Investigations on Magne-Crystallic Action. Part I: Diamagnetics

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VII. *Investigations on Magne-Crystallic Action. Part I.—Diamagnetics.*

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CONTENTS.

INTRODUCTION.

It is well known, from the investigations of COTTON and MOUTON and others* on the magnetic double-refraction of liquids, that diamagnetic molecules in general are

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* Various papers in 'C.R. Acad. Sci. Paris' and 'Ann. Chim. Phys.' (1908) to (1913); M. RAMANADHAM, 'Ind. J. Phys.,' vol. 4, p. 15 (1929). For calculation of the anisotropy, see RAMAN and KRISHNAN, 'Proc. Roy. Soc.,' A, vol. 113, p. 511 (1927).

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magnetically anisotropic. When such molecules are arranged in a regular manner as they are in a crystal, the crystal, as a whole, will usually exhibit differences in susceptibility in different directions. The magnitude of these differences will evidently depend on the relative *orientations* of the molecules in the unit cell; their *positions* in the cell will have no direct effect, since the diamagnetic moments induced in the molecules are so feeble that their mutual influences are negligible.* Thus a correlation of the magnetic anisotropy of the crystal with that of the individual molecules constituting it, calculated from measurements on magnetic double-refraction in the liquid state, or from other considerations, is likely to give us useful information regarding the orientations of the molecules. This method of analysis of molecular orientations in crystals, which was first suggested by one of us,† promises, at any rate, in favourable circumstances, to be a useful supplement to X-ray methods of crystal analysis. Indeed, in certain crystals—as will be seen in the body of the present paper—the molecular orientations can thus be determined more easily and with greater accuracy than by X-ray methods.

Optical measurements in theory have the same value, but owing to strong mutual influences of the optical dipoles induced in the neighbouring molecules of the crystal, even in those cases where the molecules happen to be orientated in the same manner, the birefringence of the crystal, as a whole, does not *directly* give that of the individual molecules. In order to correlate the optical constants of the crystal with those of the molecules, the relative *positions* of the latter in the crystal have also to be considered; thus the problem is more complicated than in the corresponding magnetic case.

Measurements on paramagnetic single crystals are also of interest for very different reasons. The mutual interactions of the atomic magnetic moments are no longer negligible, so that the anisotropy of the crystal is not determined solely by that of the individual units of the crystal. Investigations over an extensive range of temperatures, by FOËX‡ on siderite and by JACKSON§ on some sulphates and double-sulphates, show that the principal magnetic susceptibilities of a paramagnetic crystal obey Weiss relations of the type

$$\chi_i = \frac{C}{T - \theta_i}, \quad i = 1, 2, 3,$$

where the Curie constant C is the same for all three axes, while θ's are different. This suggests that the anisotropy of the crystal arises from differences in the value of the

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* See RAMAN and KRISHNAN, 'Proc. Roy. Soc.,' A, vol. 115, p. 549 (1927).

† KRISHNAN, 'Proc. Ind. Sci. Cong.,' Madras Session, January, 1929. Naphthalene was mentioned in this communication as a suitable crystal for the application of this method; the approximate molecular orientations in this crystal were first determined by this method. (BHAGAVANTAM, 'Proc. Roy. Soc.,' A, vol. 124, p. 545 (1929).) BHAGAVANTAM's results have been confirmed by more recent X-ray measurements (BANERJEE, 'Ind. J. Phys.,' vol. 4, p. 557 (1930)).

‡ 'Ann. Physique.,' vol. 16, p. 174 (1921).

§ 'Phil. Trans.,' A, vol. 224, p. 1 (1923) and vol. 226, p. 107 (1927).

inner Weiss field in different directions. Measurements on the magnetic anisotropy of paramagnetic crystals may, therefore, throw light on the dependence of the Weiss field on crystal structure, which, in our present state of knowledge regarding the nature of the Weiss field, would be very desirable.

In view of the above remarks regarding the importance of magne-crystallic investigations, extensive measurements on single crystals were undertaken by us about two years ago. This paper describes the results of these measurements. Part I of the paper deals with diamagnetic crystals; Section I refers to inorganic compounds; in Section II are given measurements on organic crystals, selected exclusively from the class of aromatic compounds on account of their remarkable magnetic anisotropy; in Section III some measurements on the change of susceptibility of crystals on melting are described; the results on organic crystals are discussed in Section IV, with special reference to molecular orientations in crystals. Extensive measurements have also been made on paramagnetic crystals, and they will form the subject-matter of Part II of the paper.

SECTION I.—INORGANIC CRYSTALS.

1. *Methods of Measuring Magnetic Anisotropy.*

One method of measuring the magnetic anisotropy of a crystal is to locate its principal magnetic axes, and to determine the actual susceptibilities along these directions. This has been done by VOIGT and KINOSHITA* and others. The method, however, is not sufficiently accurate to give the exact *differences* in susceptibility in different directions; this can be measured more precisely by a direct method.

When any diamagnetic crystal is suspended by a thin fibre, say, of quartz, in a magnetic field, besides the lateral force acting on the crystal which tends to move it to the weakest part of the field, there are also two different couples tending to rotate the crystal about the axis of suspension: (*a*) the couple due to the asymmetry of shape of the crystal and the non-homogeneity of the field, which tends to place its length perpendicular to the field, and (*b*) the couple due to the magnetic anisotropy of the crystal tending to set the axis of greater† susceptibility in the plane of oscillation, along the field. The former couple can be eliminated by using the material in the form of a sphere, and then the only couple that acts is that due to the anisotropy of the crystal. When the torsion of the fibre is known, this couple can be deduced either by observing the twist of the fibre, or preferably from the period of oscillation of the crystal sphere in the magnetic field. This method has been used by STENGER‡ and by KÖNIG§ for measurements on quartz and calcite.

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[*] 'Ann. Physik.,' vol. 24, p. 492 (1907).

[†] In the following pages the terms "greater" and "smaller" applied to susceptibility refer to its *algebraic* value.

[‡] 'Wied. Ann.,' (Ann. Physik.), vol. 20, p. 304 (1883) and vol. 35, p. 331 (1888).

[§] 'Wied. Ann.' (Ann. Physik.), vol. 31, p. 273 (1887).

It is not, however, necessary to use the crystal in the form of a sphere. The couple due to the asymmetry of shape can be eliminated almost as effectively by using a homogeneous magnetic field; such fields as are obtained in ordinary large magnets fitted with large-sized plane parallel pole-pieces, are found to be sufficiently homogeneous for the purpose. The crystal can then be used in whatever shape it is available, which is a great convenience, though the moment of inertia of the crystal about the axis of suspension is not easy to calculate; but it can be readily eliminated by making another observation on the period of oscillation outside the magnetic field. This method was, therefore, adopted in the following measurements.

Theory of Oscillations in a Magnetic Field.—Suppose that a crystal is suspended in a uniform magnetic field H. Let χ_1 and χ_2 be the maximum and the minimum values, respectively, of the gram molecular susceptibility of the crystal in the plane of oscillation. The χ_1-axis will naturally tend to place itself along the magnetic field. Let the torsion-head now be rotated, so that, when the crystal is in this position, the torsion of the fibre is zero. If the crystal be allowed to execute torsional oscillations about this position, and if T and T′ be the periods of oscillation when the field is on and when it is removed, it can easily be shown that

$$\chi_1 - \chi_2 = \frac{T'^2 - T^2}{T^2} \cdot \frac{c}{H^2} \cdot \frac{M}{m},$$

where c is the torsional constant of the fibre, m is the mass of the crystal, and M is its molecular weight. All the quantities on the right-hand side of the above equation being determinable, $\chi_1 - \chi_2$ is known.

Thus in order to determine the magnetic anisotropy of a crystal, it is sufficient to measure its periods of oscillation in a uniform magnetic field when suspended along different axes, and to compare them with the corresponding periods of oscillation outside the field.

2. *Experimental Arrangement.*

The Magnetic Field.—The magnet used in these measurements was of the usual type with replaceable pole-pieces. For the present purpose the plane parallel pieces were used. The current for the magnet was taken from a 110-volt storage supply of constant voltage, and was regulated by a water-cooled resistance. Before any measurements were made, the magnet was brought to a steady state by repeated reversals of the current, the final direction of the current in the coils always being kept the same. The field was measured in the usual manner with the help of an exploring coil and a ballistic galvanometer, with a standard mutual inductance for calibrating the latter.

In order to test the homogeneity of the field, a thin plate of Merck's "Extra Pure" sodium chloride (which crystallises in the cubic system and is therefore magnetically isotropic) was suspended centrally between the pole-pieces by a thin quartz fibre of known torsional constant. The dimensions of the plate in the horizontal plane were

13 mm. × 2 mm., one of them thus being more than six times the other. When a field of 5050 gauss was put on, there was a feeble rotation of the plate towards the equatorial position, evidently due to a small deviation from homogeneity in the field. The maximum value of the rotating couple—which obtains when the plate is nearly at 45° to the field—was measured. It was found to be equivalent to the couple which would act on the plate in an ideal homogeneous field if the susceptibility of the plate along its length were smaller than along its breadth by about 3 parts in 2,000.* Thus even for such extreme asymmetry of shape as in this plate, the effect of the non-homogeneity of field is very small, so that for the usual asymmetries involved, the effect will be negligible in comparison with that due to the magnetic anisotropy of the crystals.

