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INTRODUCTION

The characteristic magnetic properties of non-cubic crystals were anticipated by Poisson[1] in his papers on the theory of magnetism, as early as 1821 The actual discovery of magne-crystallic action was made by Plucker [2 3] (1847-1851) who observed that in the case of anisotropic crystals the attractive or repulsive force acting upon them when placed in a strong non-uniform magnetic field was different along different directions in the crystal Such crystals also showed a tendency to take up a preferred orientation when freely suspended in a magnetic field Almost simultaneously with Plucker's discovery, Faraday[4] and and Tyndall[5] in a series of investigations established the generality of the phenomenon to which the name "magne-crystallic action" was given The theory of this effect was first developed by Thompson[6] (1851) based on the earlier work of Poisson which required only a slight extension

Following on the early work of Plucker, Faraday and Tyndall, a large amount of experimental work of a more or less qualitative character on the dia- and para-magnetic anisotropy of crystals was done by Grailich and Lang[7] (1858) But the subject did not receive much attention for a long time after, and the only important experimental work in the field until very recent times has been that of Stenger[8] (1883-1888), Konig[9] (1887), Finke[10] (1910) and Voigt and Kinoshita[11] (1907) The reason for this was that not only had very accurate methods of magnetic measurements been not developed, but also precise information regarding the atomic and molecular structure of crystals was then unknown, and an interpretation of the results relating magnetism to atomic and crystalline structure was not possible In recent years, due to great advances in physics in various directions, especially as regards our knowledge of the nature of magnetism and its origin in the atomic and molecular structure of matter and in view of the great achievements in the field of X-ray analysis of crystals, it has been increasingly realized that an exact knowledge of the magnetic properties of crystals can throw much useful light on the relation between magnetism and crystal structure This realization has been responsible for many developments in the subject, both theoretical and experimental

For realising the significance of magne-crystallic phenomena in dia- and para-magnetic crystals, we have in the first place to know the nature of diamagnetism and paramagnetism Secondly, we have to investigate how in crystalline solids, which consist of an aggregation of atoms and molecules in regular array bound together by electric forces, dia- and para-magnetism become *directional* properties, conditioned by crystal structure and the electrostatic fields which act upon the atoms in the crystal lattice Significant progress has been made in all these directions in recent years and this will be briefly reviewed in the following pages in so far as it concerns the author's work

Diamagnetism and the Diamagnetic Anisotropy of Crystals

The first successful attempt at an electronic theory of diamagnetism was made by Langevin[12] (1905) The characteristic behaviour of a diamagnetic is that when placed in a non-uniform magnetic field, it tends to move from the stronger towards the feebler parts of the field, and Weber[13] (1852) had tried to explain this by assuming the existence of " electric fluids which can be set up in molecular streaming motion " But since the development of the electron theory at the hands of Lorentz, a more precise significance had to be attached to " the streaming Amperean currents " According to Langevin's theory, the electrons are supposed to move in closed circuits in each molecule or ion giving rise to effects similar to those produced by current circuits In diamagnetics, the molecules do not possess any resultant magnetic moment due to the electrons going round in orbits, and the application of a magnetic field to the electronic system of the molecule, in a state of equilibrium under the action of a centre of force, is equivalent, according to a theorem by or, to giving it an angular velocity of precession The ssional motion of the electronic orbits gives rise to dia- etism The atomic diamagnetic susceptibility of a substance en by the expression

$$\chi_{at} = -\left(\frac{e^2}{6mc^2}\right)\sum_N r^2$$

$$= -2.832 \times 10^{10} \sum_N r^2$$

there are N electrons in the atom This result obtained from cal considerations does not require any modification even ding to quantum mechanics

The problem of calculating the diamagnetic susceptibility of tom from its electronic structure reduces to estimating the value ^{2} This, however, is rather difficult owing to the complex

cter of atomic systems and, at best, theoretical computations ive only approximate values of the magnitude of the observed ptibilities For atoms containing several electrons an estimate e contribution to the diamagnetic susceptibility by any of electrons is possible by introducing appropriate screening nts, which will give the *effective* nuclear charge (The actual s of nuclear charge cannot be used in the calculations owing to fluence of the other electrons) Pauling[14] (1927) has made ations for many simple atoms and ions More satisfactory ways nputing diamagnetic susceptibilities, introduced later, are those ner[15] (1929) based on Hartree's self-consistent field method and ater[16] (1930) employing approximate atomic wave functions led computations have been recently made by Brindley[17] (1931) ngus[18] (1932)

The above calculations are confined to spherically symmetric c systems of the simplest type, each being considered to be free n-influenced by other factors In general, external factors do ave any great influence on diamagnetism, so much so that, scal[19] showed, diamagnetism is *additive* The molecular susceptibility of any compound is related to that of its constituent atoms by the simple relation

$$\chi_m = \sum_k n_i \chi_i + \lambda$$

where n_1, n_2, n_3 are the number of atoms of susceptibilities χ_1, χ_2, χ_3 respectively and λ is a correction factor whose value depends upon the nature of the chemical bonds This additivity relation has another great significance It indicates that the state of aggregation also has got little influence on diamagnetism In almost all organic crystals, the molecule preserves its characteristic diamagnetism, which is little influenced either by the electric forces in the lattice or the mutual interaction of neighbouring induced magnetic dipoles which must be extremely feeble Before considering diamagnetism in relation to crystal structure, a brief account of the characteristic magnetic properties of crystals will be given

In the most general case there are three mutually perpendicular directions in a crystal along which the direction of the applied field coincides with the direction of magnetization These are the principal axes of magnetization in the crystal and the susceptibilities in these directions are known as the principal susceptibilities In analogy with the optical properties of crystals, the magnetization in crystals may be represented by an ellipsoid of magnetic induction In uniaxial crystals the ellipsoid becomes a spheroid, and in cubic crystals it is a sphere The axes of the ellipsoid of induction are the directions of the principal susceptibilities of the crystal The principal volume susceptibilities are generally denoted by κ_1, κ_2 and κ_3, and the corresponding mass susceptibilities by χ_1, χ_2 and χ_3

In triclinic crystals, χ_1, χ_2 and χ_3 are all unequal and may have any orientation with respect to the crystallographic axes In monoclinic crystals, the three principal susceptibilities are all unequal, but one of them will coincide in direction with the '*b*'-crystallographic axis In the orthorhombic system, the principal susceptibilities which are all unequal will, however, coincide in direction with the three mutually perpendicular crystallographic axes In uniaxial

ystals two of the principal susceptibilities are equal, while the third,
fering in value from the other two, will lie in the direction of the
tic axis of the crystal

The mean susceptibility of the crystal is related in the three
ncipal susceptibilities by the equation

$$\chi_{mean} = \frac{1}{3}(\chi_1 + \chi_2 + \chi_3)$$

The large diamagnetic anisotropy of benzene and other
omatic ring-shaped molecules was first clearly pointed out by Raman
l Krishnan[20] (1927) from the data of light scattering and magnetic
ible-refraction This important property at once suggested the
sibility of determining the orientation of such molecules in their
stals, and approximate determinations in the case of naphthalene
re attempted by Bhagavantam[21] (1929) Recently, the method
been established on a sure basis by the investigations of K S
shnan and his collaborators[22, 23] (1933-1935) and Lonsdale and
shnan[24] (1936) The essential idea involved is that the magnetic
sotropy of the crystal depends entirely upon the mode of arrange-
nt of the molecules in the lattice The principal susceptibilities of
crystal are obtained merely by adding tensorially the susceptibili-
of the individual molecules which compose it The results of such
ation have been worked out by Lonsdale and Krishnan[24] (1936)

It has been shown that the less symmetry the crystal possesses,
greater is the possibility of determining molecular orientations by
magnetic method In general, the principal crystal susceptibilities
oted by χ_1, χ_2 and χ_3 are related to the molecular susceptibilities
K_2 and K_3* (referred to a gm mol in each case) by the three
ations,

$$|\chi_1| = |K_1|\alpha_1^2 + |K_2|\beta_1^2 + |K_3|\gamma_1^2$$
$$|\chi_2| = |K_1|\alpha_2^2 + |K_2|\beta_2^2 + |K_3|\gamma_2^2$$
$$|\chi_3| = |K_1|\alpha_3^2 + |K_2|\beta_3^2 + |K_3|\gamma_3^2$$

re α_1, β_1, γ_1 are the direction cosines of K_1 K_2 and K_3 with respect

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*According to the usual convention, K_1 K_2 denote the principal molecular
ptibilities in the plane of flat molecules, while K_3 denotes the susceptibility
ndicular to the plane

to χ_1, etc In the case of triclinic crystals, which possess the least symmetry, the principal molecular susceptibilities must coincide with the directions of χ_1, χ_2, and χ_3 respectively and since the latter may be determined experimentally, we can directly get the values of $|K_1|$, $|K_2|$ and $|K_3|$

In the case of monoclinic crystals complications arise and no complete solution of the equations is possible for getting the molecular orientations unless such simplifications as $|K_1| \approx |K_2|$ are made, or in special cases when the molecule is plane and normal to the (010) plane, or when K_1 actually lies in the (010) plane

Again, for orthorhombic crystals, it is not practicable to deduce the orientations of the molecules, even if χ_a χ_b, and χ_c are known and $|K_1|$, $|K_2|$ and $|K_3|$ can be accurately estimated If, however, we assume $|K_1|$ and $|K_2|$ to be equal, then in the case of a plane molecule, we can locate the orientation of the molecular plane with respect to the crystallographic axes

In tetragonal, trigonal and hexagonal systems, (uniaxial crystals) if $\chi_{\parallel'}$ and $\chi_{\perp'}$ are known, it will not still be possible to deduce the values of $|K_1|$, $|K_2|$ and $|K_3|$, unless we assume two of the principal molecular susceptibilities to be equal Conversely if $\chi_{\parallel'}$ and $\chi_{\perp'}$ are measured, and $|K_1| \approx |K_2|$ and $|K_3|$ is estimated, the inclination of K_3 to the crystal axes may be obtained

In cubic crystals, which possess the highest symmetry, even though they might consist of anisotropic molecules, the arrangement of the molecules will be such that their anisotropies will cancel out in the crystal and the crystal becomes isotropic No information in such cases can be obtained regarding molecular orientations

The above considerations show how, in favourable cases, the molecular orientations in crystals can be determined by measurements of diamagnetic anisotropy The fact that in many aromatic compounds with ring-shaped molecules, $|K_3| \neq |K_1|$ and $|K_2|$, and $|K_1| \approx |K_2|$ provides us with an important method of structure analysis From experimental determinations of the diamagnetic anisotropy of the crystal, and by estimating the value of $|K_3|$ and $(K_3 - K_1)$ using iscal's additive law and the known value of (ΔK) for the benzene ng, the orientation of the plane of the molecule with respect to the ystal axes can be calculated Recent experimental work on the amagnetic anisotropy of organic crystals deserving special mention, e those of Krishnan and his collaborators[25,26] (1933, 1935, 1939) and nsdale[27] (1936, 1938, 1939) This method is applicable to other in aromatic compounds also For instance, the orientations of the O_3) and (CO_3) groups, which possess considerable diamagnetic isotropy, in crystalline nitrates and carbonates, has been investigated this method (Krishnan and Raman,[28] 1927, Krishnan, Guha and nerjee,[22] 1933, Nilakantan,[29] 1937) Rhombic sulphur, which is own to possess a molecular structure consisting of ring-shaped lecules, has been investigated in the same manner (Nilakantan,[30] 36)

The large diamagnetic anisotropy found in bismuth and phite has been explained by Ehrenfest[1] (1925, 1929) and Raman[12] 29) as being due to electrons describing large planar orbits losing several atoms A similar argument holds good in the case he aromatic ring-shaped molecules, and recently Pauling[32] (1936) tried to calculate the diamagnetic anisotropy of a number of zene derivatives In the case of benzene, six L electrons which responsible for '*resonance*' in the structure, are assumed to be to move from one carbon atom to another in a magnetic field, describing large orbits coinciding with the circumference of the zene ring The anisotropy

$$(\Delta K) = \frac{-6Ne^2}{4\,mc^2} \Sigma r$$

re r is the radious of the benzene ring itself The value so ned agrees satisfactorily with the value assumed by Krishnan his collaborators[22,24] in their experiments By introducing suitable ections, Pauling has calculated the diamagnetic anisotropy of ral benzene derivatives also Calculations on similar lines have independently made by Lonsdale,[34] who has extended them to case of metal-free phthalocyanines More recently, London[5] has considered these molecular orbitals from the standpoint of quantum mechanics. He has utilised a method of approximation applied by Bloch in his theory of metals, which corresponds to the method of molecular orbitals in the theory of chemical linkages, and finds that interatomic currents are set up under two conditions, namely, (1) the existence of a cyclic chain of equivalent pairs of atoms and (2) a number of unpaired electrons associated with each valence bond. Such interatomic currents cannot occur in saturated compounds, like cyclohexane. London's theory has been successful in explaining the difference between the diamagnetic properties of isomeric molecules like anthracene and phenanthrene, which the semi-classical theory of Pauling is unable to do.

