

## Diamagnetism and molecular structure

Lecture delivered\* on November 8, 1929.

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Physicists at the present day do not need to be reminded of the great importance of the subject of magnetism considered from the standpoint of chemistry, i.e. in relation to molecular structure. The subject of diamagnetism in relation to molecular structure, however, has not been so much to the fore as that of paramagnetism. At Calcutta we have approached the subject from a rather unusual standpoint in connexion with our investigations on the scattering of light. We were led to discuss the question how far it was possible to obtain a quantitative expression for the magnetic double refraction observed in liquids. I will remind you of a discovery in about 1912 by two French physicists—Cotton and Mouton<sup>†</sup>—who found that if they placed an organic liquid in a strong magnetic field  $H$ , figure 1, and observed the effect of the liquid on a beam of light

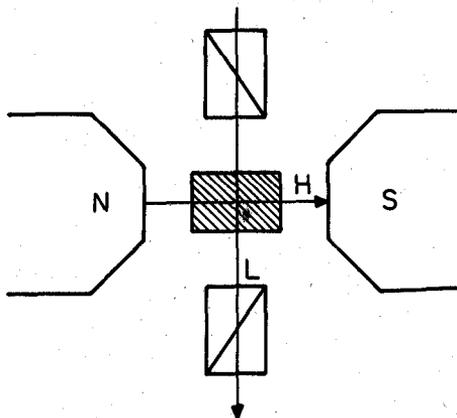


Figure 1

\*Completed and revised, in the absence of the author, by J S G Thomas, D.Sc.

<sup>†</sup>A Cotton and H Mouton, *Comptes Rendus* (1905) 141, 317-319 and 349-351.

*L*, passing through it transversely to the lines of magnetic force, certain liquids such as nitro-benzene showed a feeble double refraction, so feeble that it was at first only in very special classes of organic compounds, viz. benzene and its derivatives, that it was possible to observe it at all. Later on, improved methods of observation have extended very considerably the list of organic liquids in which this magnetic double refraction can be observed. These two French physicists also succeeded in detecting it in a very small number of aliphatic compounds, such as chloroform, bromoform, etc. and in a great many common liquids such as water and paraffins and the ordinary aliphatic hydrocarbons, ethers, alcohols, acids, etc. With some of the acids they were not able to observe the effect, and thus the great importance of the subject did not receive adequate attention.

Magnetic double refraction is exhibited by certain substances owing to their molecules possessing a magnetic susceptibility. That, of course, is obvious, but what is not quite so obvious is how exactly the magnetic double refraction arises.

About the time of the discovery by Cotton and Mouton there was already available certain work by Voigt\*, who showed that, as a consequence of the dispersion theory, if a beam of light passes through a substance placed in a transverse magnetic field, there must be a feeble double refraction produced; and this refraction was shown to be related to the Zeeman effect. You will find some reference to Voigt's work in his well-known book on magneto-optics published by Methuen.

When Cotton and Mouton made their observations on magnetic double refraction in liquids they found that the actual effect observed by them was nearly 1000 times larger than what would be roughly estimated from Voigt's theory of the phenomenon. The consequence was that they realised that an entirely different explanation must be sought. Prof. Langevin was the first to suggest what is now fairly generally accepted as the real explanation of the effect†. I would like to make the thing clear by a little diagram, figure 1. If the incident light is plane-polarised and, in the absence of the magnetic field, is completely cut off by an analyser, suitably arranged, then we find that as soon as a transverse magnetic field is established there is a feeble restoration of light. This restoration is not a matter of the ordinary Faraday effect at all, as here we are dealing with light that is passed through a *transverse* magnetic field. The light has become elliptically polarised, and the ellipticity can be measured by suitable experimental methods. The idea, however, with which Langevin started was that the molecules of the liquid possess magnetic anisotropy. Langevin's theory has been developed by Born, who assumes that the molecules possess permanent magnetic moments and that in the condition of statistical equilibrium of the molecules in the magnetic field a small percentage of the molecules becomes preferentially oriented. The

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\*W Voigt, *Gesell. Wiss. Göttingen Nachr. Math.-Phys. Klasse* (1913) 2, 215-220.