The Mounting of the Crystals.—Fine quartz fibres were used for the oscillation measurements. The upper end of the quartz fibre was fixed to a graduated torsion-head. To the lower end was attached permanently a short length (about 7 or 8 mm.) of moderately thin glass fibre, to which the crystals could be attached readily.† The glass fibre being very short, and much stouter than the quartz fibre, the torsion of the whole suspension was that due to the latter alone. The torsional constant of the suspension was determined by oscillating from its end a circular disc of glass, about one of its diameters.

The attachment of the crystal to the fibre, so as to make any specific direction in the crystal vertical, was a matter of some difficulty, and had to be adjusted by repeated trials. A short focal length telescope fitted with a graduated eye-piece scale, which could be rotated through any known angle about the axis of the telescope tube, served for measurements in connection with the mounting of the crystal. In fact, with the help of the torsion-head for measuring rotations about a vertical axis, the graduated circle of the telescope for rotations about a horizontal axis, and the eye-piece scale for linear displacements, all the necessary adjustments and measurements on the crystal could easily be made.

3. *Results.*

Before proceeding to describe the experimental results, we explain the notation adopted in the paper.

In the case of magnetically uniaxial crystals, the gram molecular susceptibilities along and perpendicular to the axis are represented by $\chi_{\parallel}$ and $\chi_{\perp}$ respectively. In crystals that belong to the orthorhombic system, the three crystallographic axes are also the magnetic axes, and the values of the susceptibilities along them per gm. mol. are denoted by χ_a, χ_b and χ_c, respectively. For the monoclinic crystals (010) plane being a plane of symmetry must naturally contain two of the magnetic axes ; we denote

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* A similar measurement with a paramagnetic single crystal of ferric ammonium alum—which is also cubic—whose horizontal dimensions were 8 mm. × 1 mm. gave practically the same value, $\Delta\chi/\chi = 2 \times 10^{-3}$.

† Traces of shellac, which was tested and found to be feebly diamagnetic, were used as cement in all cases.

the gram molecular susceptibilities along them by χ_1 and χ_2, χ_1 *being greater than* χ_2 The angle which the χ_1-axis makes with the "*c*" axis of the crystal, *taken positive towards the obtuse angle* β between the "*c*" and the "*a*" axes, determines the positions of these two magnetic axes. (Since in most of the monoclinic crystals the (001) plane was well developed, the inclination of the χ_2-axis to this plane was directly measured. Calling this angle θ, measured positive from the "*a*" axis towards the obtuse angle β, it is connected with ψ by the simple relation $90° + \theta + \psi =$ obtuse β). The third axis is, of course, along the "*b*" axis, and the gm. mol. susceptibility along it is denoted by χ_3.

The results are shown in Table I. Column 3 of Table I gives the axis of suspension, column 4 the direction of setting of the crystal in the field, the fifth column the maximum difference in susceptibility $|\Delta\chi|$ in the plane of oscillation, and the sixth column the magnetic anisotropy of the crystal. In the case of orthorhombic and monoclinic crystals, though oscillations about two axes are sufficient to determine completely the anisotropy, measurements were made also with a third direction of suspension, so as to be able to check the results.

4. *Discussion of Results.*

The most striking result is the large value of the magnetic anistropy of the nitrates, carbonates and the chlorate, as contrasted with the more or less complete isotropy of the sulphates. We have seen that calcite and sodium nitrate have an axis of magnetic symmetry, while aragonite, strontianite, witherite, potassium nitrate and potassium chlorate may for practical purposes be considered to have the same in view of the close approximation in value of two of the principal susceptibilities. In Table II are collected together the differences in susceptibility of these crystals, along, and perpendicular to, their axes of symmetry. The last column in the table gives the differences between the principal gram molecular refractivities (defined as usual by $R = M(n^2-1)/(n^2+2)\rho$).

In striking contrast with these values are those for the sulphates which are given in Table III.

The strong anisotropy of the nitrates and carbonates receives a natural explanation in terms of the intrinsic anisotropy of the NO_3^- and CO_3^{--} ions and the parallel orientations of all the ions in the crystal. (The contribution to the susceptibility of the crystal from the metallic ions is presumably isotropic.) The fact that $\chi_\perp - \chi_\parallel$ has the same value for both the nitrates and nearly the same value for the four carbonates is then readily understood. Indeed, it is possible, as has been shown in a recent paper,* to calculate the actual magnetic anisotropy of the NO_3^- ion from the Cotton-Mouton constant of nitric acid (or of aqueous solutions of nitrates) and this value is found to be in satisfactory agreement with the observed value of $\chi_\perp - \chi_\parallel$ for the crystal.

Why the nitrate and the carbonate ions are so strongly anisotropic is difficult to understand. Presumably it is connected with their plane structure; graphite, benzene,

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* C. V. RAMAN and K. S. KRISHNAN, 'Proc. Roy. Soc.,' A, vol. 115, p. 549 (1927).

TABLE I.

The unit adopted for the χ's is 10^{-6} of a c.g.s. electromagnetic unit.

Crystal.	Crystal system.	Mode of suspension.	Orientation in the field.	$\|\Delta\chi\|$.	Magnetic anisotropy.	Remarks.
1. **Quartz** (SiO_2) . .	Trigonal . .	Trigonal axis horizontal	Trigonal axis normal to field	$0\cdot12$	$\chi_\perp - \chi_\parallel = 0\cdot12$	KÖNIG's value = 0·14. STENGER's value = 0·10 to 0·12.
2. **Calcite** ($CaCO_3$) . .	,,	,,	,, ,,	$4\cdot0_9$	$\chi_\perp - \chi_\parallel = 4\cdot0_9$	KÖNIG's value = 3·98 to 4·28.
3. **Sodium nitrate** ($NaNO_3$)	,,	,,	,, ,,	$4\cdot8_9$	$\chi_\perp - \chi_\parallel = 4\cdot8_9$	
4. **Aragonite** ($CaCO_3$) .	Orthorhombic	" *a* " axis vertical	" *b* " axis along field	$4\cdot2_0$	$\chi_a - \chi_c = 4\cdot0_2\ldots$ $\chi_b - \chi_c = 4\cdot2_0\ldots$	" *c* " axis is an axis of approximate magnetic symmetry.
		" *b* " ,,	" *a* " ,,	$4\cdot0_2$		
		" *c* " ,,	" *b* " ,,	$0\cdot1_3$		
5. **Strontianite** ($SrCO_3$)	,,	" *b* " ,,	" *a* " ,,	$4\cdot8_1$	$\chi_a - \chi_c = 4\cdot8_1\ldots$ $\chi_b - \chi_c = 4\cdot8_4\ldots$	,, ,,
		" *c* " ,,	" *b* " ,,	$0\cdot0_3$		
6. **Witherite** ($BaCO_3$) .	,,	(110) horizontal	" *c* " axis normal to field	$5\cdot0_3$	$\chi_a - \chi_c = 4\cdot9_3\ldots$ $\chi_b - \chi_c = 5\cdot0_7\ldots$	,, ,,
		(110) vertical and " *c* " axis horizontal	,, ,,	$4\cdot9_7$		
		" *c* " axis vertical	" *b* " axis along field	$0\cdot1_4$		
7. **Potassium nitrate** (KNO_3)	,,	" *a* " ,,	" *b* " ,,	$4\cdot8_7$	$\chi_a - \chi_c = 4\cdot8_2\ldots$ $\chi_b - \chi_c = 4\cdot8_7\ldots$	,, ,,
		" *b* " ,,	" *a* " ,,	$4\cdot8_2$		
		" *c* " ,,	" *b* " ,,	$0\cdot0_5$		
8. **Barite** ($BaSO_4$) . .	,,	" *a* " ,,	" *b* " ,,	$0\cdot7_2$	$\chi_b - \chi_c = 0\cdot7_2$ $\chi_c - \chi_a = 0\cdot6_2$	
		" *b* " ,,	" *c* " ,,	$0\cdot6_3$		
		" *c* " ,,	" *b* " ,,	$1\cdot3_4$		
9. **Celestite** ($SrSO_4$) . .	,,	" *a* " ,,	" *b* " ,,	$0\cdot7_4$	$\chi_b - \chi_c = 0\cdot7_4$ $\chi_c - \chi_a = 0\cdot9_9$	
		" *b* " ,,	" *c* " ,,	$0\cdot9_9$		
		" *c* " ,,	" *b* " ,,	$1\cdot6_8$		
10. **Anhydrite** ($CaSO_4$) .	,,	" *a* " ,,	" *b* " ,,	$0\cdot2_7$	$\chi_a - \chi_b = 0\cdot4_0\ldots$ $\chi_b - \chi_c = 0\cdot2_5\ldots$	Since the order of the magnetic axes is different from that in $BaSO_4$ and $SrSO_4$, the measurements were repeated with two other specimens with practically the same results.
		" *b* " ,,	" *a* " ,,	$0\cdot6_5$		
		" *c* " ,,	" *a* " ,,	$0\cdot4_0$		
11. **Sulphur**	,,	" *a* " ,,	" *b* " ,,	$0\cdot0_7$	$\chi_b - \chi_c = 0\cdot0_7$ $\chi_c - \chi_a = 0\cdot2_5$	
		" *b* " ,,	" *c* " ,,	$0\cdot2_5$		
		" *c* " ,,	" *b* " ,,	$0\cdot3_0$		
12. **Selenite** . . . . . ($CaSO_4$–$2H_2O$)	Monoclinic .	" *b* " ,,	" *c* " ,,	$1\cdot0_6$	$\psi = 0$ $\chi_1 - \chi_2 = 1\cdot0_6$ $\chi_1 - \chi_3 = 0\cdot6_1$	
		" *c* " ,,	" *b* " ,,	$0\cdot4_3$		
		(100) horizontal	" *c* " ,,	$0\cdot6_1$		
13. **Potassium chlorate** ($KClO_3$)	Monoclinic $\beta = 109^\circ\cdot7$	" *b* " axis vertical	$\theta = -39^\circ\cdot5$	$3\cdot7_1$	$\psi = +59^\circ\cdot2\ \ldots$ $\chi_1 - \chi_2 = 3\cdot7_1\ldots$ $\chi_1 - \chi_3 = 3\cdot9_1\ldots$	χ_1—axis is an axis of approximate magnetic symmetry.*
		" *a* " ,,	" *b* " axis normal to field	$2\cdot3_7$		
		(001) horizontal	,, ,,	$1\cdot7_3$		