These theoretical considerations are capable of being extended to other conjugated structures as well, such as (NO_3) and (CO_3) groups, although the problem becomes very complicated in such cases. The author, as described later, has attempted to compute the diamagnetic anisotropy of the (NO_3) group in a somewhat similar manner as Pauling has done in the case of benzene.

Although considerable work has been done on the temperature dependence of the diamagnetic susceptibility of crystalline solids, the influence of temperature on the diamagnetic anisotropy of crystals has been investigated for a few substances only, mostly metals. Faraday[36] (1848 and 1855) first observed that the difference between the principal susceptibilities of bismuth decreased considerably between 40°C and 140°C, falling to less than half its original value. He could not, however, observe any change in the diamagnetic anisotropy of calcite although it was heated up to a very high temperature. Recently Goetz and Focke[37] (1934) and Shoenberg and Zaki Uddin[38] (1936) have studied the principal susceptibilities of bismuth over a wide range of temperature. The variation of the magnetic anisotropy of bismuth from room temperature up to the melting point has been investigated by W. J. John[39] (1939). Thallium has been studied by Rao and Subramaniam[40] (1936) who have observed changes in the diamagnetic anisotropy and susceptibility of the element occurring at

235°C Krishnan and Ganguli[41] (1937) have studied the anomalous temperature variation of the diamagnetic anisotropy of graphite It will be seen that all the previous work in recent years has been confined to elements only The author has investigated the temperature variation of the diamagnetic anisotropy of several inorganic and organic crystals by the more delicate experimental methods now available for investigating feeble anisotropies and their changes As will be seen later, many phenomena of the solid state such as crystal polymorphism, gradual transitions in the lattice, disorders in the lattice structure caused by impurities in the vicinity of the melting point, and molecular oscillations and rotations that set in at high temperatures, can be studied by the investigation of the variations of diamagnetic anisotropy with temperature, in favourable cases

Polymorphism has been studied so far by X-ray analysis, change of optical birefringence and thermal and dilatometric methods. It has been shown by the author (1937) that polymorphic transitions are also revealed by striking changes in the diamagnetic anisotropy of crystals, since, when transitions take place in crystals containing anisotropic groups, the relative positions and orientations of the anisotropic ions or molecules are also altered generally, and as a consequence there are corresponding changes in the anisotropy of the crystal These changes will obviously be very marked in highly anisotropic crystals in which the anisotropy is essentially due to that of the molecules or ions, as is the case in crystals of organic aromatic compounds and inorganic nitrates (we do not, of course, consider here, elements like bismuth and graphite, whose characteristic magnetic properties have to be explained on the electron theory of metals and semi-conductors), and are essentially different in character from the feebler effects observed by some authors in several diamagnetic substances during polymorphic transitions. It is possible to study many aspects of polymorphism in favourable cases, such as, the velocity of reaction from one phase to another, the influence of temperature on the rate of reaction and the relative orientations of the axes of the crystals in the two modifications.

Just as molecular orientations in crystals may be c
by magne-crystallic action, the analysis of the structure o
talline aggregates can also be accomplished in a simil
Nature abounds in such substances, to name only a fe
varieties of shells, fibres, marble, ivory, bone, teeth etc
crystallites in many of these are more or less regularl
and it will be obvious that if the crystallites are aniso
poly-crystalline aggregate itself will be anisotropic. Henc
lation of the anisotropy of the crystallites with that of the
will enable *the orientations of the former to be determi*
method has been successfully applied by the author in
mother-of-pearl from molluscan shells, and egg shells, wh
of aragonite and calcite crystals respectively

An interesting field of investigation has been opene
author's work on the diamagnetic anisotropy of crystalline n
carbonates Although it is known that the crystalline ele
can produce deformation of the ions in crystal lattices,
influence of the fields on the diamagnetic properties o
radicals had not been so far investigated because of
character of these effects It has been found by the auth
diamagnetic anisotropy of (NO_3) and (CO_3) groups is v
influenced by the character of the environment of ions s
them In fact, the feeble diamagnetic anisotropy exh
all non-cubic crystals consisting of ions like Ag^+, F^-, Cl
Cd^{++}, Ca^{++}, Mg^{++} etc, (which may all be expected to be
symmetrical in the free state), e g, crystals of Ag_2F, Ca
$CdCl_2$, $MgCl_2$ etc, is to be attributed to the deformations p
these ions in the crystal lattice by the electrostatic fields, th
of the deformations depending upon the symmetry of
consistent with the conditions of stability of the lattice
the character of the ionic deformations and of the crysta
may, in fact, be obtained from a study of the feeble d
anisotropy of these crystals.

Paramagnetism and Paramagnetic Anisotropy of Crystals

According to the classical theory of Langevin[42] (1905) and Weiss[43] (1907), we get the relation, known as the Curie-Weiss law,

$$\chi_M = \frac{C_M}{T-\theta}, \qquad \text{where } C_M = \frac{\sigma_0^2}{3R},$$

and $\theta = \frac{N\sigma_0^2\rho}{3MR}$, (Stoner, " Magnetism and Matter ", 1931)

expressing the variation of susceptibility with temperature The experimental results are, for convenience, expressed in Bohr Magneton values, and we have

$$P_B = \frac{\sqrt{3R}}{5564} \sqrt{\chi_M (T-\theta)}$$
$$= 2.839 \sqrt{\chi_M (T-\theta)}$$

and when θ is not known, the effective magneton value is expressed as

$$P_{B_{eff}} = 2.839 \times \sqrt{\chi_M T}$$

as though the Curie law were valid

The first satisfactory derivation of the magneton values of simple ions based on spectroscopic theory was given by Hund[44] (1925) who obtained the formula $P_B = g\sqrt{j(j+1)}$, where g is the Lande factor This reduces to $\sqrt{4s(s+1)}$ when the ions are in the *S*-state Hund's theoretical expression gives remarkably good values for the susceptibility of the rare-earth ions, but for the first transition group of elements, the agreement is very poor A modification of Hund's formula was therefore suggested by Sommerfeld and Laporte[46] (1926) taking into account the fact that the multiplet intervals in these ions are not very large Hund's expression assumes that $h\,\Delta\nu >> kT$ while Sommerfeld and Laporte considered the case for $h\,\Delta\nu << kT$ and the following expressions were obtained

$$P_B = g\sqrt{j(j+1)} \qquad \text{for } h\,\Delta\nu >> kT$$
$$\text{and} = \sqrt{4s(s+1) + l(l+1)} \quad \text{for } h\,\Delta\nu << kT$$

A similar expression was obtained by Van Vleck[45] (1932) by a more rigorous treatment.

The actual magneton values of the ions of the
ments do not fall between the two extreme values repre
above equations Bose[48] (1927) suggested that essent
spins contribute to the magneton value of the first tra
of elements An explanation of the paramagnetism of t
tion group of elements was offered by Stoner[47] (1929) w
the interaction effects between the neighbouring ions
In the rare-earth ions, the magnetically effective electr
the *4f* group which is incomplete, and they are effecti
from interaction effects by a complete group of higher
number But it is the *3d* group which is incomplete i
the first transition series, and since they are outerm
subject to the action of the environment The intera
the magneton values for these ions, which will lie betw
represented by

$$P_B = \sqrt{4s(s+1)} \quad \text{and}$$
$$= \sqrt{4s(s+1) + l(l+1)}$$

Recently, Van Vleck[49] (1932) has tried to exp
value of the susceptibility of the iron group of elem
due to the 'quenching' or 'freezing' of the orbital
the asymmetric crystalline fields Van Vleck's treat
to many interesting results The departure from the
be satisfactorily accounted for by the theory The rela
tions of the spin and orbital moments to the paramagne
lity can be studied and what is important for our purpos
the magnetic anisotropy of crystals is satisfactorily e
anisotropic crystals of the rare-earth salts, a crystal fiel
cular orientation and noncubic symmetry acting on the
ion, will produce a splitting of its lower levels, as a re
the magnetic moments of the levels and the suscept
different along different directions, depending on the c
field In salts of the iron group, the orbital moment is
partially quenched in an anisotropic manner and the re

through the spin-orbit coupling make the spin contribution also anisotropic.

According to quantum theory, for a free paramagnetic ion in any j–state, the number of possible *m*-states are (2j + 1) and in the absence of a magnetic field, all these states are equivalent and there is complete degeneracy But in a magnetic field, a redistribution of the ions among the (2j+1) states takes place, and this spacial quantisation gives rise to a resultant magnetic moment in the direction of the field If, however, initially the degeneracy is removed by, say, an asymmetric crystalline field such that the separation between the various energy levels is large compared to kT, then the application of a magnetic field cannot lead to any redistribution among the different states, and the substance will have zero susceptibility Such complete removal of degeneracy does not, however, take place The orbital degeneracy may be wholly or partially removed, but the spin degeneracy is conserved In any case, the partial removal of degeneracy implies a lowering of the paramagnetic susceptibility

In paramagnetic crystals, the paramagnetic ions are under the influence of the strong crystalline fields due to the ions surrounding them An asymmetric crystalline field is able to produce a Stark splitting of the energy levels of the ion, partially or even wholly removing the orbital degeneracy in salts of the iron group of elements The spin moments are not, in general, affected and are free to respond to the magnetic field and this explains why the magneton value tends to approach the *spin-only* value The spin moments might indirectly be affected due to their coupling with the orbital moments

The Stark splitting of the energy levels will depend on the character of the crystal fields, and the ground states of the paramagnetic ions A field of cubic symmetry should be expected to make no contribution to the anisotropy, whereas a departure from cubic symmetry will give rise to magnetic anisotropy as well as a departure from the Curie law and also different values for θ, the Curie temperature in the Curie—Weiss law $\chi_M = \frac{C_M}{T-\theta}$, in the directions of the principal axes of magnetization.