†See also C V Raman and K S Krishnan, *Proc. R. Soc. A* (1927) 117, I.

magnetic field only acts on the molecule if the latter has a permanent magnetic moment whose axis is fixed so that the field exerts a couple on it. If the molecule is magnetically non-isotropic, i.e. if it is not equivalent to a magnetic sphere in its behaviour, the magnetic moment has in general a direction inclined to the lines of force and, in consequence, a couple acts on the molecule. In every case the tendency of this couple is to orient the molecule so that the magnetic susceptibility of the system tends to a minimum value. This orientation, however, is unable to exert its full effect.

When dealing with a liquid in which the molecules are in a state of continual thermal agitation we have a kind of statistical equilibrium and the magnetic field tends to orient the molecules. We do not have the molecules oriented at random in all directions but there is a certain preferential orientation of the molecules in that direction in which their potential energy in the field of force is a minimum. This statistical equilibrium can be evaluated, by a well-known method, and if we postulate further that the molecules are not optically isotropic, i.e. that the electrical moments induced in the molecules by the electric field in the light wave are not always parallel to the field, we have as a consequence which, I think, is fairly obvious, that the liquid exhibits a feeble double refraction and acquires some of the characteristics of a crystal. This effect is, however, extraordinarily feeble; in fact, I doubt very much whether, except perhaps in one or two laboratories in the world, the phenomenon has been observed in the course of the ordinary work of the physicist.

I myself have observed it with a small electromagnet and when on one occasion I got the effect in a few minutes I was very jubilant, but in half an hour I discovered that I was observing a small residual Faraday effect, and not magnetic double refraction at all. The position is that the observation is extremely difficult.

Now, obviously, while Langevin's theory gives us a general account of the phenomenon, its real significance is that if we knew the magnetic characteristics and also the optical characteristics of the molecule we could calculate the double refraction and see if this agreed with observation. On the other hand, if we knew the actual magnitude of the double refraction and the optical characteristics of the molecule we could go back and infer from them the magnetic characteristics of the molecule, or at least the degree of magnetic anisotropy of the molecule. That is the importance of double refraction from the standpoint of the theory of magnetism generally.

Perhaps I can make the importance of this clearer by referring to the work of Pascal who some years ago paid a great deal of attention to the examination of the magnetic properties of a great variety of compounds, both organic and inorganic, and attempted to find some general relationship between them. Pascal's work led to the belief that there was nothing startling about diamagnetism and that you could, in general, determine the diamagnetic susceptibility of an organic compound simply by adding up certain contributions from the separate atoms of which the molecule is composed, that is to say, diamagnetic suscepti-

bility is an additive molecular property. In a few cases there were certain residual differences, but later on Pascal made further observations, though I think they are relatively of minor importance from the quantitative point of view. Nevertheless, Pascal emphasised that they constituted an influence of diamagnetism that was not altogether negligible. Pascal's work was concerned largely with liquid or crystalline bodies and in consequence what he was actually measuring was the average susceptibility of molecules oriented in all possible directions relative to the lines of magnetic force. The average susceptibility so measured does not really tell us very much about individual molecules. The results of X-ray work and the fundamental conceptions of chemistry suggest that the molecules are not even approximately isotropic. This being so, if we really wish to understand the architecture of the molecule and determine its magnetic properties we have to study the diamagnetic properties of single molecules, and unless we have such information we cannot really even begin to understand how the problems of structural chemistry are related to the fundamental properties of diamagnetism.