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* $KClO_3$ usually crystallises in the form of a pseudo-rhombohedron bounded by (001) and (110) planes. The above axis of approximate magnetic symmetry is found, on calculation, to be nearly along the trigonal axis of the rhombohedron, which is also known to be an axis of approximate optical symmetry.

TABLE II.

Crystal.	$\chi_{\perp} - \chi_{\parallel}$.	$R_{\omega} - R_{\epsilon}$ for sodium line.
$NaNO_3$	4·9	4·86
KNO_3	4·9	4·32
$CaCO_3$ (calcite)	4·1	2·99
$CaCO_3$ (aragonite)	4·1	2·41
$SrCO_3$ (strontianite)	4·8	2·77
$BaCO_3$ (witherite)	5·0	3·03
$KClO_3$	— 3·8	2·12

TABLE III.

Crystal.	$\chi_b - \chi_c$.	$\chi_c - \chi_a$.	$R_b - R_c$.	$R_c - R_a$.
$BaSO_4$	0·72	0·62	0·02	—0·28
$SrSO_4$	0·74	0·99	0·04	—0·20
$CaSO_4$	0·25	—0·65	0·12	—0·93

and naphthalene molecules may be cited as showing this connection. But, also, we know, independently, that a plane close-packing of atoms conduces to a large optical anisotropy, so that if the above relation is general we have an explanation of the relationship remarked by RAMAN and BHAGAVANTAM* that strong magnetic anisotropy is always associated with strong optical anisotropy.

On the other hand, in the case of the SO_4^{--} ions it appears from X-ray investigations† that the four oxygen atoms are disposed more or less symmetrically about the sulphur atom, being situated at the corners of a tetrahedron with the latter atom at the centre. In that case, the observed isotropic nature of the sulphates, both as regards their magnetic and optical properties, follows as a direct consequence. Here, too, may be mentioned the strong contrast in the depolarisation of the light transversely scattered by nitric and sulphuric acids, observed by VENKATESWARAN‡.

The magnetic behaviour of potassium chlorate is interesting and deserves special mention. The strong resemblance of this crystal to calcite and to sodium nitrate in several of its properties is well-known.§ Even though it belongs to the monoclinic system, it crystallizes in the form of rhombohedra like the latter crystals, and their planes of cleavage are also similar. Also the trigonal axis of the pseudo-rhombohedron,

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* 'Ind. J. Phys.,' vol. 4, p. 57 (1929).

† EWALD and HERMANN, 'Strukturbericht,' p. 340 (1913–1926).

‡ 'Ind. J. Phys.,' vol. 1, p. 235 (1927).

§ See P. GROTH, "Chemische Kristallographie,' Leipzig, vol. 2, p. 81 (1908).

as has already been remarked, is at once an axis of approximate optical and of magnetic symmetry. Optically, the crystal is negative just like the other two crystals; even the magnitude of the molecular birefringence is of the same order. But, magnetically, whereas for nitrates and carbonates $\chi_{\perp} - \chi_{\parallel} > 0$ for potassium chlorate $\chi_{\perp} - \chi_{\parallel} < 0$. This difference in sign is probably due to the fact that the ClO_3^- ion is not plane as the NO_3^- and CO_3^{--} ions are, but pyramidal with Cl at the apex. Whatever may be the explanation, the above fact regarding the signs of $\chi_{\perp} - \chi_{\parallel}$ when taken together with the known negative birefringence of these crystals, would suggest a *negative* sign for the magnetic double-refraction of ClO_3^- ions in solution as contrasted with the positive sign for nitrate solutions. This is indeed so for the nitrate solutions; the magnetic double-refraction of chlorate solutions, however, does not seem to have been tested.*

SECTION II.—ORGANIC CRYSTALS.

1. *Measurements on Organic Crystals.*

In this section are described measurements on organic crystals. Investigations on magnetic double-refraction show that molecules of the aromatic class exhibit a pronounced magnetic anisotropy. In this respect, molecules having two or more benzene rings stand in a class by themselves; all the crystals studied in this paper are selected exclusively from this class of compounds. For reasons given in the introduction, our choice of crystals has been guided to a considerable extent by the list of substances for which preliminary X-ray measurements are available, we may then expect to supplement the information regarding the orientations of molecules in these crystals by that already obtained by the X-ray methods.

The differences in susceptibilities in different directions were measured in the same manner as described in the previous section by oscillating them about different axes. The organic crystals, however, were generally in the form of plates, and hence the influence of the residual non-homogeneity of the field on the setting of the crystal will naturally be greater than for the inorganic crystals. But the magnetic anisotropy of the organic crystals is also several times larger, so that the effect of the non-homogeneity of the field is also negligible in these crystals.

2. *Absolute Susceptibilities.*

Method of Measurement.—Since existing data for the magnetic susceptibilities of organic crystals are very meagre, the absolute susceptibilities have also been measured for these crystals. The method adopted is a null method of the type used recently by RABI† for measurements on paramagnetic crystals. The principle of the method is as

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* [*Note added November* 7, 1932.—In the 'Ind. J. Phys.' vol. 7, p. 317 (1932), Mr. CHINCHALKAR reports measurements on the magnetic double-refraction of aqueous solutions of sodium chlorate. The double-refraction is *negative* as predicted here; further, its numerical value is in agreement with that deduced from the magnetic and optical anisotropies of the ClO_3^- ion given in Table II. of the present paper.]

† 'Phys. Rev.,' vol. 29, p. 174 (1927).

follows. The crystal is suspended in a strong non-homogeneous field in a bath of liquid whose susceptibility can be varied at will. In general, there will be a lateral motion of the crystal when the field is put on, which will vanish when the volume susceptibility of the solution is the same as that of the crystal *in the direction of the field*. Thus the method of measurement of the susceptibility of the crystal along any specific direction consists in suspending the crystal so as to have this direction along the field and adjusting the susceptibility of the bath till there is no lateral motion when the non-homogeneous field is put on. If this direction does not correspond to the maximum susceptibility of the crystal in the horizontal plane, the crystal will tend to rotate from the above direction. RABI prevents this rotation by using for the suspension a fibre of glass of sufficient thickness. The fibre must not be very thick since the lateral movements of the crystal will then be diminished considerably. Thus the fibre has to possess a large torsional couple and, at the same time, a small bending moment. These conditions being to some extent mutually unaccommodative, there is a limit to the sensitiveness of the above arrangement.

But in our investigations, since the differences in the principal susceptibilities are already known from the oscillational measurements, it is sufficient to determine the absolute susceptibility along *any one* direction in the crystal. We can conveniently choose the direction which actually sets itself along the field. In this case, we can replace the glass fibre of RABI by a thin quartz fibre and thus the sensitiveness of the arrangement is considerably increased.

The Balancing Liquid Bath.—In all the crystals studied by us there was at least one principal magnetic axis along which the volume susceptibility was greater than that of water. Also the crystals were only sparingly soluble in water. Hence an aqueous solution of a paramagnetic salt was used as the liquid for the balancing bath. Manganese chloride was chosen as the solute in view of its large susceptibility. A standard solution of about one per cent concentration of Kahlbaum's pure manganese chloride was first prepared (the water used for the solution, as well as for later dilutions, was specially distilled for the purpose), and its exact strength was determined by chemical analysis by converting the chloride to the pyrophosphate. In the actual experiment, 50 c.c. of the solution at 29° C. gave on analysis 0·5717 gm. of $Mn_2P_2O_7$, which corresponds to 0·01014 gm. of $MnCl_2$ per c.c. of the solution. This standard solution was suitably diluted with known amounts of water and used in the bath, the precise dilution necessary for magnetically balancing the crystal being determined by repeated trials.

