and seem to provide evidence for the presence of discontinuities in the

lattice which cannot be detected by the microscope. The effect of inclusions on the magnetic anisotropy of the biotites will be comparatively negligible since, on one hand they are much less prominent and on the other the iron forming part of the lattice is present in very large amounts.

The close correspondence between the magnetic properties of the micas and their structure is very striking. In muscovite, as is to be expected from its pseudo-hexagonal structure, two of the principal susceptibilities lie in the cleavage plane and are nearly equal, while the susceptibility perpendicular to the plane is much less than either of the other two. In biotite and phlogopite two of the principal susceptibilities not only lie in the cleavage plane but are also of the same value. It must be emphasised, however, that the determination of the magnetic anisotropy in the cleavage plane was complicated by two factors namely, (1) strains and distortions set up when cutting out the specimens in the shape of discs and (2) the presence of microscopic inclusions. The spurious effects due to the first cause could be eliminated by exercising proper care in the preparation of the discs. The effect due to the second cause was studied by determining the magnetic anisotropy in the cleavage plane of a large number of spotted and stained samples of muscovite. The heavily spotted varieties always showed enormous anisotropy in the cleavage plane while those with perceptible traces of inclusions (magnetite) were anisotropic to the extent to which they contained the inclusions and this was considerable.

From the results it could be inferred that the contribution due to the minute traces of inclusion should be much less than the observed anisotropy in the cleavage plane, and that at least part of the observed anisotropy in the cleavage plane is genuine. The definite orientation of the *b*-axis in the magnetic field in all cases also leads to the same conclusion. In this connection the isotropy of phlogopite and the biotites in the cleavage plane is interesting. It proves that the disturbing effects due to any inclusions present are negligible. Samples of phlogopite which exhibited marked asterism showed considerable anisotropy in the cleavage plane. There is a close similarity between the optical and magnetic properties also, when we remember that the muscovite showed a biaxial interference figure whereas the phlogopite and the biotites were sensibly uniaxial.

*Magnetic Anisotropy and Chemical Constitution.*—The specific magnetic anisotropy is plotted as a function of the total iron, ferrous iron and ferric iron respectively in Fig. 5. Since phlogopite and biotite belong to the same group we can study the characteristics of this group from the results obtained. In the first place there seems to be no obvious connection between

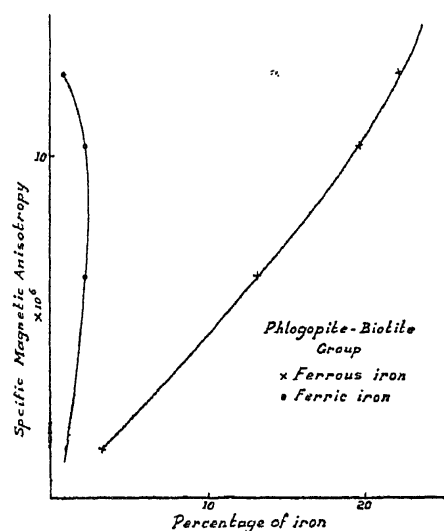


FIG. 5.

the ferric iron content and the anisotropy. On the other hand, the magnetic anisotropy increases smoothly with the percentage of ferrous iron. But the relationship is not linear and for large percentages of iron the curve becomes steeper. In Table IV the gram ionic anisotropy for  $\text{Fe}^{++}$  is given. This shows a remarkable increase with the percentage of ferrous iron in the biotites (Fig. 6). It is likely that this increase is due to interaction between

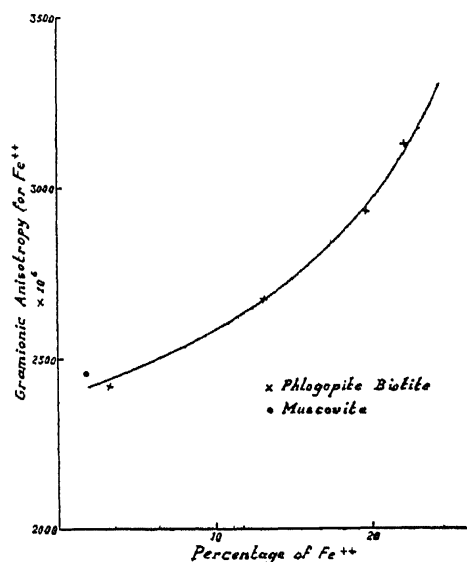


FIG. 6.

neighbouring iron atoms in the sheet. The nature of this interaction will be discussed later.

The results obtained are significant in the light of recent theoretical developments due to Van Vleck and Penney and Schlapp.