We have, therefore, to seek for some method of investigating the diamagnetic character of molecules. We have dealt hitherto with liquids but when we pass from liquids to crystals we have a complication introduced by the fact that the actual structure of the crystal is not known in many cases; in fact, in most cases it is not known at all. Therefore the work on liquids tends in the direction of simplicity, and it is of importance to try and interpret magnetic double refraction in a quantitative manner and then to deduce the ultimate qualities of the molecules themselves.

This has been the fundamental idea with which we set out. There was, however, a very serious limitation in that the work of Cotton and Mouton was practically confined to certain specified classes of organic compounds, namely the aliphatic compounds, whilst in regard to a great many inorganic compounds they do not, for some reason, appear to have been able to get a measurement or even to observe the effect.

One of the first things we did, therefore, was to try and improve the technique of the subject in such a manner as to bring all known substances within the scope of the research. We felt quite certain that the failure of Cotton and Mouton to observe magnetic double refraction in water or one of the common paraffins was due to the insufficient sensitiveness of their apparatus. Moreover we knew from optical work on the scattering of light that there is no reason to suppose, if a molecule is electrically isotropic, that it must be magnetically isotropic as well. On the other hand, we know that the electrical and magnetic behaviour are counterparts of each other and that there must be correlation between these aspects. Therefore we felt that if the technique of Cotton and Mouton were improved it should be possible to study double refraction in all substances in the liquid state. The problem is twofold. First there must be a sufficiently intense magnetic field, and secondly there must be sufficiently delicate methods of observation. It is obvious that in order to increase the sensitiveness of the method of observation the liquid must be placed in an *intense* magnetic field.

Not possessing the financial resources which seem to lie so close to hand in the case of many American physicists, and perhaps also to some physicists in this country, I wandered about the streets of Calcutta and looked into the old iron shops and discovered a huge dynamo of the Edison type, which had probably figured in some nobleman's house but had been thrown away in favour of some newer model. This dynamo happened to be in perfect order and we got it for the price of the old copper it contained. The old Edison dynamos are enormous and the marked feature of the electromagnet was its great length of 35 cm, while the gap was very small, only about  $1\text{ cm}^2$ . We found that with a current of about 10 amp we had a field of 25,000 gauss. Using the electromagnet we were able to observe magnetic double refraction in practically all the substances we examined. In order to obtain quantitative results we have had also to develop more sensitive methods of measurement and for this purpose we employed a very interesting device, due to the late Lord Rayleigh\*, which proved to be of great service. The set up of the apparatus is given in figure 2, which shows diagrammatically the apparatus employed by one of my students, M Ramanadham†.

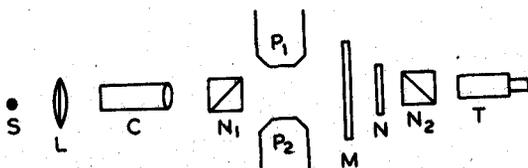


Figure 2

*S* is a "Pointolite" source of light, *L* a converging lens illuminating the slit of the collimator *C*. *N*<sub>1</sub> and *N*<sub>2</sub> are respectively the polarising and analysing Nicols. *P*<sub>1</sub>, *P*<sub>2</sub> are the poles of the electromagnet and *T* the observing telescope. The glass strips *M* and *N* form the compensator. A piece of flint glass, *M*, supported at its ends, is bent in a vertical plane by a small adjustable force applied at its centre. The glass thus strained is interposed between the crossed Nicol prisms. The double refraction induced in the glass plate by the applied stress manifests itself by the restoration of light everywhere in the field of the telescope *T* except along a horizontal dark band corresponding to the neutral axis of the plate *M*. If any doubly refracting medium is interposed between the strained glass and the polariser *N*<sub>1</sub> a shift of the dark band occurs and can be measured with reference to the cross wire of the observing telescope. In order that both kinds of double

\**Philos. Mag.* (1902) 4, 678.