The Susceptibility of the Balancing Solution.—The volume susceptibility of the balancing bath has next to be calculated from its known concentration. Accurate measurements have been made by CABRERA and DUPERIER,* on the susceptibilities of solutions of $MnCl_2$ of different concentrations, and they find that the calculated susceptibility of $MnCl_2$ is very nearly the same for all concentrations. The smallest concentration measured by them was, however, about 3 per cent, which is much greater than the concentrations

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* 'J. Phys. Rad.,' vol. 6, p. 121 (1925).

used here. Hence the value was carefully redetermined by comparing the susceptibility of the above solution with that of water by a modified Quincke method, which will be described in the next section in connection with the measurements on molten crystals. These measurements gave for the susceptibility of $MnCl_2$ at such low concentrations, the value $117 \cdot 9 \times 10^{-6}$ at 28·5° C., as against $115 \cdot 3 \times 10^{-6}$ calculated for the same temperature from the results of Cabrera and Duperier for higher concentrations. (The value for solid $MnCl_2$ is much lower, being equal to $105 \cdot 3 \times 10^{-6}$ per gm.)

The above value has been adopted in the following calculations. For small deviations of temperature from 28·5° C. the temperature coefficient of susceptibility of $MnCl_2$ in solution has been taken to be $- 0 \cdot 43 \times 10^{-6}$ per 1° C.

3. *Densities of Organic Crystals.*

Since the volume susceptibility of the balancing solution gives at once that of the crystal along the field, it remains only to know the density of the crystal in order to calculate the corresponding gram molecular susceptibility. On a reference to the standard literature, one finds that the values for the densities of organic crystals given by different experimenters vary widely. This is not surprising; even in the case of substances which can be obtained in the form of large single crystals, Tutton* remarks that measurements on several crystals are made and the *highest* value is adopted. The difficulties of measurement on organic substances, which are usually in the form of micro-crystals, are naturally greater, and hence the above discrepancies. In fact, it has been suggested by Bragg† that the calculation of the density from the size of the unit cell determined by X-ray methods is likely to give a more accurate value than direct methods of measurement.

Thus it is clear that in our calculation of the gram molecular susceptibility of a crystal from its volume susceptibility we have to use the proper value of the density for the particular crystal used. This was determined by the "immersion" method, using a solution of zinc sulphate for the purpose.

The following observation made in the course of the measurements on densities appears to be worth mentioning. By taking a large crystal and continually subdividing it, the density of the heaviest piece is found to be considerably higher than that of the original crystal. The limiting value of the density so determined agrees in general with the value calculated from X-ray measurements.

Assuming that the deviation of the density of the actual crystal from the ideal density is due to inclusions of air, the gram molecular susceptibility χ of the crystal is connected with its volume susceptibility k (both χ and k being expressed in the usual unit, viz., 10^{-6} of a c.g.s. e.m.u.) by the relation,

$$\chi = \frac{kM}{\rho} - \left(\frac{1}{\rho} - \frac{1}{\rho_0}\right) M \cdot 0 \cdot 029,$$

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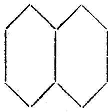
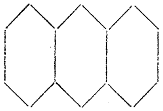
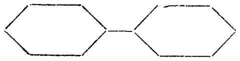
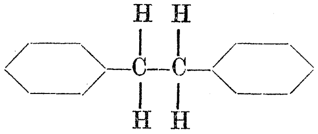
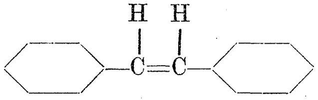
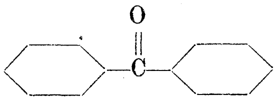
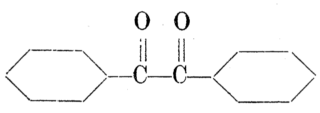
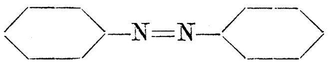
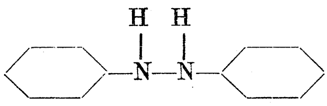
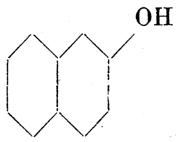
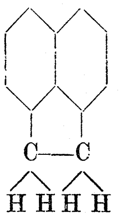
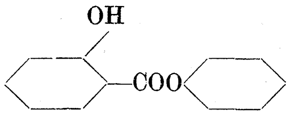
* "Crystallography," p. 625.

† 'Proc. Phys. Soc.,' vol. 35, p. 167 (1923).

TABLE IV.

Crystal.	Crystal system.	Mode of suspension.	Orientation in the field.	$\|\Delta\chi\|$.	Magnetic anisotropy.	Remarks.
1. Naphthalene . . . . . 	Monoclinic $\beta = 122°\cdot 8$	“ b ” axis vertical “ a ” ,, (001) vertical and the intersection of (001) and (110) horizontal	$\theta = + 20°\cdot 8$ “ b ” axis normal to field (001) at 68°·5 to field	122 13·9 92·5	$\chi_1 - \chi_2 = 122$ $\chi_1 - \chi_3 = 29\cdot 3$ —	Calculated value of setting angle = 67°·3 and of $\Delta\chi = 92\cdot 0$.
2. Anthracene . . . . . 	Monoclinic . . $\beta = 124°\cdot 4$	“ b ” axis vertical	$\theta = + 26°\cdot 4$	Oscillation measurements were not made with this crystal. Absolute measurements were made along three directions. See Table V.		
3. Biphenyl . . . . 	Monoclinic $\beta = 94°\cdot 8$	“ b ” ,, “ a ” ,, (001) horizontal	$\theta = - 15°\cdot 3$ “ b ” axis normal to field “ a ” ,,	83·1 29·7 40·1	$\chi_1 - \chi_2 = 83\cdot 1$ $\chi_1 - \chi_3 = 35\cdot 5$ —	Cal. $\Delta\chi = 41\cdot 8$.
4. Dibenzyl . . . . 	Monoclinic $\beta = 115°\cdot 9$	“ b ” axis vertical (001) horizontal “ a ” axis vertical	$\theta = - 58°\cdot 0$ “ a ” axis along field “ b ” ,,	83·1 5·1 29·9	$\chi_1 - \chi_2 = 83\cdot 1$ $\chi_1 - \chi_3 = 28\cdot 4$ —	Cal. $\Delta\chi = 31\cdot 4$.
5. Stilbene . . . . 	Monoclinic $\beta = 114°\cdot 1$	“ b ” ,, (001) horizontal “ a ” axis vertical	“ a ” ,, “ b ” ,, “ b ” ,,	56·6 0·8 58·0	$\chi_1 - \chi_2 = 56\cdot 6$ $\chi_3 - \chi_1 = 0\cdot 8$ —	Cal. $\Delta\chi = 57\cdot 4$.
6. Benzophenone . . . . 	Orthorhombic	“ c ” ,, “ c ” axis horizontal and (110) vertical (110) horizontal	“ a ” ,, “ c ” axis normal to field “ c ” ,,	0·6 61·0 61·3	$\chi_a - \chi_b = 0\cdot 6$ $\chi_b - \chi_c = 60\cdot 7$ —	Cal. $\Delta\chi = 61\cdot 0$.

7. Benzil . . . . 	Trigonal . . .	Trigonal axis horizontal	Trigonal axis along field	45·6	$\chi_{\parallel} - \chi_{\perp} = 45{\cdot}6$	
8. Azobenzene . . . . . 	Monoclinic $\beta = 114°{\cdot}4$	" *b* " axis vertical	" *a* " ,,	42·7	$\chi_1 - \chi_2 = 42{\cdot}7$	
		(001) horizontal	" *b* " ,,	4·4	$\chi_3 - \chi_1 = 4{\cdot}4$	
		" *a* " axis vertical	" *b* " ,,	46·3	—	Cal. $\Delta\chi = 47{\cdot}1$.
9. Hydrazobenzene . . . . 	Orthorhombic	" *a* " ,,	" *c* " ,,	48·5	$\chi_a - \chi_b = 15{\cdot}0$	
		" *c* " ,,	" *a* " ,,	15·0	$\chi_c - \chi_b = 48{\cdot}5$	
		" *b* " ,,	" *c* " ,,	33·9	—	Cal. $\Delta\chi = 33{\cdot}5$.
10. β-Naphthol . . . . . 	Monoclinic $\beta = 119°{\cdot}8$	" *b* " ,,	$\theta = +\ 20°{\cdot}4$	86·0	$\chi_1 - \chi_2 = 86{\cdot}0$	
		" *a* " ,,	" *b* " axis normal to field	7·6	$\chi_1 - \chi_3 = 18{\cdot}1$	
		(001) horizontal	" *b* " axis along field	54·2	—	Cal. $\Delta\chi = 57{\cdot}4$.
11. Acenaphthene . . . . 	Orthorhombic	" *b* " axis vertical	" *a* " ,,	28·0	$\chi_a - \chi_c = 28{\cdot}0$	
		" *c* " ,,	" *b* " ,,	45·5	$\chi_b - \chi_c = 73{\cdot}5$	
		" *a* " ,,	" *b* " ,,	72·7	—	Cal. $\Delta\chi = 73{\cdot}5$.
12. Salol . . . . 	Orthorhombic	" *b* " ,,	" *a* " ,,	31·5	$\chi_a - \chi_c = 31{\cdot}5$	
		" *c* " ,,	" *b* " ,,	30·3	$\chi_b - \chi_c = 61{\cdot}8$	
		" *a* " ,,	" *b* " ,,	61·9	—	Cal. $\Delta\chi = 61{\cdot}8$.

where ρ and ρ_0 are the densities for the actual crystal and for the ideal crystal respectively and M is its molecular weight. The second term is, in general, negligible.