The general nature of the paramagnetic anisotropy of hydrated double sulphates of the iron group of salts may be understood by considering the typical case of ferrous ammonium sulphate, ($FeSO_4.(NH_4)_2SO_4.6H_2O$). Although the complete X-ray analysis of this crystal is not available yet, it is known that the Fe++ ion is surrounded by six water molecules in an approximately octahedral arrangement (Gorter[60], 1932). According to Lipson and Beevers[61] (1935), two types of arrangement of water molecules are possible, the octahedral and tetrahedral. In the Tutton salts the former type of arrangement occurs. The electric fields due to such an arrangement of polar molecules about the ion have been found to be markedly asymmetric. For instance, Krishnan and Mookherji[62] (1937) have observed a large paramagnetic anisotropy in rare-earth salts like, $Pr_2(SO_4)_3.8H_2O$ (in which also there is an octahedral arrangement of water molecules round the paramagnetic ion) which points to a crystalline field departing largely from cubic symmetry. The group, $Fe(OH)_6$, forms the "paramagnetic complex," and the anisotropy of the crystal should be referred to that of the 'complex'. These complexes or clusters are regularly arranged in the crystal lattice and are orientated in a definite manner with respect to the crystallographic axes (the unit cell comprising several such complexes) and a detailed X-ray examination would be very useful in correlating the anisotropy of the individual complexes with that of the crystal. The anisotropic paramagnetic complexes like $Fe(OH)_6$, persist even in the dissolved state, and this explains the phenomena of magnetic double-refraction strongly exhibited by many paramagnetic salts in solution (Chinchalkar[63], 1931; Haenny[64], 1937).

One of the important deductions of Van Vleck's theory[65] is that crystals containing ions in the *S* state, as for example, those of manganous and ferric salts, should not show any appreciable magnetic anisotropy. This has been verified by experiments of Rabi[66]

(1927), Jackson[57] (1933) and Krishnan and his collaborators[48, 53] (1934–1936) on Manganous (Mn^{++}) and Ferric (Fe^{+++}) salts, the paramagnetic ions of which are in the *S* ground-states. A further confirmation of the theory is available from studies on the magnetic double-refraction of solutions of paramagnetic salts, the salts containing ions in the *S* states exhibiting practically no double-refraction e.g., Ferric, Manganous and Gadolinium chlorides (Chinchalkar, 1931, Haenny, 1937).

Detailed calculations of the influence of crystalline electric fields on the paramagnetism of Pr and Nd among the rare-earth ions, and Ni, Co and Cr in the Iron group, have been made by Penney and Schlapp[60] (1932). In the rare-earths, there is no quenching of the orbital moments by the crystalline fields, and their susceptibilities are given by the Hund expression. However, a field of rhombic symmetry acting on the rare-earth ion will produce an asymmetric splitting of the lower levels, and hence give rise to anisotropy of paramagnetic susceptibility. Experimentally a fairly large anisotropy has been observed in the rare-earth salts, $M\,(SO_4)\;8H_2O$, (M = Sm, Pr, Er, Nd) by Krishnan and Mookherji[52] (1937).

In the ions of the first transition group of elements, the incomplete sub-shell of electrons lies outermost, and the spin-orbit coupling is weak. The orbital moments are, therefore susceptible to the influence of the crystalline fields, and will be partially frozen. The ions are all in the *F*-state, with $l = 3$, and the seven-fold degeneracy is removed by the crystalline field wholly or partially, according to the nature of the field. A rhombic field will completely remove the orbital degeneracy, while a cubic field will split the *F*-level into one single and two triply degenerate levels. Penney and Schlapp have assumed a field of predominantly cubic symmetry with a smaller rhombic term. The Hamiltonian function in a magnetic field *H* is given by

$$\begin{aligned} H = {} & D(x^4 + y^4 + z^4) + Ax^2 + By^2 \\ & - (A+B)\, z^2 + \lambda(L\,S) + \beta H\,(l + 2s) \end{aligned}$$

Assuming a cubic field of the same sign and magnitude for all the three ions, the spin orbit interaction together with the rhombic field is shown to be able to remove the degeneracy of the lowest level in Ni++ and Cr++ only in a high approximation, while, in the case of Co++ the degeneracy is removed to a first approximation This difference accounts for the isotropy of Ni++ and Cr++ as compared with the high anisotropy of Co++ In the case of Ni++ and Cr++, the splitting of the ground levels under the influence of the crystal fields is similar, the non-degenerate orbital level being lowest The susceptibility of Cr++ is lower than the *spin-only* value while that of Ni++ is higher In the case of Co++ there would be an inversion of levels, as pointed out by Van Vleck, with respect to Ni++, the triply degenerate level being lowest, and, therefore, a splitting of these levels by the rhombic part of the field or by the spin-orbit interaction takes place giving rise to deviation from the Curie law, and high paramagnetic anisotropy

Fe++ and Cu++ are both in the D-state ($d^6$5D and $d^9$2D respectively) There is a reciprocal relationship between Fe++ and Cu++ just as in the case of Ni++ and Co++ as shown by Van Vleck. The case of iron is of special interest in connection with the authors' investigations on biotite mica, but unfortunately, detailed computations are not available yet The splitting of the levels takes place as shown in figure below

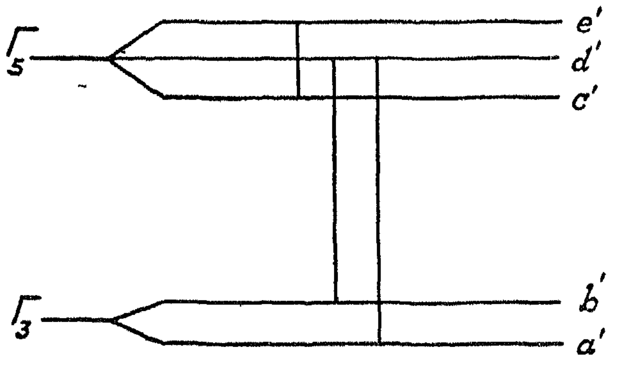

Fig 1

The figure will be upright in Cu++ and inverted in Fe++ The separation of the components of Γ and Γ is due entirely to the rhombic field The character of the ground states would indicate that the magnetic anisotropy of Fe++ should be much greater than that of Cu++, but actually, this is not found to be the case This anomaly is explained by Van Vleck as being due to various other causes Recently Van Vleck[61] (1939) has also considered the crystalline Stark splitting for clusters of the type (XY_6) in relation to the Jahn—Teller effect

In Van Vleck's original theory, the dipole-dipole interactions, between neighbouring paramagnetic ions are not considered and only salts of considerable magnetic dilution such as the hydrated sulphates and double sulphates of iron, cobalt, nickel etc, are discussed When, however, the concentration of the paramagnetic ion is raised, it is natural to expect interaction effects to influence the magnetic properties perceptibly Recently Van Vleck[62] (1937) has considered the effect of dipole-dipole coupling on the susceptibility, but the influence on the anisotropy has not been worked out The existence of such interactions in anhydrous salts of the iron group like $CoCl_2$, $CrCl_2$, $NiCl_2$ and $FeCl_2$ has been demonstrated by De Haas and Schultz[63] (1939) from susceptibility measurements at low temperatures when their effects become marked No data, however, are available regarding the effect of the interactions on the magnetic anisotropy at room temperatures, except the feeble effects mentioned by Krishnan and Banerjee (1936) in manganous salts of considerable dilution Joglekar[64] (1937) has studied some paramagnetic Tutton salts of the type, $MSO_4\,(NH_4)_2SO_4\,6H_2O$, where M is a divalent atom of the iron group, and he has examined the effect of partially replacing the paramagnetic ions M++ by Mg++ and Zn++ He has found that the order of magnitude of the anisotropy is not materially affected by dilution and the observed changes were attributed to slight alterations in the crystalline fields acting on the paramagnetic ion

The difficulty of investigating the effect of magnetic interactions lies in discovering a suitable substance, the concentration of the paramagnetic ion in which can be varied at will Biotite offers a suitable material for study since different varieties contain different amounts of iron The crystal structure of biotite is also fairly well known, and a satisfactory interpretation of the results of magnetic measurements is possible It has been found by the author that a high concentration of the paramagnetic ion enhances the gram ionic anisotropy referred to Fe++, to a considerable extent.

In many paramagnetic crystals, strong paramagnetic anisotropy is also associated with a marked pleochroism The absorption bands of the rare-earth salts consist of sharp lines and the inhomogeneous Stark splitting of the energy levels of the paramagnetic ion in an asymmetric crystalline field should produce strong pleochroism of the absorption bands The dichroism of biotite appears to be due to the asymmetry of the crystalline field of the Fe++ ion, as a consequence of which, light vibrations parallel to the cleavage plane are strongly absorbed, while those perpendicular to the plane are not absorbed to the same extent Krishnan and Chakrabarty[65] (1937) also have observed polarization of the absorption bands in some hydrated sulphates of rare-earths, which strongly suggests a high asymmetry of the crystalline fields in these salts Since paramagnetism and colour are related properties in the salts of the transition series of elements, any theory of paramagnetic susceptibility should also be able to explain the characteristics of the absorption spectra of these salts

A great deal of work on the absorption spectra of the rare-earth and iron group of salts has been recently done by Spedding and his collaborators[66] It has been found rather difficult to explain quite satisfactorily both the magnetic as well as the absorption data, on the basis of the work of Van Vleck, Schlapp and Penney This unsatisfactory state of affairs is partly due to the discrepancy in the magnetic data obtained by different workers, and accurate work in the field is needed According to Spedding and co-workers, the data of absorption of salts like Neodimium sulphate octahydrate $(Nd_2(SO_4)_3, 8H_2O)$

may be explained satisfactorily on the assumption that the crystalline fields in these are predominantly cubic in character. But from measurements of the paramagnetic anisotropy of these salts, Krishnan and Mookherji[62] (1937) have postulated fields of considerable asymmetry since the magnetic anisotropy of these salts is pronounced. The strong pleochroism of the absorption bands in these salts also lends support to this view. A rigorous treatment of absorption in paramagnetic salts on the basis of the Stark splitting of the energy levels of the paramagnetic ion in the crystal fields is highly desirable. In the absence of any satisfactory theory of absorption and pleochroism in iron salts, the author has attempted a qualitative explanation of pleochroism of biotite, based on Saha's theory of the colour of inorganic salts.

The most important experimental work on the paramagnetic anisotropy of crystals in recent years has been that of Finke[16] (1910), Jackson[67] (1924-1938), Rabi[56] (1927), Bartlett[58] (1932) and Krishnan and his collaborators[69-73] (1934-1939). Of these, the extensive investigations of Krishnan and his collaborators are note-worthy. They have studied such different aspects as the magnitude and asymmetry of the electric fields acting on the paramagnetic ion in the crystal, the geometry of distribution of the negatively charged atoms surrounding the ion, and hence its co-ordination number, the strength of coupling between the orbital and spin angular moments of the electrons in the incomplete shell of the ion, and in those crystals in which the paramagnetic ions are in the S-state, the magnitude of separation of the S-levels, which plays an important part in determining the thermal properties of the crystal at very low temperatures.