*Van Vleck's Theory of the Paramagnetism of Solids.*—The object of the theory is to account for the following features in the magnetic behaviour of paramagnetic solids, such as (1) the departure from the Curie law and the

appearance of cryomagnetic anomalies at low temperatures, (2) the relative contributions of the spin and orbital moments to the susceptibility and (3) the magnetic anisotropy of the crystals. It is based on the earlier work of Bethe and Kramers on the Stark splitting of the energy levels of atoms and ions under the influence of crystalline electric fields. Detailed computations have been made by Penney and Schlapp, who have considered Pr and Nd among the rare earths and Co, Cr and Ni in the iron group. Jordahl has made calculations in the case of the cupric salts. The main results for the salts of the iron group are as follows: Since the magnetically effective 3d electrons are in the outermost shell, the influence of the crystalline electric fields due to the neighbouring atoms will be strong enough to break the coupling between the orbital and spin moments. The orbital degeneracy is partially or completely removed and the orbital moment makes practically no contribution to the susceptibility. The orbital moment is then said to be quenched. The spins, however, are not directly affected by the crystalline fields and hence contribute fully to the susceptibility. An asymmetric crystalline field produces asymmetric partial freezing of the orbital moment and due to the coupling between orbit and spin, since the remnants of the orbital moment are anisotropic, the freedom of the spins to orient themselves along different directions will be different. Hence the crystal exhibits magnetic anisotropy. Due to the partial quenching of the orbital moments the susceptibility lies between the limits given by  $P_{B'} = \sqrt{4S(S+1)}$  and  $P_{B'} = \sqrt{4S(S+1) + L(L+1)}$ . In fact we have pointed out earlier that in the case of the biotites this is the case, the Bohr magneton values approaching the spin only value. One important consequence of Van Vleck's theory is that manganous and ferric salts should not exhibit any marked anisotropy, since the  $Mn^{++}$  and  $Fe^{+++}$  ions are in the S-state and therefore have no orbital moment to be quenched. The present investigation also shows how the magnetic anisotropy of biotite is not dependent on the amount of ferric iron in the specimens, and thus lends support to the theory.

In many hydrated paramagnetic crystals which exhibit large magnetic anisotropy, there is evidence from X-ray analysis that we have an octahedral arrangement of water molecules round the paramagnetic ion. Recent experimental work shows that the crystalline electric field due to such an arrangement deviates widely from cubic symmetry<sup>13</sup> and most probably possesses only hexagonal symmetry. Usually in such paramagnetic crystals there are a number of these complexes (formed by the paramagnetic ion and its environment of six water molecules) in the unit cell, differently oriented with respect to each other, such that crystalline magnetic properties may have only the lower rhombic symmetry. But in the micas the case is much



simpler. Here the octahedral group around the  $\text{Fe}^{2+}$  ion consists of four oxygen atoms and two hydroxyl groups and all the groups are arranged parallel to each other in layers in the crystal lattice. Hence the anisotropy of the crystal actually corresponds to that of these individual paramagnetic complexes. The hexagonal symmetry of phlogopite and biotite as regards the magnetic properties lends support to the view that the crystalline electric fields due to the octahedral grouping possess the same symmetry. In the case of muscovite, however, the departure from hexagonal symmetry may be attributed to the staggering of the sheets relative to each other which is responsible for the monoclinic angle of  $95^\circ$  and which probably introduces slight departures from the octahedral symmetry of the environment round the  $\text{Fe}^{2+}$  ion. Since the 3d electrons occupy the outer shell they are very susceptible to slight changes in the positions of the surrounding atoms which can cause considerable variation in the character of the crystalline fields influencing these outer electrons. The magnetic anisotropy of the paramagnetic complex  $[\text{Fe}(\text{OH})_6]$  referred to a gram ion is most probably the value obtained for phlogopite since, here, the magnetic dilution is large enough for the interaction due to neighbouring paramagnetic atoms to be ignored.

The rapid increase in the magnetic anisotropy of the biotites with the percentage of iron is a new feature and gives an insight into the effect of the concentration of the paramagnetic ion on the magnetic anisotropy. The explanation in this case seems to be that it is due to the interaction between neighbouring iron atoms. The peculiar structure of mica is very favourable for such interaction to take place since the iron atoms lie all in the same plane and their population is sufficiently high in the biotites for most of them to occupy neighbouring positions of six co-ordination. Interactions of this character are not taken into account by Van Vleck's theory which is strictly applicable only in the case of salts of considerable magnetic dilution, e.g., the highly hydrated sulphates and double sulphates of the transition elements.