4. *Results.*

The results of the oscillation measurements are given in Table IV. The different columns have the same significance as the corresponding columns in Table I and do not require any explanation. One extra oscillation measurement was also made with these crystals, as a check on the accuracy of the measurement, and the results are included in the Table. The calculated value of $|\Delta\chi|$ for this suspension is given in the final column for comparison with the observed value.

The results of the measurements on absolute susceptibilities are given in Table V. The second column gives the direction along which the susceptibilities were measured, and the next column the volume susceptibility of the bath and therefore of the crystal along the above direction, in the usual unit, viz., 10^{-6} of a c.g.s. e.m.u. The fourth column gives the density of the crystal. The principal gram molecular susceptibilities can thence be calculated with the help of the data given in Table IV. The principal magnetic constants for the crystal so calculated are given in column 5. The sixth column gives the arithmetic mean of the three principal susceptibilities of the crystal and the last column the value of the susceptibility of the substance calculated from the well-known additive law of PASCAL. The constants required in this calculation were all taken from the "International Critical Tables," vol. VI.

SECTION III.—CHANGE OF SUSCEPTIBILITY OF CRYSTALS ON MELTING.

1. *Some Remarks on Measurements in the Solid State.*

Before proceeding to discuss the results on organic crystals, described in the foregoing section, we may give here an account of some experiments on the change of susceptibilities of crystals on melting. In a well-known paper OXLEY* has given measurements of this change for a number of organic crystals. He finds that, in general, the susceptibility in the solid state is greater than that for the fused substance. The difference is usually of the order of 5 per cent; in exceptional cases, however, it is much higher, as, for example, in nitrobenzene, where it is 13 per cent. The value for the solid state in OXLEY's experiment refers to the substance as obtained by solidifying the molten liquid in a glass bulb; the substance would naturally be in the form of micro-crystals. The question arises how far the orientations of such micro-crystals, when placed in a magnetic field can be assumed to be random. Especially in crystals like naphthalene, which are markedly anisotropic—the extreme values for this crystal are in the ratio of 4 : 1—there will be a strong orientative couple acting on the micro-crystals. Even a small rotation of the crystals under the influence of this couple will give a value for the susceptibility of the aggregate which will be appreciably higher than the mean value

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* 'Phil. Trans.,' A, vol. 214, p. 109 (1914).

TABLE V.

Crystal.	Direction along which susceptibility was measured.	Vol. susceptibility.	ρ	Principal gm. mol. susceptibilities.	Mean susceptibility.	PASCAL'S additive value.
1. Naphthalene	⊥ to (001)	—0·461	1·081	χ_1 = — 39·4	— 89·8	— 89·5
				χ_2 = — 161·4		
				χ_3 = — 68·7		
				ψ = + 12·0°		
2. Anthracene	Along χ_1 — axis	—0·320	1·24	χ_1 = — 45·9	—123·7	—123·9
	⊥ to (001)	—0·578		χ_2 = — 233·2		
	Along χ_3 — axis	—0·641		χ_3 = — 91·9		
				ψ = + 8·0°		
3. Biphenyl	Along χ_1 — axis	—0·466	1·132	χ_1 = — 63·4	—102·9	—104·3
				χ_2 = — 146·5		
				χ_3 = — 98·9		
				ψ = + 20·1°		
4. Dibenzyl	,, ,,	—0·540	1·086	χ_1 = — 90·5	—127·7	—128·0
				χ_2 = — 173·6		
				χ_3 = — 118·9		
				ψ = + 83·9°		
5. Stilbene	,, ,,	—0·626	1·155	χ_1 = — 97·4	—116·0	—116·7
		—0·605	1·124	χ_2 = — 154·0		
				χ_3 = — 96·6		
				ψ = — 65·9°		
6. Benzophenone . . .	Along "*a*" axis	—0·583	1·206	χ_a = — 88·0	—108·6	—108·6
				χ_b = — 88·6		
				χ_c = — 149·3		
7. Benzil	Along trig. axis	—0·474	1·244	$\chi_{\parallel}$ = — 80·0	—110·4	—112·9
				$\chi_{\perp}$ = — 125·6		
8. Azobenzene	Along χ_1 — axis	—0·576	1·198	χ_1 = — 87·5	—100·3	—113·6
				χ_2 = — 130·2		
				χ_3 = — 83·1		
				ψ = — 65·6°		
9. Hydrazobenzene . .	Along "*c*" axis	—0·524	1·179	χ_a = — 115·4	—109·2	—121·3
				χ_b = — 130·4		
				χ_c = — 81·9		
10. β-Naphthol	Along χ_1 — axis	—0·546	1·263	χ_1 = — 62·3	— 97·0	— 96·1
				χ_2 = — 148·3		
				χ_3 = — 80·4		
				ψ = + 9·4°		
11. Acenaphthene . . .	Along "*b*" axis	—0·557	1·191	χ_a = — 117·6	—111·8	—107·4
				χ_b = — 72·1		
				χ_c = — 145·6		
12. Salol	,, ,,	—0·551	1·299	χ_a = — 121·1	—121·5	—122·9
				χ_b = — 90·8		
				χ_c = — 152·6		

The figures given in the last two columns of the Table agree in general. Azobenzene and hydrazobenzene are, however, striking exceptions.

for a single crystal. Hence, instead of comparing the susceptibility of the fused substance with that of the solidified micro-crystals, it was considered preferable to compare it with the mean of the three principal susceptibilities for a single crystal. Naphthalene and benzophenone were chosen for these measurements.

2. *Susceptibility of Fused Crystals.*

The susceptibility of the molten substance was compared with that of water by a modified Quincke method. Since a similar arrangement has been described in a recent paper by RANGANADHAM* we refer to this paper for the details of the arrangement. The principle of the method is as follows. The two liquids whose susceptibilities are to be compared are contained in two similar U-tubes. One limb of each tube is of small bore and lies in a uniform magnetic field, while the other, which lies outside the field, is of much larger diameter. The levels of the liquid menisci in the two narrow tubes are adjusted so as to be in the centre of the magnetic field. When the field is removed, the liquid menisci which were originally depressed will move up. The positions of the menisci both when the field is on and when it is removed, are photographed on the same plate with a camera having a large magnification—about 20 times. Since the images of the menisci are sharp lines, the changes of level of the two liquids which occur when the field is removed, can be compared accurately.

It can easily be shown that the above change of level, say, h, in the narrow tube when a field H is removed, is given by

$$h = \frac{H^2}{2g} \cdot \left(\frac{S}{S + \sigma}\right) \cdot \frac{k}{\rho} \quad ,$$

where k is the volume susceptibility of the liquid, ρ is its density, g is the acceleration due to gravity, and σ and S are respectively the cross-sectional areas of the inner (*i.e.*, the narrow limb inside the magnetic field) and the outer limbs of the U-tube. Since the two U-tubes are of identical dimensions,† the ratio of the changes in level of the two liquids gives directly the ratio of their *specific* susceptibilities. As the temperature co-efficient of the specific susceptibility of a diamagnetic substance is very small (if not zero) any small uncertainty in the measurement of the temperatures of the two liquids will have no influence on the ratio.

3. *Results.*

Naphthalene (m.p. = 80·1° C.). The two U-tubes were wound separately with nichrome wires, so that each could be raised to any desired temperature. The tube containing molten naphthalene was kept exhausted, and was at 94° C. The other U-tube contained water at 32° C., and was kept exposed to air through a small side tap.

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* 'Ind. J. Phys.,' vol. 6, p. 421 (1931).

† S being much greater than σ—actually about 60 times—any small difference in the diameters of the two U-tubes will not affect the results.

The ratio of the rise of molten naphthalene to that of water when the field was removed was 0·928, whence the susceptibility of the former comes out on calculation as $-0 \cdot 694 \times 10^{-6}$ per gm. In another series of measurements molten naphthalene at 100° C. was first compared with that of nitrobenzene at 90° C.; the latter was, in its turn, compared with nitrobenzene at 30° C., which was finally compared with water at the same temperature. All the tubes were kept exhausted. The experimental values for the ratios were 1·418, 0·976, and 0·707, respectively. Hence, the susceptibility of molten naphthalene at 100° C. $= -0 \cdot 704 \times 10^{-6}$, which agrees within the limits of experimental error with the previous value. Their mean corresponds to

$$\chi_{\text{liq.}} = -89 \cdot 5 \times 10^{-6} \text{ per gm. mol. at about } 100^\circ \text{ C.}$$

This value may be compared with the mean value for the crystal $[= \frac{1}{3}(\chi_1 + \chi_2 + \chi_3)]$

$$\chi_{\text{crys.}} = -89 \cdot 8 \times 10^{-6} \text{ per gm. mol. at about } 30^\circ \text{ C.}$$

The difference is less than one-half of one per cent.

Benzophenone (m.p. = 48·5° C.). The specific susceptibility of the molten substance at 50° C. was 0·852 times that of water at 30° C., and is therefore equal to $-0 \cdot 612 \times 10^{-6}$ per gm. This corresponds to $-111 \cdot 5 \times 10^{-6}$ per gm. mol., whereas the mean gm. mol. susceptibility for the crystal $= -108 \cdot 6 \times 10^{-6}$ which is, numerically, about 2·5 per cent. less than for the liquid.