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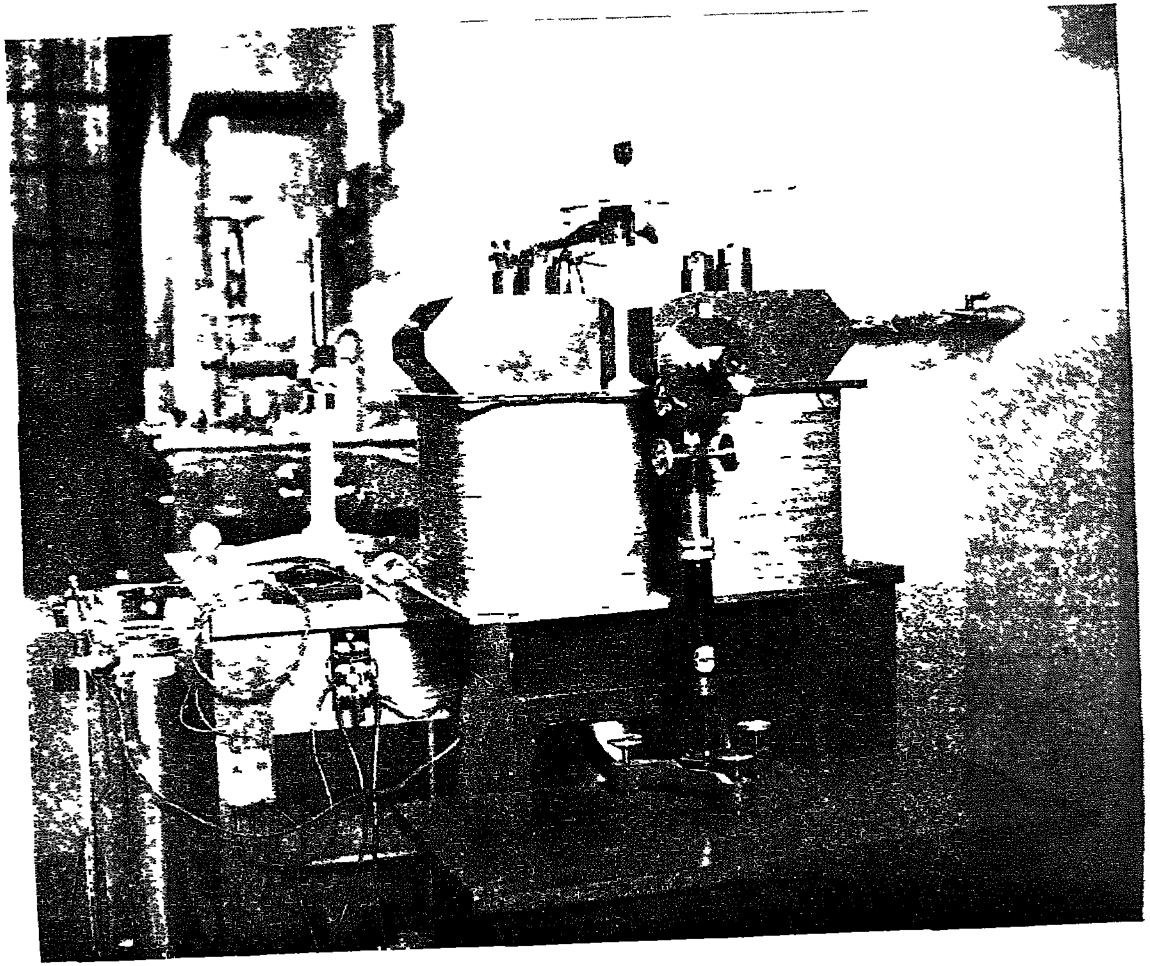


CHAPTER I

EXPERIMENTAL METHODS AND DETAILS

1. The Electromagnet

The electromagnet used for the measurements was supplied by Charles W Cook and Sons, Ashby de la Zouch, England, the pole pieces being made according to design submitted by the author (Fig 2, Plate I) Since perfectly uniform fields were necessary for the determination of the diamagnetic anisotropy, the pole-pieces were made massive with a large area of pole-face (66-sq cms) For susceptibility determinations with the torsion-balance, a pair of specially designed conical pole-pieces was employed, the semi-angle of the cone being made 55° for obtaining maximum intensity of the field These pole-pieces could be kept with their axes inclined to each other, producing an inhomogeneous field of the same type as in Curie's experiments

A current of ten amperes could be passed through the magnet for about 15 minutes without any sensible heating of the coils The current was adjusted by means of a system of rheostats Before each experiment the iron was brought to a cyclic state by reversing the current, kept at a low value, a sufficient number of times so that the field corresponding to any value of the current through the electromagnet was always of definite strength and exactly reproducible With the flat pole-pieces at a distance of 2 5 cms apart and a current of 7.0 amperes through the electromagnet, a field of 7710 Oersteds was obtained With the pole-faces 1 cm apart fields of the order of 12000 Oersteds could be easily attained But such high fields are not necessary for the anisotropy measurements The saturation value of magnetisation was reached with a current of 7 amperes through the magnet For the susceptibility measurements using the conical pole-pieces, fields of the order of 22000 Oersteds were attainable

For determination of the diamagnetic anisotropy at high temperatures, a second electromagnet designed by Dr C S Venkateswaran and constructed in the work-shop of the Indian Institute of Science, was employed (Fig 3, Plate II).

2. *Measurement of Field Strength*

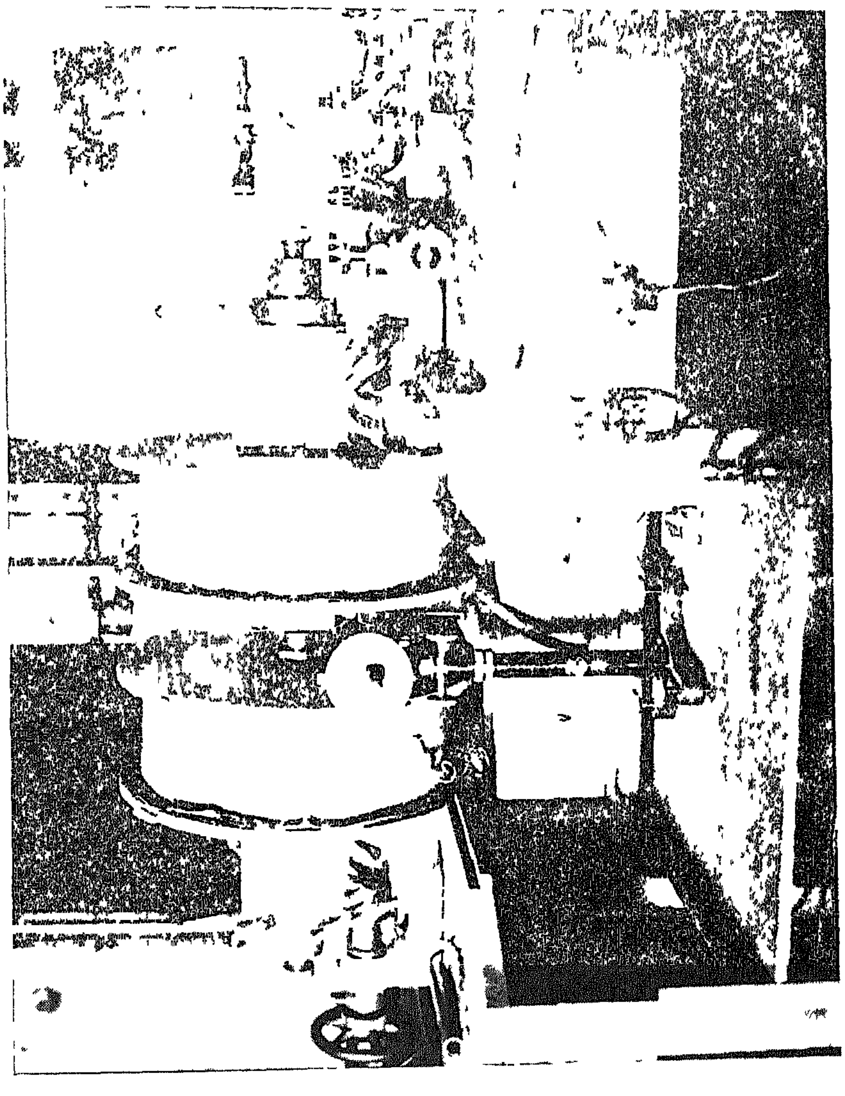
The field-strength was measured by means of a standard search coil made by the author and a calibrated Grassot fluxmeter. The search coil consisted of 30 turns of No. 40 S.W.G. double silk-covered pure copper wire, wound round an accurately turned cylinder of non-magnetic marble of diameter 2.359 cms. The fluxmeter was calibrated with a campbell standard mutual inductometer. Field strengths up to 8000 Oersteds were employed for anisotropy determinations on diamagnetic crystals. The values obtained in a typical field determination are given below.

Fluxmeter calibration = 14050 Maxwells per division
Search coil diameter 2.359 cms, Number of turns = 30,
resistance = 3.34 ohms
Mean fluxmeter deflection = 72.0 ± 0.4 divisions
This corresponds to a field of 7710 Oersteds (± 0.5%)

3. *Determination of Diamagnetic Anisotropy*

The direct determination of the principal magnetic susceptibilities of crystals cannot give very accurate values of the anisotropy, especially when the anisotropy is small. A method which directly gives the anisotropy is preferable. Such a method was first employed by Stenger[1](1883-1888) and König[2](1887), who used the crystal cut and ground in the form of a sphere and suspended by means of a *silk* fibre in the magnetic field. If χ_1 and χ_2 are the maximum and minimum values (algebraically) of the susceptibility in the plane of oscillation, the crystal will tend to set itself with the χ_1–direction parallel to the field-direction. Let initially the torsion-head, to which the fibre is attached, be turned round so that the χ_1–direction coincides with the field direction and there is no twist in the fibre. If the crystal is now allowed to make small torsional oscillations about its equilibrium position, and T_1, T_2 are the periods of oscillation with the field on and with zero field respectively, then the gram molecular anisotropy is given by

$$(\Delta\chi) = \chi_1 - \chi_2 = \frac{T_2^2 - T_1^2}{T_1^2}\,\frac{CM}{mH^2}$$



where m = the mass of the crystal, M its gram molecular weight, H the field strength in Oersteds and C the modulous of torsion of the fibre

Now, in the above method, strict uniformity of the field is not required, since the crystal has got a spherical shape Krishnan and his collaborators[3] (1933) have, however, used the crystals in their natural shape, making the field strictly homogeneous by using large flat pole-pieces (They have also employed quartz instead of silk fibres) There is a two-fold effect when the crystal has an arbitrary shape Even if the field is strictly uniform, there will be a couple acting on it tending to set it axially with the field direction This effect will, however, be undetectable by ordinary experimental methods and is generally negligible If, however, there is any residual inhomogeneity of the field, the combined effect of this and the anisotropy of shape of the crystal may be considerable This may be estimated in the following manner (Stansfield[4], [1938])

Consider a rectangular lamina of thickness t and mass m and susceptibility χ If $2a$ and $2b$ are the sides parallel to the coordinates X and Y, the potential energy of the lamina in a magnetic field H will be given by

$$V = -\tfrac{1}{2}\kappa t \int_{-a}^{+a}\int_{-b}^{+b} H^2 \, dX \, dY$$

$$= -\tfrac{1}{12} m\chi \left[6H_0^2 + a^2 \left(\frac{\partial^2 H^2}{\partial X^2} \right)_0 + b^2 \left(\frac{\partial^2 H^2}{\partial Y^2} \right)_0 \right],$$

higher powers of a and b being neglected, and the suffix $_0$ indicating zero value at the origin On transformation to new axes x, y, rotated through an angle θ in the plane of the lamina relative to the axes X, Y, the expression becomes

$$V = -\tfrac{1}{12} m\chi \Big\{ 6H^2 + (a^2\cos^2\theta + b^2\sin^2\theta) \frac{\partial^2 H^2}{\partial x^2} +$$

$$(a^2 \sin^2\theta + b^2 \cos^2\theta \frac{\partial^2 H^2}{\partial y^2} +$$

$$2 \sin\theta \cos\theta \, (b^2 - a^2) \frac{\partial^2 H^2}{\partial x \, \partial y} \Big\}$$

The couple C_z acting on the crystal tending to rotate the lamina about the Z axis is given by

$$C_z = -\frac{\partial V}{\partial \theta} - \frac{b^2-a^2}{6} \, m\chi \left\{ H_1 \left(\frac{\partial^2 H_1}{\partial x^2} - \frac{\partial^2 H_1}{\partial y^2} \right) + \left(\frac{\partial H_1}{\partial x} \right)^2 \right\} \sin 2\theta,$$

assuming the field to be symmetrical about x, y and x, z planes

If $a=b$, this couple disappears and comparing this expression with the expression for the couple due to the crystalline anisotropy,

$$C = \tfrac{1}{2} m \left(\chi_1 - \chi_2\right) H^2 \sin 2\theta,$$

for a crystal of mass m, it will be evident that the ratio of the two couples contains a factor involving the squares of the linear dimensions, and if the dimensions are small, then the effect due to any residual inhomogeneity of the field can be considerably minimised Hence the crystals should preferably be chosen of such dimensions that they approximate to a spherical shape