These interactions are the 'exchange effects' or 'Austausch' discovered by Heisenberg. The exchange effects are formally equivalent to a strong coupling between the spins of the interacting electrons and take place when the interatomic distance has a critical value in ferromagnetics ( $2.7-3 \text{ \AA}$  according to Forrer, in the case of iron). In the biotites, however, the distance between positions of six co-ordination is of the order of  $2.6 \text{ \AA}$  which is less than this critical value. For explaining the experimental results it is enough to assume that the effect of these interactions is equivalent to imposing a further restriction on the freedom of orientation of the orbital moments. This will naturally increase the magnetic anisotropy. At the

same time we should expect a decrease in the Bohr magneton value due to the further quenching of the orbital moments. This is actually found to be the case, for we find that with the increase in the percentage of iron there is a corresponding decrease in the approximate effective Bohr magneton value. Thus the explanation offered seems to be quite satisfactory although the exact nature of the interaction has to be investigated further.

#### 10. *Pleochroism of the Biotites.*

There is, as yet, no satisfactory explanation of the pleochroism of the biotites. The intimate relationship between colours of inorganic salts and paramagnetism is well known, for salts of the transition elements which are coloured are also paramagnetic. Saha<sup>14</sup> has put forward a theory of the origin of colour in inorganic salts according to which absorption in the visible region of light is due to transitions involving the reversal of the spin vector of the one of the 3d electrons of the paramagnetic ion. Such transitions although forbidden for the free paramagnetic ion are assumed to be possible in solids and in solutions. Subsequent work by Bose and others lends support to this view.

The connection between colour and paramagnetism at once suggests a corresponding relationship between pleochroism and paramagnetic anisotropy and the examination by the author of the available data on the pleochroism and paramagnetic anisotropy of salts of the iron group of elements has revealed that strong paramagnetic anisotropy is generally associated with marked pleochroism. This enquiry proved to be fruitful in another way. The author could not find any reference to the pleochroic properties of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  in the literature on the subject. This substance is known to be highly anisotropic magnetically and we should expect a marked pleochroism also. A large single crystal was examined in the (010) plane and it was found that the colour is pale green for light vibrations in the  $\gamma$  direction and yellow when the vibrations are in the  $\alpha$  direction.

The bearing of the above on the pleochroism of the biotites is obvious, for we have seen that pleochroism is most pronounced in the varieties rich in ferrous iron and the magnetic anisotropy also increases with the iron content. The two phenomena are evidently closely related. If the mechanism of absorption of light in biotite by the iron atom is the same as suggested by Saha (The positions of the absorption maxima are slightly different in the different specimens and seem to correspond roughly with the  ${}^6\text{D} - {}^4\text{P}$  and  ${}^6\text{D} - {}^4\text{F} =$  transitions for  $\text{F}_c^{++}$ ) the pleochroism implies that the reversal of the spin vector can take place only when the light vibrations are parallel to the cleavage plane and not when they are perpendicular. This

restriction in the orientation of the spins is evidently due to the influence of the asymmetric crystalline fields which, according to Van Vleck, act indirectly on the spins through the spin orbit coupling and which are responsible for the large magnetic anisotropy.

The close correspondence between the ease of magnetisation parallel to the cleavage plane (the paramagnetic susceptibility parallel to the cleavage plane is much greater than that perpendicular to it) and the readiness with which the spins respond to the electric field of light wave when this is parallel to the cleavage plane is very striking and is strongly suggestive of the fact that the polarisation of absorption in the biotites is chiefly due to the influence of the asymmetric crystalline fields acting on the paramagnetic ion enhanced, however, by the spin-spin interactions. The recent work of Krishnan and Chakrabarty<sup>15</sup> on the polarisation of the absorption lines of single crystals of the hydrated sulphates of Pr and Nd is interesting in this connection. They find that "many of the absorption lines are strongly polarised, some of them being confined almost wholly to vibrations along one or another of the principal axes of the optical ellipsoid of the crystal and that these variations in the direction of polarisation occur even among the lines of the same group, in other words, among the Stark components which originate from the same absorption line of the free ion, some are polarised strongly in one direction and some strongly in another." These crystals also show strong magnetic anisotropy. From these facts Krishnan concludes that the crystalline electric fields which produce the Stark splitting are also highly anisotropic.