†M Ramanadham, Magnetic birefringence in liquids, *Indian J. Phys.* (1929) 4, 15.

refraction may be determined quantitatively this shift is compensated by the interposition of a second glass strip  $N$  which can be compressed either horizontally (for positive birefringence) or vertically (for negative birefringence). The plate  $N$  is connected with a pan in which weights can be placed so that the applied stress necessary to compensate the shift can be measured.

In this manner Mr Ramanadham has been able to measure the double refraction occurring in a great many common substances, including something like 35 compounds in which Cotton and Mouton failed to observe the effect, and in which it is exceedingly small. There is a large difference between the aliphatic compounds and the aromatic compounds and I have some figures here relating thereto. If we take the double refraction observed with nitrobenzene as 100, the figure for water is only 0.4, and that for ethyl alcohol is of the same order. There is a very remarkable difference referring not only to the magnitude but also to the signs of the double refraction and their relation to chemical constitution. A characteristic feature of the effect as observed by Cotton and Mouton is that all compounds of the benzene series—naphthalene and similar aromatic compounds—show a positive birefringence, whilst the aliphatic compounds show a negative birefringence. In other words, aromatic compounds behave like positive uniaxial crystals, aliphatic compounds like negative uniaxial crystals. The chemist has divided organic compounds into the aliphatic and aromatic classes and the distinction, which is fundamental in chemistry, is reflected magnetically in the fact that one class gives a positive and the other class a negative birefringence. Only, however, by very refined arrangements such as I have outlined is it possible to observe and measure this characteristic difference.

In aliphatic series, the effect of substitution is to produce considerable change in the magnitude of the magnetic double refraction observed. This is shown in the following series of relative experimental values: [nitrobenzene, 100]; formic acid, + 2.5; acetic acid, + 1.1; propionic acid, + 1.1; butyric acid, 0.7; capronic acid, + 0.7; heptylic acid, + 0.5; caprylic acid, 0. We have obtained these results and you will see that formic acid shows a strong positive birefringence. I have no doubt that if we proceed further with the series—we have not yet studied some of the higher acids—we shall obtain a negative birefringence. This reversal of the sign of the birefringence is analogous to the reversal of the long chains of fatty acids observed by Müller by X-ray methods. We have shown that a negative birefringence is characteristic of the aliphatic compounds, and the same sort of influence is shown in the ketones and as we proceed up the series we obtain a negative birefringence. On the other hand there is evidence that double compounds have a positive birefringence.

I have given you a few illustrations, but do not run away with the idea that the method is only applicable to organic compounds. It is just as possible to investigate inorganic compounds. In this case, of course, we have only to use solutions of such compounds. Results with some of the nitrates, such as sodium nitrate and nitrites, show that any kind of unsaturation increases the positive

birefringence and decrease the negative birefringence. In all this I am merely indicating the field of work that has been opened up by the extending of the work of Cotton and Mouton and the making of their method of investigation applicable to a great variety of substances.

Now I come to the question of the interpretation and use we make of these results. It is not sufficient to say that there occurs positive or a negative birefringence. We must try to deduce the magnetic characteristics and here we are face to face with considerable difficulties. Langevin considered the case of a molecule with an axis of symmetry, and the mathematics becomes much simpler in such a case. We, however, in the general case, have to assume that the magnetic ellipsoid and the optical ellipsoid of the molecule have unequal axes and that these axes may have no obvious relationship to each other. You will find an account of Langevin's theory given in Prof. Born's monograph, *Handbuch der Radiologie*. This theory of Langevin, complicated as it may seem, is inadequate because he has assumed that the polarisation field, i.e. the optical field acting on the molecule, is of an isotropic character.