OXLEY's value for this change is 6 per cent., which is much higher.

It is known that benzophenone possesses a large dipole moment, viz., $2 \cdot 5 \times 10^{-18}$ e.s.u., whereas naphthalene is non-polar. It would therefore be interesting to determine whether the difference in behaviour of benzophenone and naphthalene, as regards the change of susceptibility on melting, is typical of polar and non-polar molecules respectively. Experiments on other compounds which are in progress in the author's laboratory may be expected to throw light on this point.

SECTION IV.—MAGNETIC ANALYSIS OF MOLECULAR ORIENTATIONS IN CRYSTALS.

We now proceed to discuss the magnetic constants of organic crystals in relation to the orientations of the molecules in their unit cells. Among the crystals studied by us, naphthalene, anthracene, biphenyl and dibenzyl are of special interest from this point of view, since their unit cells contain only two molecules.

1. *Naphthalene.*

Naphthalene crystal belongs to the monoclinic prismatic class. Its structure has been studied by X-ray methods by BRAGG* and ROBERTSON,† and more recently by BANERJEE (*loc. cit.*). The unit cell contains two molecules, for which BANERJEE suggests

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[*] "X-Rays and Crystal Structure," p. 233 (1924).

[†] 'Proc. Roy. Soc.,' A, vol. 125, p. 546 (1929).

a plane structure. As regards their orientations, he finds, in the first place, that both the molecules in the unit cell have their lengths (*i.e.*, the lines joining the centres of the constituent benzene rings) in the (010) plane making an angle of 12° with the "*c*" axis in the obtuse angle β. Since from direct considerations of symmetry the long axis of the naphthalene molecule must be one of its magnetic axes (the other two being along its breadth in the plane of the benzene rings and along the normal to the plane of the rings, respectively) we should expect the above direction in the crystal to be one of the magnetic axes of the crystal. This is indeed so, because our measurements gave for the direction of the χ_1-axis $\psi = +12\cdot0°$, which is precisely the angle deduced by BANERJEE from his X-ray measurements.*

Having fixed the directions of the *lengths* of the molecules, we next consider the orientations of their *planes*. BANERJEE finds that they are inclined at $+65°$ and $-65°$ respectively, to the (010) plane. In order to deduce the value of this angle from the magnetic measurements, a knowledge of the principal susceptibilities of the individual molecules, say, K_1, K_2 and K_3 along their lengths, their breadths and the normals to their planes, respectively, is necessary. A calculation of these constants has been made by one of us from direct considerations of the structure of the molecule, by a method which has recently been used with success for the benzene molecule.† The susceptibility normal to the plane of the naphthalene molecule comes out on this calculation to be about four times as much as for directions in the plane.‡ Correlating this result with the known values for χ_1, χ_2 and χ_3 for the crystal the orientations of the molecules can easily be calculated.

Magnetic Constants of the Naphthalene Molecule.—However, in view of the accurate information, already available from X-ray measurements, regarding the molecular orientations in the crystal, it will be more logical to use this to calculate the precise values of the magnetic constants of the molecules, rather than to determine their orientations from their magnetic constants deduced from structural considerations, which at best must be considered as only approximate. We directly proceed to do so. The calculations are simple since we have the following relations :—

$$\chi_1 = K_1$$

$$\chi_2 = K_2 \cos^2 65° + K_3 \sin^2 65°$$

$$\chi_3 = K_2 \sin^2 65° + K_3 \cos^2 65°.$$

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* It may be remarked here that the value of this angle given by the magnetic method is more accurate than the X-ray value, since the former is obtained by a direct measurement of the orientation of the crystal when suitably suspended in a magnetic field. It is, however, a matter for satisfaction that the values given by the two methods agree so closely.

† RAMAN and KRISHNAN, 'C. R. Acad. Sci. Paris,' vol. 184, p. 449 (1927).

‡ The calculations have not been published. The results are quoted by BHAGAVANTAM, *loc. cit.*, p. 546.

Using the known values of the χ's for the crystal, we obtain for the principal susceptibilities of the *molecule*[*]

$$K_1 = -39\cdot4$$

$$K_2 = -43\cdot0$$

and

$$K_3 = -187\cdot2.$$

Thus, the plane of the naphthalene molecule is almost a plane of magnetic symmetry. Also the susceptibility along the normal to the plane is about 4½ times as much as for directions in the plane; this confirms the results of our calculations from its structure, referred to in an earlier paragraph.

Optical Constants of the Naphthalene Molecule.—Since any information regarding the physical constants of individual molecules is of great interest, we remark in passing that the above data for the magnetic constants of the naphthalene molecule enable us to calculate its optical constants also; other data necessary for the calculation are (1) refractivity, (2) depolarisation factor of light-scattering, and (3) Cotton-Mouton constant. The calculation[†] gives for the polarisabilities of the molecule along its length, its breadth and normal to its plane the values $26\cdot7 \times 10^{-24}$, $14\cdot2 \times 10^{-24}$ and $11\cdot5 \times 10^{-24}$ respectively, for the sodium line.

These values when taken together with the known orientations of the molecules in the crystal would suggest for the plane of its optic axes (010). This agrees with observation.

2. *Anthracene.*

We next consider anthracene. This crystal also belongs to the monoclinic prismatic class, and there are two molecules in the unit cell. On the basis of his X-ray measurements Banerjee finds that the lengths of both the molecules (*i.e.*, the lines joining the centres of the three component benzene rings) lie in the (010) plane in the obtuse angle β at 9° to the "*c*" axis. The planes of the molecules, as in the case of naphthalene, are inclined at + 65° and − 65° to the (010) plane.

The above inclination of the long axes of the molecules to the "*c*" axis, viz., + 9°, is directly confirmed by our magnetic measurements, since $\psi = +8\cdot0°$. Concerning the orientations of the molecular planes, we will adopt, as we did for naphthalene, the results of the X-ray measurements and calculate the molecular magnetic constants. We thus obtain for the principal susceptibilities of the molecule along its length, along its breadth and along the normal to its plane respectively, the values

$$K_1 = -45\cdot9$$

$$K_2 = -52\cdot7$$

$$K_3 = -272\cdot5.$$

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[*] The K's, just like the χ's, refer to one gm. mol. and are also expressed in the same unit, viz., 10^{-6} of a c.g.s. electromagnetic unit.

[†] The details of the calculation will be published elsewhere.

Here, also, the normal to the plane of the molecule is practically an axis of magnetic symmetry, in spite of the large geometric asymmetry in the plane.

3. *Benzene, Naphthalene and Anthracene.*

Knowing now the molecular magnetic constants of naphthalene and anthracene, it is desirable to calculate the constants for benzene in order to be able to compare the values for the three molecules. The necessary X-ray investigations, as well as magnetic measurements on crystalline benzene, are not available. The constants for benzene can, however, be calculated from its Cotton-Mouton constant and the depolarisation factor of its light-scattering, since we may without appreciable error assume the molecule to possess an axis of symmetry. Taking the Cotton-Mouton constant for liquid benzene at 18° C. as $5\cdot90 \times 10^{-13}$ and the depolarisation factor for transverse scattering of unpolarised incident light at the same temperature as $0\cdot417$, we get for the principal susceptibilities of the molecule, viz., K_1 and K_2 in the plane of the ring and K_3 normal to it, the values

$$K_1 = K_2 = -37\cdot3$$
$$K_3 = -91\cdot2.$$

The values for the three molecules are collected in Table VI.

TABLE VI.

Molecule	K_1	K_2	K_3	Mean K
Benzene	37·3	37·3	91·2	55·3
Naphthalene . . .	39·4	43·0	187·2	89·8
Anthracene	45·9	52·7	272·5	123·7

It is remarkable that as we proceed from benzene to naphthalene and from naphthalene to anthracene, the numerical increases in diamagnetic susceptibility are confined practically to one direction, viz., normal to the plane of the benzene rings.*

4. *Biphenyl and Dibenzyl.*

We next consider biphenyl and dibenzyl, which, in view of the fact that the X-ray measurements at present available are not sufficiently precise to determine the

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* In the previous article, we have assumed the orientations of anthracene molecules given by X-ray measurements and calculated the K's. On the other hand, if complete X-ray analysis of the crystal had not been made, we could still have deduced the K's either from structural considerations, as for naphthalene, or preferably from the relation

$$K_i^{C_{14}H_{10}} - K_i^{C_{10}H_8} = K_i^{C_{10}H_8} - K_i^{C_6H_6}, \quad i = 1, 2, 3,$$

and thence determined solely from magnetic data the correct orientations of molecules in the unit cell.

orientations of the molecules in their unit cells, offer good scope for analysis by the magnetic method.