The nature and disposition of the magnetic carriers in biotite may now be understood from the following picture. The orbital moments being mostly frozen, the freedom of orientation of the spins is also restricted considerably. We assume that the spins are mostly oriented with the magnetic axes nearly parallel to the cleavage plane, randomness of orientation existing in azimuth, so that there is no residual magnetisation as should be the case in paramagnetics. The magnetic carriers possess complete freedom of orientation in the cleavage plane. Under the influence of a magnetic field parallel to the cleavage plane, we get the usual paramagnetism although considerably diminished in magnitude. But when the field is normal to the cleavage plane, the resolved part of the spin moments perpendicular to the cleavage plane is much less on account of the restrictive action of the crystal fields, and we get a much lower susceptibility. Thus the high magnetic anisotropy may be explained. Our picture also reveals how the reversal of the spin vector can take place in the cleavage plane but not perpendicular to it since the spins are directed more or less parallel to

the cleavage plane. The pleochroism also is thus satisfactorily explained. This physical picture although somewhat naive is sufficient to explain both phenomena in a crude way. A rigorous treatment of pleochroism taking into account the Stark splitting of the energy levels in the crystal fields is very desirable.

It seems very likely that the mutual interaction of neighbouring paramagnetic ions, to which we ascribed the enhanced anisotropy in the varieties rich in iron, plays a significant part in intensifying the pleochroism, although at present we cannot say to what extent. But it is seen that when the percentage of ferrous iron exceeds a certain value, the effect due to the interaction of the iron atoms may become enormous as compared with the usual Van Vleck effect of the asymmetric fields, and both the magnetic anisotropy and the pleochroism become exceedingly large.

Although the connection between pleochroism and paramagnetic anisotropy seems to be obvious in the biotites, further quantitative investigation is necessary in the case of other paramagnetic salts to establish the generality of the relationship. Some anomalous features also have to be explained. For instance, Murmann and Rotter have observed pleochroism in  $\text{MnSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ <sup>16</sup> although this crystal is almost isotropic magnetically. Again in the case of a rose-coloured variety of tourmaline containing a considerable percentage of manganese the author has observed pronounced pleochroism, the absorption band in green being very strongly polarised, while the magnetic anisotropy is very feeble. The crystal is paramagnetic.  $\chi = 0.31 \times 10^{-6}$ ,  $\chi_{\perp} - \chi_{\parallel} = 0.008 \times 10^{-6}$  c.g.s. E. M. units. This would indicate that at least as regards relative magnitudes, in all cases, pleochroism and magnetic anisotropy bear no simple relationship to each other.

A quantitative study of the polarisation of the absorption bands of paramagnetic crystals of salts of the iron group of elements, in relation to their magnetic anisotropy is under progress in order to further elucidate the connection between the two phenomena.

My heartfelt thanks are due to Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his encouragement and helpful criticism. I also wish to express my indebtedness to Mr. N. Jayaraman for his assistance while doing the chemical analysis and to Dr. K. R. Krishnaswami, D.Sc., for kindly providing me with facilities for the same.

#### *Summary.*

The paramagnetic anisotropy and susceptibility of three different varieties of biotite and one each of muscovite and phlogopite have been

determined. The ferrous and ferric iron contents of the specimens have also been found by chemical analysis and their pleochroism estimated quantitatively. It is found that the biotites are highly anisotropic and that both the anisotropy and the pleochroism increase with the iron content. The magnetic anisotropy is seen to depend only on the amount of ferrous iron and not on the ferric iron. The relationship between the gram ionic anisotropy referred to  $\text{Fe}^{++}$ , and the percentage of iron is not linear when the latter is high. The anisotropy, in fact, increases more rapidly and this is attributed to the mutual interactions of neighbouring paramagnetic atoms, which cannot be neglected for high concentrations of the latter. The results, in general, are in agreement with the theory of the paramagnetism of solids recently developed by Van Vleck and Penney and Schlapp based on the Stark splitting of the energy levels of the paramagnetic ion under the influence of the strong asymmetric crystalline electric fields. The pleochroism of biotite is discussed in the light of Saha's view that absorption of light in inorganic salts of elements of the transition series is due to transitions involving the reversal of the spin vector of one of the 3d electrons of the cation. In biotite where the absorption is essentially due to the ferrous iron, the pleochroism is explained as being due to the fact that the reversal of the spin vector of the 3d electrons of the  $\text{Fe}^{++}$  ion can take place only when the light vibrations are parallel to the cleavage plane. This restriction on the spins is attributed to the influence of the asymmetric crystalline fields which according to Van Vleck's theory give rise to the magnetic anisotropy also. This affords a satisfactory theoretical explanation of the origin of pleochroism besides indicating the character of its intimate relationship with paramagnetic anisotropy, observed experimentally.

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