When we have a beam of light passing through a liquid, the actual electromagnetic field acting on the light wave is due to two causes; one, the external field of the light wave itself, and the other, the optical polarisation of the molecules in the immediate neighbourhood. Langevin and Voigt used the well-known theory of refraction in this matter, but our investigations show that Langevin's theory is quite inadequate, even as an approximation, and when we come to deal with such recondite phenomena as double refraction it is wholly inadequate. Molecules are not spherical in form. They are highly anisotropic. Much depends on how the molecule is oriented in the light wave. Mr Krishnan and myself\* have developed a general theory of optical and electrical properties of a liquid and we have been able to show that the influence of the shape of the molecule is, in consequence of its environment, effectually diminished in a manner that can be experimentally determined. The reason I have had to speak about optical anisotropy is that magnetic birefringence depends on *both* optical and magnetic anisotropy.

The value of  $C_m$ , the Cotton-Mouton constant<sup>†</sup>, which is a measure of the optical birefringence exhibited by a liquid in a strong magnetic field is given by the equation

$$\begin{aligned} C_m &= (n_p - n_s)/\lambda H^2 \\ &= -3(n_0^2 - 1)^2[(A - B)(A' - B') + (B - C)(B' - C') \\ &\quad + (C - A)(C' - A')]/8\pi n_0 \lambda \kappa T v (A + B + C)^2, \end{aligned}$$

\**Loc. cit.*

†S Bhagavantam, *Indian. J. Phys.* (1929) 4, 1.

where  $A, B$  and  $C$  are the moments induced by unit electric force in the incident light wave acting along the three mutually perpendicular axes of the optical ellipsoid of the molecule, and  $A', B', C'$  are the magnetic moments for unit magnetic fields acting in the same directions. The remaining symbols have their customary significance. It is clear that the sign of  $C_m$  depends on that of the factor

$$\Sigma(A' - B)(A' - B').$$

If the optical moments  $A, B, C$  are in descending order of magnitude and if  $A', B', C'$  are in the reverse order, then  $\Sigma(A - B)(A' - B')$  is positive and the value of  $C_m$  is positive. But if  $A, B, C$  and  $A', B', C'$  are in the same order, either descending or ascending, then the value of  $C_m$  is negative. The quantities  $A, B, C$  are connected with the refractive index,  $n$ , by the relation

$$(A + B + C)/3 = 3(n_0^2 - 1)/4\pi v(n_0^2 + 2),$$

so that we have

$$C_m = -(n_0^2 - 1)(n_0^2 + 2)[\Sigma(A - B)(A' - B')]/60n_0\lambda\kappa T[\Sigma A].$$

If  $A = B$ , and  $A' = B'$ , we have

$$C_m = -(n_0^2 - 1)(n_0^2 + 2)(A - C)[3C' - (A' + B' + C')]/60n_0\lambda\kappa T(2A + C)$$

also, if  $\delta$  be the optical anisotropy, then

$$\delta = (A^2 + B^2 + C^2 - AB - BC - CA)/(A + B + C)^2.$$

It is because the molecule is both optically and magnetically anisotropic that we get double refraction. If we knew the quantities  $A, B, C$  and  $A', B', C'$  it would be possible to compute the Cotton and Mouton constant absolutely and see if it agrees with observation. I think the principal feature of the theory that Mr Krishnan and I have worked out is the determination of  $A, B, C$  and if we could get  $A', B'$  and  $C'$  we should get a value for the Cotton and Mouton constant. But we do not know  $A', B'$  and  $C'$ . What we want to do is to know  $A, B$  and  $C$  and to calculate  $A', B'$  and  $C'$ . If we assume the molecule to have an axis of symmetry the method becomes a perfectly practicable one. This assumption is definitely permissible in a number of cases. Take carbon bisulphide or benzene. In these cases the assumption of an axis of symmetry is justified and we can go ahead and compute the magnetic characteristics. This was done some time ago\* and the remarkable fact was discovered that in the case of benzene the magnetic susceptibility is nearly twice as large in a direction normal to the plane of the ring as in a direction parallel to the ring. In the case of anthracene the magnetic susceptibility in a direction normal to the plane of the benzene ring was four and a

\*See e.g. Magnetic birefringence in liquids of the aliphatic series, by M Ramanadham, *Indian J. Phys.* (1929) 4, 15 and the anisotropy of the polarisation field in liquids, *ibid.* p. 39.

half times that in a direction parallel to the ring. This is sufficiently remarkable but I should mention that these compounds show positive and negative birefringence and I come to the simple conclusion that in the case of certain compounds, as for example benzene, maximum diamagnetic susceptibility coincides in direction with minimum optical polarisation-susceptibility. We have here an effect deduced from observation which awaits interpretation, and there is no doubt that it is extremely significant from the point of view of molecular structure.