We do not of course consider here the small lateral bodily movements of the crystal This effect will be quite unimportant in diamagnetics, especially when the inhomogeneity is very small, and will not affect the anisotropy determinations

The method of oscillations has been adopted by the author in some of the determinations to be described hereafter The influence of non-uniformity of the field was tested experimentally by suspending a rod of quartz 1 mm in diameter and 10 mm in length with its axis horizontal by means of a fine quartz fibre in the field The expression for the couple acting on the rod shows that the couple will be a maximum when the rod makes an angle of 45° with the field Hence, initially, the rod is kept at this inclination with the field-direction, and the twist produced on the fibre when the field is put on, in order to restore the rod to its original position, was determined with a field-strength of 7990 Oersteds We can easily calculate the "anisotropy" $\frac{\chi_{\parallel r}}{\chi_{\perp r}}$ to which this will correspond, and it was found that this ratio was as 1 1 0003 This is negligibly small compared to the magnitude of the crystal anisotropies actually measured

Krishnan and Banerjee[5] have later employed a torsional method This method is, in many ways, more convenient than the oscillational method when very small crystals are used, and has been extensively used by the author The theory of the method will be dealt with in detail here since the original formula of Krishnan and Banerjee[5] (1935) is only an approximation and valid only under certain conditions [Krishnan and Banerjee[6], (1938), and K Banerjee and Bhattacharya[6] (1938)]

We have to consider the equilibrium of a crystal suspended in a uniform magnetic field by means of a quartz fibre, such that two of the principal axes of magnetic susceptibility are in the horizontal plane We shall consider the field to be strictly uniform so that the effect of anisotropy of shape of the crystal need not be taken into account

Let μ_1 and μ_2 be the permeabilities in the horizontal plane of the suspended crystal ($\mu_1 > \mu_2$ algebraically) Then in the uniform magnetic field, the crystal will tend to set itself with the μ_1-direction parallel to the field If, initially, the torsion-head is set in such a position that the μ_1-direction coincides with the field direction, when the field is on, there will be no couple acting on the crystal and no twist in the fibre If now the torsion-head is turned round through an angle α, the crystal also will turn round in the same direction through a smaller angle θ The couple acting on the crystal is then given by the expression

$$G = \frac{9(\mu_1 - \mu_2)\, VH^2}{4\pi(\mu_1 + 2)\,(\mu_2 + 2)} \quad \sin\theta\cos\theta$$

where V is the volume of the crystal and H is the field strength Substituting κ, the volume susceptibility in the expression ($\mu = 1 + 4\pi\kappa$), we have

$$G = \tfrac{1}{2}(\kappa_1 - \kappa_2)\, VH^2 \sin 2\theta$$

approximately, since κ_1 and κ_2 are very small compared to unity (in the case of diamagnetic and feebly paramagnetic crystals) This couple is balanced by the twist in the fibre, and we have the general condition of equilibrium,

$$C(\alpha-\theta)=\tfrac{1}{2}(\kappa_1-\kappa_2)\ VH^2 \sin 2\theta$$
$$=\tfrac{1}{2}(\chi_1-\chi_2)m\ H^2 \sin 2\theta, \qquad (1)$$

where C is the torsional constant of the fibre, m is the mass of the crystal and χ_1, χ_2 are the mass susceptibilities. Hence,

$$(\Delta\chi)=\chi_1-\chi_2=\frac{2(\alpha-\theta)C}{mH^2 \sin 2\theta} \qquad (2)$$

This general relation enables us to evaluate $(\Delta\chi)$, since α and θ can be measured directly, and C, m and H can be accurately determined by the usual methods.

Let the torsion-head be turned round further until it reaches a critical position when the crystal is in an unstable state of equilibrium and the slightest further rotation of the torsion-head makes it turn round suddenly. If θ_0 is the angle which the χ_1–direction in the crystal then makes with the magnetic field, and α_0 is the critical angle of rotation of the torsion-head, we have from (2)

$$(\Delta\chi)=\frac{2\ (\alpha_0-\theta_0)}{\sin 2\theta_0}\ \frac{C}{mH^2} \qquad (3)$$

Since at the critical position, $\frac{\partial\alpha}{\partial\theta}$ is evidently zero we have from (1)

$$\frac{\partial\alpha}{\partial\theta}=(\Delta\chi)\frac{mH^2}{C}\cos 2\theta_0+1=0$$

$$\cos 2\theta_0=-\frac{C}{mH^2(\Delta\chi)}$$

Putting $\theta_0=\frac{\pi}{4}+\delta$ we get $\sin 2\delta=\frac{C}{(\Delta\chi)\ mH^2}$,

which is always positive. Hence the critical angle θ_0 is always greater than 45°. It must be remembered however that the couple acting on the crystal is a maximum when $\theta=45°$. In some previous experimental work it has been assumed that $\theta_0=45°$. This is valid as a close approximation only for large values of α_c when δ is negligibly small This will become clear from the following considerations.

From (3), we have

$$C\,(\alpha_c-\theta_c)=\tfrac{1}{2}(\Delta X)\ mH^2 \sin 2\theta_c$$

$$\alpha_c-\theta_c=\tfrac{1}{2}(\Delta X)\ mH^2 \cos 2\delta$$

Hence, since

$$\sin 2\delta=\frac{C}{(\Delta X)\ mH^2},$$

$$\tan 2\delta=\frac{1}{2(\alpha_c-\frac{\pi}{4}-\delta)} \qquad (4)$$

In the table below, the values of δ for various values of α_c are calculated from relation (4) by the method of approximations In the approximate formula

$$(\Delta X)=2(\alpha_c-\frac{\pi}{4})\ \frac{C}{mH^2} \qquad (5)$$

the quantity $(\alpha_c-\frac{\pi}{4})$ replaces $\dfrac{\alpha_c-\frac{\pi}{4}-\delta}{\cos 2\delta}$ in the rigorous expression

$$(\Delta X)=\frac{2\,(\alpha_c-\frac{\pi}{4}-\delta)}{\cos 2\delta}\ \frac{C}{mH^2} \qquad (6)$$

obtained by substituting $\theta_c=\frac{\pi}{4}+\delta$ in (3) Table I clearly indicates the error introduced in the value of (ΔX) for various values of α_c when the approximate formula is used

It is evident that when α_c is small, i e , of the order of π, the percentage error introduced by neglecting δ in the expression (6) for the magnetic anisotropy, will be considerable It will also be clear that whereas α_c can never be less than $\frac{\pi}{2}$ according to the rigorous expression, the approximate relation apparently permits values of α_c down to $\frac{\pi}{4}$ However, when α_c is of the order of 2π, the per-

TABLE I

α_0	$\delta \pm 0.1^\circ$ in degrees	$\dfrac{\alpha_0 - \frac{\pi}{4} - \delta}{\cos 2\delta}$	$\alpha_0 - \dfrac{\pi}{4}$
6π	0.8	18.057	18.064
4π	1.2	11.771	11.775
2π	2.6	5.175	5.495
π	7.1	2.302	2.355
$\overset{\longrightarrow}{\text{Lt}}\ \frac{\pi}{2}$	$\overset{\longrightarrow}{\text{Lt}}$ 45	$\overset{\longrightarrow}{\text{Lt}}$ 0.5	0.785

centage error introduced if δ is neglected is less than 0.5%. For greater values of α_0 δ is negligibly small. In such cases, therefore the approximate formula (5) is quite valid. It is always advantageous from considerations of simplicity and convenience to adjust the experimental conditions such that α_0 is at least two rotations of the torsion-head, so that the approximate formula is valid. In the author's experiments generally two to seven rotations of the torsion-head have been employed to get the critical position. It sometimes happens that although a crystal is highly anisotropic in certain directions, the anisotropy in other directions may be quite small. In such cases the rigorous expression must be employed for the feeble anisotropies and δ should be evaluated independently. The critical position, however, is not sharply defined for values of α_0 considerably less than π, and in such cases, the experimental conditions can advantageously be altered e.g., by increasing the field strength, by using thinner quartz fibres etc.

The accurate determination of the anisotropy, requires the exact measurement of the angle α_0, the field strength H, the mass m

of the crystal and the torsional constant C of the fibre The angle of rotation of the torsion-head can easily be measured with an accuracy of 1 in 1000, and the field strength H and the mass m, may be determined correct to 0 5% Since an ordinary analytical balance weighs correct to 0 1 milligram only, the crystals selected should never weigh less than 20 m g if high accuracy is aimed at For crystals of smaller mass, we have to employ a microbalance For the determination of the torsional constant of the fibre, the method of oscillating from its end, a circular disc of glass about one of its diameters (Krishnan, Guha and Banerjee[3], 1933) is unsatisfactory since the damping due to air will be very great and a correction for this will have to be introduced In the author's experiments accurately-cut glass cylinders were employed of the following masses and dimensions (I) mass 49 5 mgm, diameter 0 330 cms, (II) mass 111 0 mgm, diameter 0 329 cms, (III) mass 289 4 mgm, diameter 0 552 cms For any particular fibre, any two cylinders of suitable masses could be employed These were suspended with their axes vertical respectively and their periods of oscillation in each case determined by a Cooke and Kelvey stopwatch We have the usual relation

$$C=\frac{4\pi^2(I_1-I_2)}{T_1^2-T_2^2}$$

where I_1 and I_2 are the moments of inertia of the cylinders which can be known from their masses and dimensions, and T_1 and T_2 are the periods of oscillation, respectively

4. *Effect of Traces of Paramagnetic Impurities*

In case paramagnetic impurities are present in a diamagnetic crystal, when measurements are made at low field strengths (below 100 oersteds) the effect of these impurities will be considerable But when strong fields are employed of the order of 5,000 to 10,000 oersteds, the effect of small traces of impurity becomes negligible, since the couple due to the intrinsic anisotropy of the crystal is proportional to the square of the field-strength With a crystal of calcite, the possible effects of small traces of impurities was investigated for field-strengths ranging from 100 to 8000 Oersteds For field-strengths ranging from 100 to 500 Oersteds, a consistent departure from the actual value of the diamagnetic anisotropy could be detected But the effect was quite negligible at fields of the order of 1000 Oersteds and above The influence of slight traces of impurities in the shellac at 8000 Oersteds was estimated to affect the values of crystal aniostropy by less than 0 01 per cent

5. *Preparation of Quartz Fibres*

The quartz fibres were prepared by the technique of Nichols. A quartz rod is drawn in the Oxy-coal gas flame to about 1 mm thickness and broken in the middle Using a powerful blast and a pointed flame, the two broken ends are brought together and drawn apart in the hottest part of the flame The blast is sufficient to draw out the fibre which is received on a black velvet screen placed in front of the flame, slant-wise Fibres of any degree of fineness could be drawn by suitably adjusting the flame

6. *Mounting the Crystal and Determination of Orientations in the Field*

A torsion-head divided in degrees was employed and the fibre was attached to it by means of shellac To the lower end of the fibre, for conveniently affixing the crystal, a short glass pin was attached with its head down A trace of pure diamagnetic shellac is enough to hold the crystal firmly to the glass pin-head

The crystal axes and faces were identified with a small Herbert Smith Goniometer The mounting of the crystal was done with small pincers inside a wooden case, in order to protect it from dust and impurities Inorganic crystals which are insoluble in alcohol, were washed thoroughly with alcohol to remove any dust particles sticking to the surface of the crystal. The crystal and fibre were enclosed in a glass tube for protection from draughts when measurements were being made in the magnetic field (Fig. 4)

In order to determine the position of the crystal relative to the magnetic field, we have to fix the direction of the field first This was done by the following arrangement a glass plate, with a fine straight line scratched on it with a diamond point, is fixed to the lower end of the glass tube supporting the torsion-head (Fig 4) The line is set initially parallel to the field-direction A small mirror kept below at an angle of 45° reflects the image of the line on to the telemicroscope

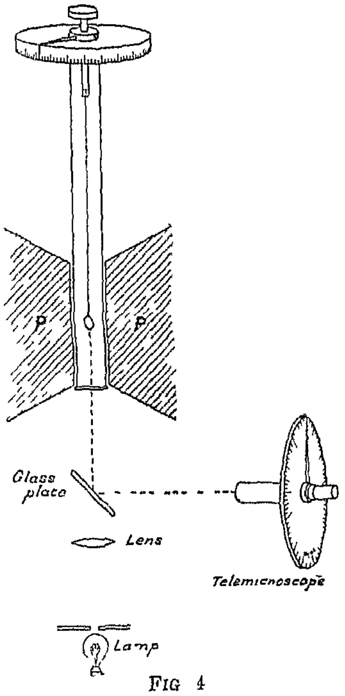


Fig 4

mounted on a circular scale The zero-reading on the circular scale corresponds to the setting of the cross wire of the telemicroscope parallel to the line The orientation of the crystal is observed with reference to well-developed faces and edges of the crystal, identified by means of a goniometer, the cross-wire being set parallel to any one of these edges as found convenient With well-developed crystals the orientations could be determined correct to 0 5°.