Biphenyl.—Biphenyl also belongs to the monoclinic prismatic class. Its structure has been investigated by X-ray methods by HENGSTENBERG and MARK* and independently by CLARK and PICKETT.† They assign it to the space group C_{2h}^5. Its unit cell contains only two molecules. Whether one takes the benzene rings in biphenyl to have a puckered structure, as HENGSTENBERG and MARK have done, or to have a plane structure by analogy with the ring in hexamethyl benzene, analysed by Mrs. LONSDALE,‡ and the rings in naphthalene and anthracene, according to BANERJEE, it is possible to satisfy the symmetry requirements of the molecule in the crystal. In either case, the planes of the two component benzene rings of any given molecule—their mean planes in the former assumption, and their actual planes in the latter—have to be orientated in the same manner. We proceed to locate the orientations of these planes,§ without making any attempt to determine whether the planes are puckered or not. *We will only assume that the benzene rings in biphenyl have the same structure as in the benzene molecule.*

In the first place, we have to calculate the magnetic constants of the biphenyl molecule from the known constants for benzene. The mean gram molecular susceptibility of biphenyl $= -102\cdot9$, which is numerically less than twice the susceptibility of the benzene molecule by $7\cdot7$. This difference is clearly the contribution from the two hydrogen atoms which have been dropped out from the benzene rings in the formation of the biphenyl molecule. As a first approximation, we assume that the above numerical diminution in susceptibility, due to dropping the H^- atoms, is the same along the three principal directions of the molecule.|| We then obtain for the principal susceptibilities of the biphenyl molecule, say, K_1 and K_2 along its length (*i.e.*, the line joining the C-atoms 1 and 4 or 4′ and 1′) and breadth respectively in the plane of the benzene rings, and K_3 along the normal to the plane, the values

$$K_1 = K_2 = - \quad 66\cdot9$$

$$K_3 = -174\cdot7.$$

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* 'Z. Krystallog,' vol. 70, p. 283 (1929).

† 'J. Amer. Chem. Soc.,' vol. 53, p. 167 (1931).

‡ 'Proc. Roy. Soc.,' A, vol. 123, p. 494 (1929).

§ The "mean plane" of the puckered benzene ring is taken by HENGSTENBERG and MARK to be the plane which contains the C-atoms, 2, 3, 5, 6, in the usual notation, the other two C-atoms, viz., 1 and 4, being one on either side of this plane. On the other hand, the "mean plane," referred to in this paper, does not contain any of the C-atoms; three of them, 1, 3, 5 lie on one side of this plane and the remaining three, 2, 4, 6, lie on the other side of it at the same distance.

|| This assumption is probably not far from the truth; even if it is, since this contribution is small compared with the susceptibility of the whole molecule (only about 7½ per cent), the particular manner in which it is distributed among the three directions is a matter of little consequence.

On the other hand, the values for the crystal are

$$\left.\begin{aligned}\chi_1 &= -\ \ 63\cdot4\\ \chi_2 &= -146\cdot5\\ \chi_3 &= -\ \ 98\cdot9\end{aligned}\right\};\ \psi = +20\cdot1^\circ.$$

A correlation of the two sets of constants given above gives the following orientations for the two molecules in the unit cell of biphenyl. Let both the molecules have their planes parallel to (100) and their lengths along the " *c* " axis. In order to bring the molecules to their actual orientations, we have to give them the following rotations :

Firstly, a rotation about the " *c* " axis of one of the molecules through an angle λ and of the other through $-\lambda$;

Secondly, a rotation of both the molecules about the " *b* " axis through an angle of μ, the positive direction of the rotation being defined as being from the " *c* " axis to the " *a* " axis through the obtuse angle β ; and

Thirdly, a rotation of the two molecules through angles $+\nu$ and $-\nu$ respectively, about the normal to the plane which contains the " *b* " axis and the direction of the lengths of the molecules obtaining after rotation (2) has been performed.

Evidently

$$\mu = \psi = +20\cdot1^\circ.$$

λ and ν can be evaluated from the following relations :*

$$\begin{aligned}\chi_1 &= K_1\cos^2\nu + (K_2\cos^2\lambda + K_3\sin^2\lambda)\sin^2\nu\\ \chi_2 &= K_2\sin^2\lambda + K_3\cos^2\lambda\\ \chi_3 &= K_1\sin^2\nu + (K_2\cos^2\lambda + K_3\sin^2\lambda)\cos^2\nu.\end{aligned}$$

Solving them, we get

$$\lambda = 31^\circ$$

$$\nu = 0.$$

We thus find that the lengths of the molecules lie in the (010) plane in the obtuse angle β at 20·1° to the " *c* " axis, while the planes of the molecules are inclined at plus and minus 31° respectively to the " *b* " axis.

It would be interesting to confirm by further X-ray measurements on biphenyl the above assignment of orientations of the molecules in its unit cell.†

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* Since we have already assumed that $\chi_1+\chi_2+\chi_3 = K_1+K_2+K_3$, only two of these relations are independent.

† [*Note added November* 7, 1932.—Further X-ray investigations on this crystal have recently been made by Mr. J. DHAR ('Ind. J. Phys.,' vol. 7, p. 43 (1932)), and they confirm the results of our magnetic analysis. In the first place Mr. DHAR finds that the lengths of the molecules lie in the (010) plane, in the obtuse angle β, at 20° to the "*c*" axis; our value for the angle is 20·1°. As regards the planes of the molecules, he finds that they are inclined at plus and minus 32° to the " *b* " axis; this is in close agreement with the values plus and minus 31° for this angle calculated by us from the magnetic data.]

Dibenzyl.—Dibenzyl also crystallizes in the monoclinic prismatic class, and has been assigned by HENGSTENBERG and MARK to the space group C_{2h}^5. The molecule is found to have a centre of symmetry, the unit cell containing two molecules.

The magnetic constants for the molecule can be calculated in the same manner as for biphenyl. In the same notation,

$$K_1 = K_2 = -91 \cdot 7$$

$$K_3 = -199 \cdot 5.$$

Correlating these with the values for the crystal, we obtain for the angular parameters λ, μ and ν that define the orientations of the molecules in the unit cell, again using the same notation as for biphenyl, the values

$$\lambda = 30^\circ$$

$$\mu = +83 \cdot 9^\circ$$

$$\nu = 0.$$

On comparing these values with those for biphenyl, we find that in both the crystals the molecular planes are inclined at about 30° to the " b " axis; also the lengths of the molecules lie in both cases in the (010) plane in the obtuse angle β. There is this essential difference, however, between the two crystals. Whereas in biphenyl the molecular lengths are inclined at 20·1° to the " c " axis, in dibenzyl they are almost normal to the "c" axis (actually at 83·9°). This difference is reflected in the dimensions of the unit cell, as we should expect; whereas the " c " axis is the longest axis for biphenyl ($a = 8 \cdot 22$ A, $b = 5 \cdot 69$ A, $c = 9 \cdot 50$ A), for dibenzyl the longest axis is the " a " axis, since $a = 12 \cdot 82$ A, $b = 6 \cdot 18$ A and $c = 7 \cdot 74$ A.

The optical observations on this crystal, viz., that the optic axes lie in (010) and that the bisectrix lies in the acute angle β, making a small angle with the " c " axis, are in agreement with the molecular orientations suggested here.

Before concluding this article, it may not be out of place to remark that the centro-symmetric structure of the molecules of biphenyl and dibenzyl points to a zero dipole moment for these molecules. This is in conformity with observation.*

5. *Azobenzene and Stilbene.*

We will first consider azobenzene. This crystal has recently been analysed by X-ray methods by PRASAD.† It is assigned to the space group C_{2h}^5 in the monoclinic prismatic class, with four molecules in the unit cell, whose dimensions are

$$a = 12 \cdot 65 \text{ A}, b = 6 \cdot 06 \text{ A} \quad c = 15 \cdot 60 \text{ A}; \quad \beta = 114 \cdot 4^\circ.$$

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* W. LAUTSCH, 'Z. Phys. Chem.,' B, vol. 1, p. 115 (1928).

† 'Phil. Mag.,' vol. 10, p. 306 (1930).

" A remarkable feature of this crystal " according to PRASAD " is the nearly complete symmetry about the (20 $\bar{1}$) plane both in respect to the geometrical relations and to the intensities of reflection by corresponding planes." Using the above dimensions for the unit cell for calculation, we find that the (20 $\bar{1}$) plane is nearly normal to the " *a* " axis. We should therefore expect the normal to the (001) plane to be an axis of magnetic symmetry. This is actually so, because, in the first place, one of the principal magnetic axes, viz., the χ_2-axis, lies along that direction and, secondly, χ_1 has nearly the same value as χ_3 ; the values are

$$\chi_2 = -130 \cdot 2$$

$$\chi_1 = -87 \cdot 5$$

$$\chi_3 = -83 \cdot 1.$$

Since the number of molecules in the unit cell is 4, which is the maximum number necessary to complete the symmetry of the class, it is presumable that the molecule itself has no element of symmetry. This result appears surprising in view of the centro-symmetry of the biphenyl and dibenzyl molecules, but is supported by the magnetic observations. Suppose we assume that azobenzene has a structure similar to that of biphenyl or dibenzyl with a centre of symmetry. The molecular magnetic constants would then be

$$K_1 = K_2 = -64$$

$$K_3 = -172.$$

Correlating these values with those for the crystal, we get for the angular parameters λ, μ, ν in our usual notation

$$\lambda = 39^\circ$$

$$\mu = -65 \cdot 6^\circ$$

$$\nu = 48^\circ.$$

These values place the lengths of the molecules in the (001) plane, at an angle of 48° to the " *a* " axis and therefore at 42° to the " *b* " axis ; *i.e.*, the long axes of the molecules lie nearer to the " *b* " axis than to the " *a* " axis. The dimensions of the unit cell, however, show that this conclusion cannot be correct. Thus, we find that the lengths of the two component benzene rings of the molecule—by the length of the ring we mean the line joining the C-atoms 4 and 1, or 1′ and 4′—cannot lie along the same line.