If I stopped here, as I ought from considerations of time, I should leave the whole subject in an extremely unsatisfactory state. You might very well say that I have discussed double refraction and spoken of light-scattering, but that you know nothing at all about magnetic anisotropy, and yet you are asked to accept the fact of this double refraction, and that this places rather a heavy strain on your credulity.

Fortunately, however, the most interesting things that have come out of our work are conclusions drawn from wholly unrelated fields of investigation. From our studies on light-scattering and other investigations of that kind we can compute the magnetic characteristics of the molecule. This matter is discussed in a paper to be published shortly. If we take, for example, hexamethyl benzene we find that it is a remarkable substance. Lonsdale has analysed its crystal structure, and as soon as we saw his results we came to the conclusion that it should be possible for us, without much difficulty, to determine the magnetic characteristics of this crystal from our investigation of light-scattering, together with our studies of its magnetic birefringence. We proceeded to fix the magnetic axes of the crystal and to find out what should be the magnetic susceptibility normal to the plane of the ring, and also in a direction parallel to it, and the observations showed themselves to be in complete agreement with the results referred to. Hexamethyl benzene, in a direction at right angles to the plane of the benzene ring, behaves as an aromatic compound, whilst in the plane of the ring its behaviour is typically aliphatic and attributable to the  $\text{CH}_3$  groups.

We appear to have developed a new technique for studying the magnetic characteristics of crystals. This is shown diagrammatically in figure 3. The apparatus is based essentially upon the gravity balance of Threlfall and Pollock\* and was used by S Bhagavantam†. A fine quartz fibre is stretched across the poles of the electromagnet *NS* as shown and is kept taut by two screws. A glass fibre carrying the crystal, *C*, between the poles of the electromagnet is attached to the quartz fibre as shown, so that the crystal hangs in the non-homogeneous field of the electromagnet. As the quartz fibre is stretched across the gradient parallel to the field, it at once responds to forces acting on the crystal in the direction of this

\**Philos Trans. A.* 193, 215 (1899).

†*Loc. cit.*

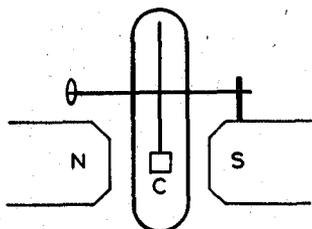


Figure 3

gradient and the resultant twist of the quartz fibre results in an angular displacement of the end of the glass fibre which is measured by a microscope.

I have taken up a large amount of time and I cannot describe to you in any detail all the various kinds of instruments we have developed for our investigations. This new technique, however, has been applied to a very large number of organic crystals, so that we now have a means for direct quantitative observation of the magnetic characteristics of organic crystals, especially naphthalene, anthracene, hexamethyl benzene and a number of others. I want you to realise that here we have the beginning of a practically limitless field of research. The organic chemist manufactures and the physicist designs for our benefit thousands and thousands of crystals, all of which await a detailed study of their magnetic construction. This field of work might perhaps at one time have been considered too unimportant because the effects exhibited were so small, but I hope you will realise from what I have been telling you that the magnetic anisotropy of an organic crystal is a remarkable phenomenon, the diamagnetic susceptibility being four or five times greater in one direction than in another. Important results must consequently follow from an extended study of the diamagnetic behaviour of organic crystals. I would be failing in my duty if I did not emphasise to you that this new technique enables us to go much farther than has been possible by older methods in the matter of crystal structure, X-ray analysis is a most powerful method of research and I would be the last to decry it because I use it myself, but there are limitations to the X-ray method, and the magnetic study of crystals has revealed properties which are at present beyond the reach of X-ray examination. I will take as an illustration the case of hexamethyl benzene. One would assume that it has axes of symmetry and that the magnetic susceptibility is the same in all direction and that likewise the optical susceptibility is the same in all directions. In one respect, as stated already, this substance is an aromatic compound but in another it is aliphatic in character, a peculiar combination. There is a difference of about 10%, in the magnetic susceptibility along the two axes of the plane of the ring and these two axes coincide absolutely with the optical axes in that plane. Here we have, therefore, the optical and the magnetic susceptibilities following each other closely. That is what we should expect from the crystal structure.