7. *Experimental Determination of the Diamagnetic Anisotropy of different classes of crystals*

The determination of the magnetic properties of a crystal involves the determination of χ_1, χ_2 and χ_3, the three principal susceptibilities, and the orientation of the axes of the magnetic ellipsoid with respect to the crystallographic axes In the procedure followed by Krishnan and his collaborators in their experiments, one of the principal susceptibilities was directly determined by Rabi's[7] null method, and then χ_1 χ_2 and χ_3 could be determined in magnitude and direction from measurements of the magnetic anisotropy Instead of directly determining one of the principal susceptibilities, we may, alternatively, measure the mean susceptibility

In the case of uniaxial crystals, a single experiment is sufficient to determine the anisotropy $\chi_\perp - \chi_\parallel$. The crystal is suspended with the symmetry-axis horizontal in the magnetic field and it will tend to set itself with the axis along or perpendicular to the field, according as it is the direction of maximum or minimum susceptibility algebraically The anisotropy may then be easily determined as described before

In the case of orthorhombic crystals, the crystal is suspended with the '*a*', '*b*' and '*c*' axes vertical respectively, so that $\chi_b - \chi_c$, $\chi_c - \chi_a$ and $\chi_a - \chi_b$ can be determined Although a knowledge of two of these quantities is sufficient, the third is also generally determined to check up

For monoclinic crystals, following Krishnan's notation, χ_3 denotes the susceptibility along the symmetry axis and χ_1 and χ_2, the principal susceptibilities in the symmetry plane ($\chi_1 > \chi_2$). ψ is the angle which the χ_1-axis makes with the '*c*'-axis of the crystal taken positive when measured towards the obtuse angle β The three modes of suspension of the crystal generally employed are '*b*'-axis vertical, '*a*'-axis vertical and (001) plane horizontal respectively Then we can know

$$\chi_1 - \chi_2,\ (\chi_2 \sin^2\theta + \chi_1 \cos^2\theta) - \chi_3$$
$$\text{and } (\chi_2 \cos^2\theta + \chi_1 \sin^2\theta) - \chi_3$$

respectively, where θ is given by $\beta = \frac{\pi}{2} + \psi + \theta$ θ or ψ can be directly determined by observing the orientation of the crystal in the field when suspended with the '*b*'-axis vertical

8. *Determination of Absolute Susceptibilities*

The determinations of absolute susceptibilities were made by a torsion balance of the Curie-Wilson type constructed by the author The principle of the balance is too well-known to need any description here Only the constructional details will be given here Fig 5 gives a schematic diagram of the balance The balance was completely enclosed in glass as shown Most of the parts of the balance were of glass except the torsion-head and wire, the riders for balancing the phial and the weights for keeping the torsion-wire taut The arms of the balance were of glass as also the extension for holding the glass container The phial was made of thin glass tubing with a close-fitting ground stopper The phial could be rigidly fixed to the arm of the balance by the simple device indicated in Fig 5

The measurements were made by the null method The most important adjustment in the Curie balance is that of bringing back the phial exactly to its original position relative to the field, in every case This was done by means of the telescope-and-scale arrangement, the image of the scale reflected from the mirror M_1 being viewed through the telescope The advantage of this arrangement lies in the fact that we can also find out easily whether the two arms are properly balanced or not If the balancing is not properly done the image of the scale will be displaced vertically relative to the crosswire of the telescope The correct balanced position was defined by a horizontal line on the scale, the image of which coincided with the point of the intersection of the cross-wires A mirror M_2 also served to indicate the position of the bottom of the phial relative to the field, the reflected image being viewed through a telemicroscope

The torsion-wire could be replaced to suit both dia- and paramagnetics, as the case may be

In the case of diamagnetics, the standard was pure double distilled water (susceptibility taken as -0.720×10^{-6}) For para-magnetics, a 33.8 per cent solution of $MnCl_2$ was prepared and its susceptibility measured by the U-tube method at room temperature It was found that $\chi_{(25^\circ c)} = 38.30 \times 10^{-6}$

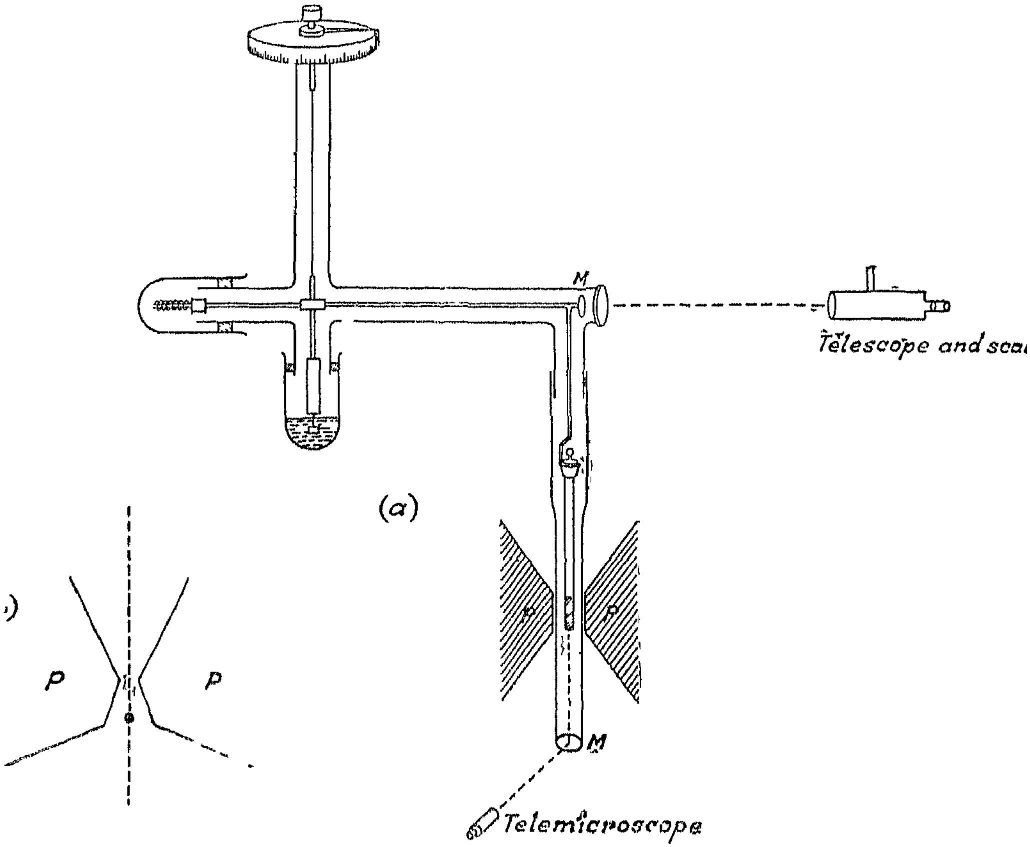


FIG 5

The usual procedure was adopted in making the measurements, first with the phial alone, then with the phial containing the standard substance and finally with the phial containing the substance in the form of fine powder if solid The phial was always filled up to a definite mark made on it We have the well-known formula

$$\chi = \frac{1}{m}\left\{ \chi_a m_a + (\chi_s m_s - \chi_a m_a)\frac{F_2 - F_1}{F_3 - F_1} \right\}$$

where χ, m, represent the susceptibility and mass of the specimen,

χ_a, m_a those of air, χ_s, m_s those of the standard substance respectively, the masses referring to equal volumes of substances in the container; F_1 denotes the force acting on the container, F_2 that on the container with the substance whose susceptibility is to be determined and F_3 that acting on the container plus the standard substance respectively. Measurements with a few well-known substances were made in order to calibrate the apparatus.

In the table below, the author's values of the susceptibility for a few cases are given along with the values obtained by other workers (International Critical Tables, Vol. VI, pp. 354–66).

TABLE

Substance	Temperature °C	Mean Susceptibility × 10^6	
		Author	Int. Crit. Tab.
NaCl	25	−0.494	−0.499
Na_2CO_3	24	−0.236	−0.24
$KMnO_4$	25	0.174	0.175
$MnCl_2$	24	106.0	107.0 (24°C)
$FeSo_4(NH_4)_2SO_4$ $6H_2O$	24	30.2	32.6 (17°C)

9. *Temperature Variation of the Magnetic Properties*

The abovementioned experimental arrangements had to be suitably modified for studying the influence of temperature on the diamagnetic properties of crystals. The details of the modifications and the heating arrangement used are described later. The heating was done electrically and special care was taken that the heating wire had no disturbing effect on the character of the magnetic field. In the anisotropy measurements, a uniform non-inductive winding of chromel wire (which was only feebly magnetic) round the glass tube within which the crystal was suspended, was found to be satisfactory. This was tested in the following manner with a crystal of calcite. The crystal suitably mounted at the end of the quartz fibre, (details given later) was placed in the magnetic field and the critical angle of rotation of the torsion-head determined at room temperature. The crystal was now heated to various temperatures by passing electric current through the heating coil from a battery and in each case the critical angle of rotation of the torsion-head was deter-