Also the *planes* of the two component benzene rings cannot be parallel to each other since in that case the value of χ_1 ought to be equal to − 64, whereas it is actually equal to − 87·5.

Thus solely from the magnetic data and the known axial ratio $a : b$, we can conclude, regarding the benzene rings of the azobenzene molecule, that they cannot have either their lengths parallel to each other, or their planes parallel to each other. Hence the molecule has no element of symmetry—a conclusion in conformity with the X-ray evidence.

If we assume, not unreasonably, that the two halves of the azobenzene molecule are identical and that the greatest length of the molecule lies along the " *a* " axis, the magnetic constants suggest that the planes of the two benzene rings of the molecule are inclined at + 39° and − 39°, respectively, to the (001) plane, and that the lengths of the rings, as defined above, lie in the (001) plane at about + 48° and − 48° to the " *a* " axis. Thus we get an estimate of the " twist " and the " folding up " of the two benzene rings of the azobenzene molecule in the crystal.

The weak birefringence of the azobenzene crystal observed by BHAGAVANTAM* is not difficult to understand on the basis of the above structure.

Coming to stilbene, which is also monoclinic and belongs to the C_{2h}^5 prismatic class, it is very similar in its crystal structure and in its magnetic properties to azobenzene. The existence of a pseudo-rhombic symmetry (just as in azobenzene) has been remarked by HENGSTENBERG and MARK)†; magnetically, the normal to the (001) plane (which is along the χ_2 axis) is an axis of symmetry.

This molecule also has no element of symmetry. The orientations of the two component benzene rings of the molecule with respect to each other, as also with respect to the crystallographic axes, can be estimated in the same manner as for azobenzene.

6. β-*Naphthol.*

Next we take β-naphthol. It belongs to the monoclinic prismatic class. The crystal has been analysed by BRAGG‡ and is found to contain 4 molecules in the unit cell.

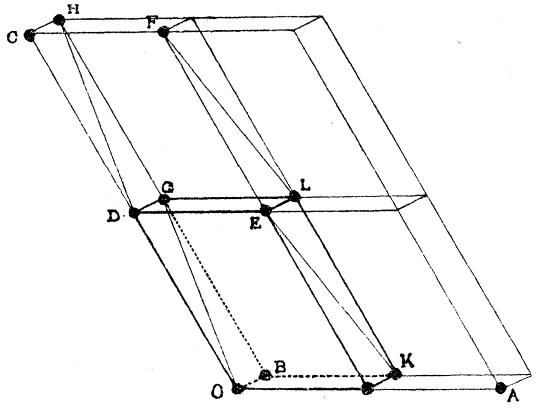

FIG. 1.—Unit cell of β-naphthol.

Taking the molecules at O, D, K and L, fig. 1, as belonging to the unit cell under consideration, their lengths are placed by BRAGG along the diagonals OG, DH, EK and

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* 'Ind. J. Phys.,' vol. 4, p. 1 (1929).

† *Loc. cit.*, footnote on p. 294.

‡ 'Proc. Phys. Soc., Lond.,' vol. 34, p. 45 (1922).

FL respectively. As regards the magnetic evidence for their orientations, the constants for the crystal are

$$\left.\begin{aligned}\chi_1 &= -\ \ 62\cdot3\\ \chi_2 &= -148\cdot3\\ \chi_3 &= -\ \ 80\cdot4\end{aligned}\right\};\quad \Psi = +9\cdot4^{\circ}.$$

Those for the molecule can be calculated from the known constants for naphthalene on the assumption that the small numerical increase in susceptibility of the molecule when we pass from naphthalene to β-naphthol, due to the replacing of a H-atom by the OH-group, takes place isotropically. Then the molecular susceptibilities along the length, breadth and the normal to the plane are, respectively,

$$K_1 = -\ \ 46\cdot6$$

$$K_2 = -\ \ 50\cdot2$$

$$K_3 = -\ 194\cdot4.$$

A correlation of the two sets of constants gives the following orientations for the molecules. Starting with all the molecules in the unit cell, having their planes parallel to (100) and their lengths along the "c" axis, we have, to give them the following rotations in order to bring them to their actual orientations in the crystal :—

(1) about the "c" axis : half the molecules through an angle λ and the other half through an angle $-\lambda$;

(2) about the "b" axis : all the molecules through an angle μ (the positive direction of μ being defined as before) ;

(3) about the normal to the plane containing the "b" axis and the directions of the lengths of the molecules obtaining after rotation (2) has been performed : half the molecules through an angle ν and the other half through $-\nu$.

The choice of the particular molecules for the positive and for the negative rotations in (1) and (3) is determined by the requirements of the symmetry of the crystal.

Calculation gives

$$\lambda = \ 34^{\circ}$$

$$\mu = +9\cdot4^{\circ}$$

$$\nu = \ 34^{\circ}.$$

7. *Acenaphthene.*

The crystal belongs to the orthorhombic class, having the fullest symmetry of that class. Its structure has been analysed by BRAGG.* There are 4 molecules in the unit cell. BRAGG provisionally places the planes of all the molecules in the (001) plane,

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* 'Proc. Phys. Soc. Lond.,' vol. 34, p. 45 (1922).

their lengths making angles of about 30½° with the " *b* " axis on either side. (See fig. 2. The positions of the molecules in the unit cell are denoted in the figure by dots, and the directions of the lengths of the molecules by arrows.)

Magnetically, if we assume with BRAGG, that the lengths of the molecules lie in (001) plane, it is found on calculation that they make angles of plus and minus 24° with the " *b* " axis, while the molecular planes are inclined at about 41½° to the (001) plane.

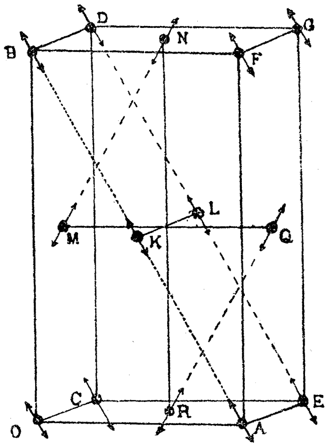

FIG. 2.—Unit cell of acenaphthene.

The known optical properties of the crystal are consistent with the orientations proposed here. Just as in the case of naphthalene, the optical polarisability of the acenaphthene molecule should be a maximum along its length and a minimum along the normal to its plane. From the molecular orientations, given in the previous paragraph, we should therefore expect the optical polarisability of the crystal to be a maximum along the " *b* " axis and a minimum along the " *c* " axis. This is actually the case, since the crystal shows a positive birefringence, the (100) plane being the axial plane and the " *b* " axis being the acute bisectrix.

8. *Conclusion.*

From what has been said in the previous pages it is clear that in favourable cases, *e.g.*, biphenyl and dibenzyl, it is possible from magne-crystallic measurements to determine the precise orientations of the molecules in the unit cell; in less favourable cases, *e.g.*, naphthalene and anthracene, some of the angular parameters defining the orientations can be so derived; even in complicated cases like stilbene and azobenzene, where it is not possible to obtain a unique solution, the magnetic data throw considerable light on the question, which would help us at least to decide between alternative orientations suggested by X-ray methods. In any case, it is obvious that no structure proposed by X-ray methods can be considered acceptable which cannot satisfactorily explain the observed magnetic properties of the crystal. Thus the magnetic method of analysis of molecular orientations in crystals promises to be a useful supplement to X-ray methods of analysis.

We have much pleasure in thanking the Government of Bengal and the University of Dacca for the grant of Research Scholarships to the two junior authors which made it possible for them to collaborate in this work.

Summary.

The paper describes a convenient method of determining the magnetic anisotropy of crystals by oscillating them about different axes in a uniform magnetic field. Amongst the inorganic crystals studied by this method were quartz, calcite, aragonite, strontianite, witherite, sodium and potassium nitrates, potassium chlorate, barite, celestite, anhydrite, gypsum and sulphur. It may be noted that while the nitrates and carbonates exhibit a large anisotropy, the sulphates are more or less completely isotropic.

The organic crystals investigated were naphthalene, anthracene, β-naphthol, acenaphthene, biphenyl, dibenzyl, benzophenone, benzil, azobenzene, hydrazobenzene and salol. In most of the above crystals the mean of the three observed principal susceptibilities agrees well with the value calculated for the substance from the well-known additive relations of Pascal. Azobenzene and hydrazobenzene are, however, exceptions in this respect, as the additive value is numerically much higher than the actual mean value for the crystal.

On comparing the mean susceptibilities of naphthalene and benzophenone crystals with the values obtained for these two substances in the fused state, it is found that while the susceptibility of naphthalene remains practically unchanged, benzophenone shows a diminution of $2\frac{1}{2}$ per cent on melting. A possible connection between the dipole character of the molecule and such a change is indicated.

A correlation of the principal magnetic constants of the crystal with those of the individual molecules constituting it may be effected with the help of the data on magnetic birefringence and light-scattering. This offers a useful method of determining the orientations of the molecules in the crystal lattice, and is found to work very satisfactorily, leading to accurate results, two typical instances being biphenyl and dibenzyl.