I cannot understand at present chemically why it should be asymmetrical, but it is asymmetrical.

I will not stop here but will trespass further on your patience and indicate a still further possibility of this work. Take that very interesting and remarkable substance azobenzene, which is the starting-point of a great industry, viz. the manufacture of dyes. Azobenzene is composed of two benzene rings bridged together by an azo group. This substance has been examined and it has been found that the crystal does not show that high degree of magnetic anisotropy which we should have expected from the existence of two benzene rings presumably in the same plane; at least this is the structure the chemists provide us with. There must be something in the crystal structure which masks the magnetic anisotropy; in other words, there must be more than one molecule in the lattice and these molecules must be so oriented relatively to each other that in the crystal itself there occurs a masking of the anticipated magnetic anisotropy. One can predict that the two molecules in the crystal lattice cannot be oriented parallel to each other. Similarly, I fear that in the case of naphthalene and benzene, the orientation which Sir William Bragg, in his book published some years ago, assigned as probable, cannot now be accepted, because it does not take into account the optical and magnetic aspects and there is evidence that more recent X-ray results will lead to a revision of their structures so as to fit in with the optical and magnetic characteristics. Optical and magnetic characteristics never mislead—X-ray results may sometimes mislead.

You see now that starting from the molecule we have entered into the crystal region and provided we have enough data in these two fields of research, magnetic study can be regarded as a most powerful auxiliary to crystal analysis. That is the point I am trying to make.

I should like to mention another very remarkable new field of research in relation to diamagnetism which we have entered upon. For a long time it has been part of our scheme of research on magnetism in Calcutta to investigate how the physical state of a substance influences the magnetic characteristics. Suggestion have been made that the diamagnetism of certain compounds is different in the liquid state from what it is in the solid state. Mr V I Vaidyanathan\* started a research some time ago in Calcutta to develop a complete technique by which the feeble diamagnetism of vapours and gases could be accurately measured. The method is an extremely simple one; it was first used by Faraday and was modified by Glaser and by Hammar.

A thin aluminium vane  $B_1B_2$ , figure 4, carrying a concave mirror,  $M$ , is suspended by a phosphor bronze strip within a vessel of the form shown, which can be filled with any gas or vapour. One end of the vane carries the evacuated

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\* *Indian J. Phys.* (1926) 1, 183.

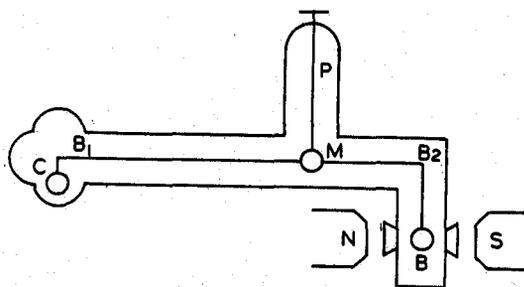


Figure 4

glass bulb, *B*, whilst the other end carries a counterpoising bulb *C*. *B* is suspended in the magnetic field of the electromagnet *NS*.