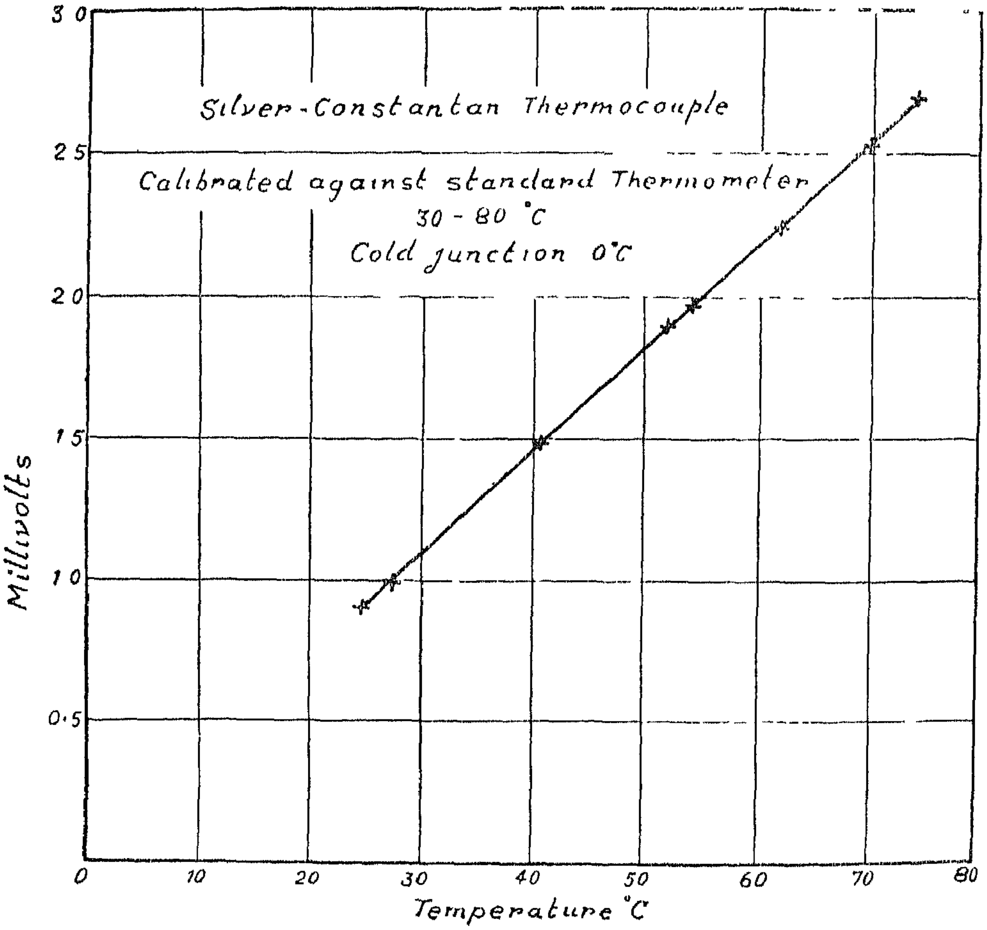


FIG 6

mined It was found that up to 300°, the diamagnetic anisotropy was practically unaffected by temperature In order to find out whether the heating current produced any disturbing effect, the current was cut off momentarily at a high temperature and the critical angle again measured It was found that any residual field

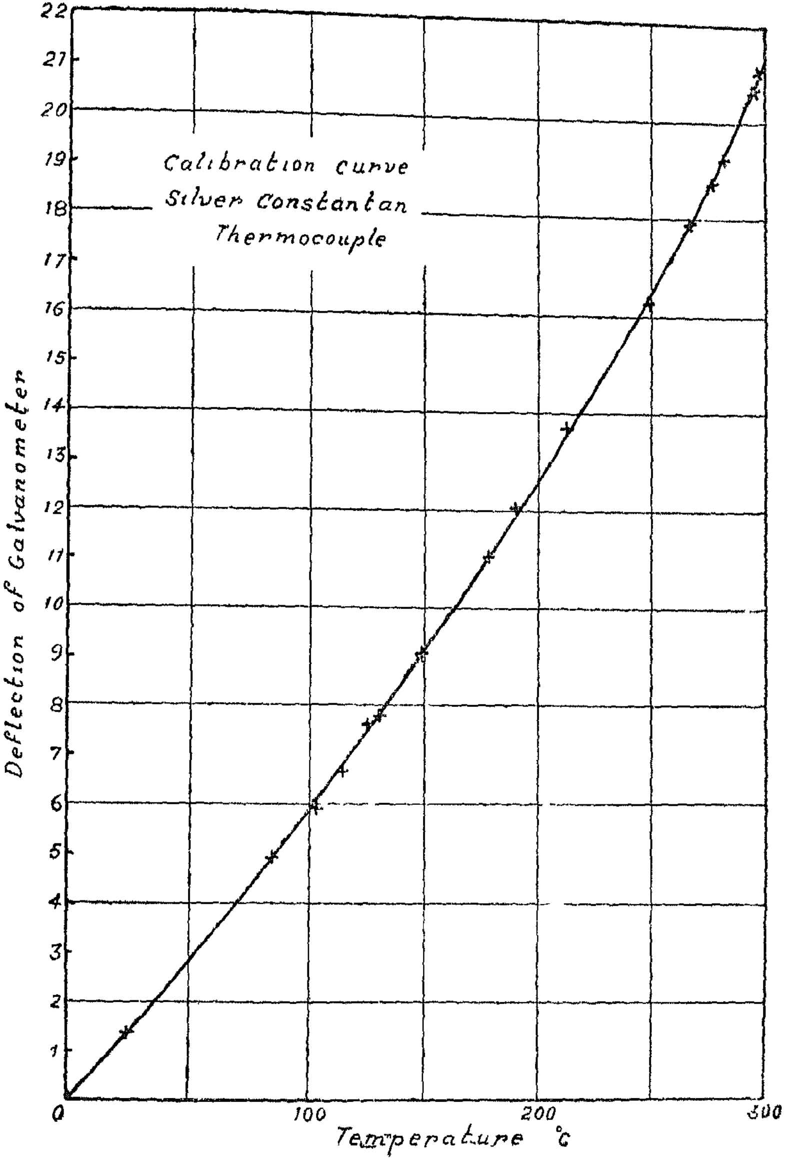


FIG 7

due to the current through the heating coil had practically no effect or the values obtained

10. Measurement of Temperature

The temperature was measured by means of silver-constantan thermocouple* (cold junction kept in melting ice) which was calibrated directly with reference to a standard certified thermometer The E M F of the thermocouple was directly measured by mean of a potentiometer The temperatures could then be read o directly from a graph showing E M F against temperature A typic temperature chart is given in Fig 6 for the range 25°–80° Similar charts were prepared for different ranges of temperatu For the nitrates a higher temperature range is necessary than f the organic crystals examined For the range 25°–300°C, therm couple was directly connected to a sensitive moving coil galvanomet through a suitable resistance, and the deflection corresponding any temperature directly read off by means of a lamp-and-sca arrangement Fig 7 shows the calibration of the thermocoup in terms of deflections of the galvanometer The potentiomet was employed when higher accuracy in any narrow range temperature was required

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* In the preliminary experiments a copper-constantan couple was used

CHAPTER II

DIAMAGNETIC ANISOTROPY OF NITRATES AND CARBONATES

1. Introduction

In connection with the author's investigations on various aspects of the diamagnetic anisotropy of crystalline nitrates and carbonates it was found necessary to make accurate determinations of the anisotropy of these substances, since, a study of the literature on the subject revealed that there are considerable discrepancies in the values obtained by different experimenters. The earliest measurements on the ratio of the principal susceptibilities of calcite were made by Tyndall[1] (1851). Later Stenger[2] (1883 and 1888) and Konig[3] (1887) determined the difference between the principal susceptibilities by the method of oscillations, employing silk fibres. They got rather discordant values, for, whereas $K_3 - K_1$ according to Stenger was -0.85×10^{-7}, Konig got the value -1.135×10^{-7}, K_3 and K_1 denoting the volume susceptibilities along and perpendicular to the trigonal axis of calcite. The possibility of this discrepancy arising from the presence of impurities was considered by Stenger although he did not investigate the matter further. Voigt and Kinoshita[4] (1907) have determined the principal susceptibilities of calcite and aragonite by a direct method but this cannot obviously give accurate values of the anisotropy, especially in the case of feebly anisotropic crystals, since there are many possibilities of error in their method incident on measuring the field and its gradient, the preparation of the crystal sections, the location of the crystal in the field etc. More recently Krishnan and his collaborators (1933) have effected an improvement in the original method of Stenger and Konig by using quartz fibres. But no special care seems to have been taken in determining the torsional constant of the fibre, which they found by the simple method of oscillating a glass disc, by one of its diameters, at the end of the quartz fibre. Krishnan and his co-workers have determined the anisotropies of calcite, aragonite, strontianite and witherite among the carbonates In regar to nitrates the determinations of Rabi[6] (1927) and Krishnan an co-workers[6] (1933) are available for sodium and potassium nitrates There is some discrepancy in the values here also

It is evident from the foregoing, that fresh determinations ar highly desirable The improved technique described earlier by th author has made it possible to determine the feeble diamagneti anisotropies of carbonates and nitrates with an accuracy of 1% Th results obtained in the case of several carbonates and nitrates a presented here and discussed in relation to their structure As wi be seen later much new information regarding diamagnetic anisotrop of (NO_3) and (CO_3) groups in relation to crystal structure has bee obtained

2. *Experimental Details*

Since the carbonates employed are all naturally occurrin minerals, their composition varies widely according to their place o origin Calcite, aragonite, strontianite and witherite are not always pur $CaCO_3$, $SrCO_3$ and $BaCO_3$ respectively It is very important to not that although the optical properties, specific gravity, transparenc etc , are not affected to any noticeable extent by the presence of trace of paramagnetic impurities, the magnetic properties are extremel sensitive to these, especially the diamagnetic anisotropy Hence, i is highly essential to examine the specimens carefully before makin the magnetic measurements Two samples of Iceland spar crystals were available for the experiments, besides a good crystal o calcite obtained from a broken Nicol prism All the crystals use were clear and colourless and optically free from defects The tw samples of Iceland spar crystals were chemically analysed in regar to their iron content One was found to contain 0 002% of iro and the other 0 005%. It was also found that iron was presen in the ferrous state Since $FeCO_3$ is isomorphous with CaCO evidently we have here a case of isomorphous substitution commo among minerals The sample obtained from the Nicol prism wa found to be practically free from iron The aragonite crystal wa also found to be iron-free The samples of witherite and strontianite were slightly opaque

The crystalline nitrates can be obtained in a high state of purity by recrystallising the 'Kahlbaum' substance from solution in dilute nitric acid In view of the fact that sodium nitrate is easily crystallizable, and is available in a very pure state, it should serve as a convenient standard for all measurements of feeble diamagnetic anisotropies Besides sodium and potassium nitrates, ammonium and silver nitrates also have been examined These have not been studied by earlier workers The silver nitrate crystals were grown in the dark in order that they might not be affected by light

The torsional method of Krishnan was employed in making the measurements The mean susceptibilities of the carbonates in the form of powder was also determined by the torsion balance

The values obtained in a typical experiment with a sample of Iceland spar are given below

Two crystals of masses 41 2 and 50 7 mgm were taken from the selected sample and the surface of the crystals was cleaned with dilute acid, followed by distilled water and alcohol, before they were fixed to the end of the quartz fibre

Field strength H=7710 Oersteds (±15)

Torsional constant of the fibre $C=2\ 586\times10^{-3}\pm(0\ 3\%)$

Mass of crystal (± 0 1 mgm)	Mean α_0 (degrees ±1°)	$(\alpha_0\text{-}45^\circ)$ degrees	$(\Delta X)=\frac{2(\alpha_0-45)\pi}{180}\times\frac{CM}{mH^2}\times10^6$
41 2 mgm	780	*735*	2 70
50 7 mgm	956	*911*	2 71

Similar determinations were made in all cases and in the table below the results obtained with various carbonates and nitrates are given

TABLE

Crystal data			$(\Delta\chi)\times 10^{6}$						χ (mean) $-\times 10^{-}$
			(A)	(Kr)	(V K)	(R)	(S)	(Ko)	
Calcite (1) (005% iron), density 2 725	$CaCO_3$ gm mol wt, 100 01, Trigonal Rhombohedral, space group D_{3d}^{6}, two molecules in unit cell	$\chi_{\perp r} - \chi_{\parallel r}$	2 71						34 9 (A)
Calcite (2) (002% iron), density, 2 720		,,	3 45						35 6 (A)
Calcite (3) density 2 713		,,	3 89	4 0_1	4 2_1		3 11	3 98-4 30	35 8 (A)
Aragonite density 2 940	$CaCO_3$ gm. mol wt 100 01, Orthorhombic, space group V_h^{16}, four molecules in unit cell	$\chi_a - \chi_c$	4 89	4 0_2	5 2				36 9 (A)
		$\chi_b - \chi_c$	5 21	4 2_0	5 7				