The glass of the bulb *B* is specially chosen so as to have the smallest possible magnetic susceptibility. It is highly paramagnetic, so that magnetically this glass bulb is practically neutral. By suspending it inside the cylinder containing the gas or vapour—a magnetic analogue of the principle of Archimedes—we can determine the magnetic susceptibility of the gas or vapour. One of the first fruits of the method which we devised was connected with results obtained by Glaser, who investigated  $\text{CO}_2$  and one or two other inorganic gases and came to the conclusion that the susceptibility of a gas is not proportional to the pressure. Glaser laid it down that at low pressures, instead of the magnetic susceptibility decreasing proportionally to the pressure, the susceptibility pressure curve departed from this linear relationship. That result caused a great deal of sensation and got into the text-books, which ought not to have happened. As a matter of fact, I saw this paper of Glaser's on a Saturday afternoon and on the following Tuesday evening I gave an Address, proving to my own satisfaction, if not to the satisfaction of my audience, that Glaser's work must be wrong and his result attributable to faulty technique. Glaser explains the result as due to some orientation of the molecules in the magnetic field. If such an orientation exists, we know from our work on double refraction that the effect of orientation is exceedingly small. The Cotton and Mouton constant contains the factor  $10^{-14}$ , so that you will realise at once what an exceedingly small effect it is. In view of that, Glaser's statement that the molecules are orientated is palpably wrong. The subsequent work of Glaser I believe to be fallacious, but that was the starting-point, and one object which led us to develop this new technique of placing the vacuum bulb in a heterogeneous magnetic field was the investigation of his conclusion\*. We have found throughout strict proportionality between pressure

\*Glaser, *Ann. Phys.* (1924) 74, 459; Hammar, *Proc. Natl. Acad. Sci.* (1926) 12, 594; Vaidyanathan, *Indian J. Phys.* (1926) 1, 183; (1928) 2, 135.

and the value of susceptibility for carbon dioxide, argon, hydrogen, and all gases examined, and are convinced that Glaser's conclusion is erroneous.

I wish to say, however, that this field of work must be extended largely. We have tried to extend it and there are two or three cases of very great interest in which the physical state does seem to produce a most remarkable change in diamagnetism. The most remarkable cases are those of graphite, charcoal and diamond. Pascal worked with many organic compounds and also with the above forms of carbon. Values of the diamagnetic susceptibilities (in  $10^{-6}$  units) found by Pascal are: graphite,  $-4.0$ ; charcoal and diamond,  $-0.5$ . In other words, magnetically diamond and charcoal are alike. Why is it that graphite has a higher value? Graphite stands out alone of all forms of carbon as having a diamagnetic susceptibility about eight times as high as the others. That suggests that there must be something peculiar about graphite and we set to work and carried out some experiments. We have found that the susceptibility of massive graphite is still higher; the average value is something like  $-7.0 \times 10^{-6}$ . Graphite is magnetically anisotropic, the diamagnetic susceptibility normal to the plane of its structural ring (in  $10^{-6}$  units) being  $-18$ , whilst in the plane of the ring the value is  $-2$ . We find with graphite that the value can be brought down to the value for sugar charcoal by powdering of the graphite; in other words, particle size determines the magnetic susceptibility of graphite. But the powdering must be extremely fine to achieve the result. The same sort of thing is found in the case of bismuth and antimony, and we now know that particle size has an influence on the diamagnetic property and there is obviously a relationship between the fact that the susceptibility is greater in the direction normal to the plane of the ring\*.

I have tried to give you some idea of the kind of work that is being attempted in Calcutta. We have only just started these investigations and they have to be pursued and developed. We have obtained some results but we are yet far from being able to picture them and explain them in terms of the newer theories. Nevertheless, I think that what I have said will indicate that there is still plenty of room for experimental work in modern physics.

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\*See S Paramasivan, Anomalous diamagnetism of graphite, *Indian J. Phys.* (1929) 4, 141.