Crystal data			$(\Delta\chi)\times10^6$						χ(mean) $-\times10^6$
			(A)	(Kr)	(V K)	(R)	(S)	(Ko)	
Strontianite	$SrCO_3$ gm mol wt, 147 6, aragonite type structure	$\chi_a-\chi_c$	5 05	$4\,8_1$					
		$\chi_b-\chi_c$	5 25	$4\,8_4$					45 0 (A)
Witherite	$BaCO_3$ gm mol wt, 197 4, aragonite type structure	$\chi_a-\chi_c$	4 34	$4\,9_3$					
		$\chi_b-\chi_c$	4 52	5 0					52 1 (A)
Sodium nitrate	$NaNO_3$ gm mol wt, 85 01, calcite type structure	$\chi_{\perp r}-\chi_{\parallel r}$	6 15	$4\,8_9$		5 4			25 6 (K)
Potassium nitrate	KNO_3 gm mol wt, 101 1, aragonite type structure	$\chi_a-\chi_c$	6 79	$4\,8_2$		5 7			
		$\chi_b-\chi_c$	6 98	$4\,8_7$		5 9			31 0 (K)

Crystal data			(ΔX) × 10						X (mean) — × 10^6
			(A)	(Kr)	(V K)	(R)	(S)	(Ko)	
Ammonium nitrate	NH_4NO gm mol wt, 80 05, Orthorhombic, space group V_h^{13}, two molecules in unit cell	$\chi_c-\chi_a$	0 58						33 6 (K)
		$\chi_c-\chi_b$	6 42						
		$\chi_a-\chi_b$	5 92						
Silver nitrate	$AgNO_3$ gm mol wt, 169 9, Orthorhombic, space group V^1-V^9, eight molecules in unit cell, complete structure analysis not yet available	$\chi_c-\chi_a$	2 47						46 5 (K)
		$\lambda_c-\chi_b$	3 63						
		$\chi_a-\chi_b$	0 97						

A—Author, Kr—Krishnan and his collaborators, V K—Voigt and Kinoshita, R—Rabi, S—Stenger, Ko—Konig, K—Kido

For calcite the three samples gave three different values. The values obtained by other workers are, Stenger, 3.11×10^{-6}, Konig, 4.2×10^{-6}, Voigt and Kinoshita, 4.2×10^{-6}, Krishnan, Guha and Banerjee, 4.09×10^{-6}. The best sample used by the author gave 3.89×10^{-6}. The earlier workers have not specified the purity of the substances used, and as Stenger has pointed out, there is likelihood of the specimens containing paramagnetic impurities like the isomorphous mineral siderose ($FeCO_3$). There is little doubt that the discrepancies between the results of Stenger and Konig are due to this.

The author's results for nitrates are seen to be higher than those of earlier workers. In general, the diamagnetic anisotropy of the NO_3 ion is found to be considerably higher than that of the CO_3 ion, in their respective crystals. The significance of this difference is discussed later.

3. Diamagnetic Anisotropy in relation to Crystal Structure in Carbonates and Nitrates

The magnetic anisotropy of crystalline nitrates and carbonates in relation to their crystal structure and the properties of the individual ions constituting them, was first investigated by Krishnan and Raman[7] (1927). They were able to demonstrate that the magnetic anisotropy of the crystal is due to the intrinsic anisotropy of the individual carbonate and nitrate groups, these groups being arranged regularly parallel to each other in the crystal lattice with their planes perpendicular to the optic axis in calcite and sodium nitrate, and perpendicular to the c-axis in aragonite and potassium nitrate respectively. They were led to this conclusion from a consideration of the data of light scattering and magnetic double refraction of nitric acid, which indicated considerable diamagnetic anisotropy for the (NO_3) group. The value of the diamagnetic anisotropy of the (NO_3) group thus deduced agreed satisfactorily with the experimental values found for crystalline nitrates, thus clearly indicating that the crystal anisotropy is essentially due to the (NO_3) group. The correlation of the crystal anisotropy with that of the individual (NO_3) and (CO_3) groups in a number of carbonates and nitrates has also been discussed by Krishnan, Guha and Banerjee[5] (1933)

The essential features in the relation between crystal anisotropy and that of the (NO_3) and (CO_3) groups, in the case of sodium and potassium nitrates, calcite, aragonite, witherite and strontianite are now well-known In all these the (CO_3) and (NO_3) groups are arranged in layers parallel to each other in the crystal lattice, interspaced by layers of metallic ions The problem is therefore very simple, and neglecting any mutual interaction of neighbouring ions, the anisotropy of the individual group is clearly that of the crystal itself, to a first approximation

In the case of rhombic ammonium nitrate, the results clearly show that the (NO_3) groups are all orientated with their planes perpendicular to the '*b*'–crystallographic axis. X-ray analysis of this crystal has been recently done by C D West (1932) and Hendricks, Posnjak and Kracek (1932) The results of the magnetic analysis are in complete agreement with X-ray analysis As C D West has pointed out, the difference between potassium nitrate and ammonium nitrate lies in the absence of the separation into alternate layers of metal ions and nitrate groups (which lie parallel to the nitrate planes) in the latter It is noticeable that the magnetic anisotropy in the *a c* plane is considerable. This may be attributed to a large distortion of the (NO_3) group by the neighbouring ions, producing asymmetry of electronic configuration of the group in its own plane

The complete structure determination of silver nitrate has not yet been made, although Zachariasen[10] (1928) has attempted to fix the space-group and the number of molecules in unit cell He has found that there are eight molecules in the unit cell The complete structure analysis, evidently, is not easy The orientations of the (NO_3) groups in the lattice may, however, be calculated from the magnetic data, assuming $K_1 = K_2$[11]

We have first of all to eliminate the contribution due to the silver ions, which may be assumed to be equal in all directions. From

χ_a, χ_b and χ_c, we can obtain the quantities, $\chi_{a(NO_3)}$, $\chi_{b(NO_3)}$ and $\chi_{c(NO_3)}$. *Then we have,*

$$\chi_{a(NO_3)} = K_1 + (K_3 - K_1)\cos^2\gamma_1$$
$$\chi_{b(NO_3)} = K_1 + (K_3 - K_1)\cos^2\gamma_2$$
$$\chi_{c(NO_3)} = K_1 + (K_3 - K_1)\cos^2\gamma_3$$
$$\cos^2\gamma_1 + \cos^2\gamma_2 + \cos^2\gamma_3 = 1$$

where, K_1 and K_3 are the principal gram molecular susceptibilities of the (NO_3) group along and perpendicular to its plane, and γ_1, γ_2, γ_3 are the angles made by the normal to the plane of the ion with the '*a*', '*b*', '*c*' axes of the crystal respectively. Any two of these equations are sufficient to determine the angles.

According to Kido[12], the susceptibility of the (NO_3) group is -20.1×10^{-6}, *and combining this with the diamagnetic aniso*tropy of the (NO_3) ion, 6.15×10^{-6}, as determined experimentally in the case of sodium nitrate, we get

$$|K_1| = -18.05\times10^{-6}$$
$$|K_3| = -24.2\ \times10^{-6}$$

If the susceptibility of the silver ion is assumed to be -26.2×10^{-6} (Klemm[13] 1936, from Kido's data), we have,

$$\chi_{a(NO_3)} = -20.8\times10^{-6}$$
$$\chi_{b(NO_3)} = -21.7\times10^{-6}$$
$$\chi_{c(NO_3)} = -18.3\times10^{-6}$$

γ_1, γ_2, γ_3, are then found to be

48°, 30′, 40°, 6′ and 79°, 36′ respectively.

This indicates that the K_3 axis of the ion is nearly perpendicular to the '*c*'-axis of the crystal and explains why the diamagnetic susceptibility in the direction of the '*c*'-axis is a minimum.

The above calculations are only approximate since the ionic susceptibilities derived from Kido's data are not very accurate. But the calculations should prove very helpful when a complete X-ray analysis of the *structure of silver nitrate is attempted.*

4. *Magnetic Anisotropy of Calcite*

For a pure specimen of calcite the author has obtained the value $\chi_{\perp r} - \chi_{\parallel r} = 3\ 89 \times 10^{-6} \pm\ 04$ This is in close agreement with the values obtained by Konig, Voigt and Kinoshita and also Krishnan and his collaborators A higher accuracy of measurements can be claimed here in view of the improved experimental methods employed, along with careful determinations of all the quantities involved, such as the field-strength and the torsional constant of the fibre

It is very significant that the diamagnetic anisotropy of specimens containing iron (presumably as $FeCO_3$) is less than that of pure calcite On examining the data of Dupouy[11] (1931) for the magnetic anisotropy of siderose ($FeCO_3$) it becomes quite clear why this should be so Siderose has got a structure similar to calcite each Fe++ ion being surrounded by six (CO_3) groups in an approximately octahedral arrangement As pointed out before, the paramagnetic anisotropy of the crystal is due to the influence of the crystalline fields on the Fe++ ion producing an asymmetric Stark splitting Experimentally it has been found that the paramagnetic anisotropy is maximum along the optic axis and least perpendicular to the axis Dupouy gets a value for $\chi_{\parallel} - \lambda_{\perp} = 47\ 9 \times 10^{-6}$ at 17°C (referred to 1 gm) with a specimen containing 35 6 per cent iron If Fe++ replaces Ca++ in calcite by isomorphous substitution, it is evident that this will introduce a paramagnetic anisotropy superposed on the diamagnetic anisotropy of the crystal, and opposed to it in character We may, therefore, expect a diminution of the diamagnetic anisotropy In fact, the results clearly show that when the percentage of iron is higher, the diamagnetic anisotropy decreases in a corresponding manner With a higher percentage of iron, the paramagnetic anisotropy may predominate over the diamagnetic anisotropy of calcite The simple calculation shown below will indicate how differences of the observed order can arise from traces of iron If the specimen of calcite contains 0 005 per cent. of iron, the amount of iron present as Fe++ in one gram molecule of $CaCO_3$ will be 0 005 gms

0.356 gms of Fe^{++} will give rise to a paramagnetic anisotropy of 47.9×10^{-6}. Hence 0.005 gms will contribute $\frac{0.005}{0.365} \times 47.9 \times 10^{-6} = 0.7 \times 10^{-6}$, which will be opposite in character to the diamagnetic anisotropy of calcite. The gram molecular diamagnetic anisotropy of calcite will therefore, be diminished by this amount. In fact, the observed changes of anisotropy are of this order. The presence of the other isomorphous carbonates such as $MgCO_3$ in calcite may also have a little influence on the crystal anisotropy, since, when Mg^{++} replaces Ca^{++}, the environment of the (CO_3) group changes to some extent owing to the different ionic sizes of Mg^{++} and Ca^{++}.

It should be pointed out that the presence of iron is not sufficient to account for the diminution of the anisotropy completely. As Stenger has pointed out, it is possible that even pure specimens of calcite may show slight deviations of diamagnetic anisotropy due to peculiarities of individual crystals. Therefore calcite seems to be unsuitable for use as a standard substance in anisotropy determinations.

5. *Diamagnetic Anisotropy and Crystal Structure*

The next important point to be noted is that the diamagnetic anisotropy of aragonite is definitely higher than that of calcite. The significance of this difference has not been so far discussed at all although Voigt and Kinoshita have noticed this difference experimentally. It is now known that the powerful electrostatic fields in crystals produce considerable deformations in the ions, and as a result, the electronic configuration of the ion in the crystal lattice might differ considerably from that of the ion in the *free* state. The deformation will depend on a number of factors, such as the nature of the surrounding ions, the charges they carry, and their relative positions governed by the character of the crystal lattice. Goldschmidt[15] (1926) has pointed out how the distances between the atoms in polyatomic ions in crystals will depend on the nature of the other ions in the lattice. For instance, small differences in the N–O distances of the NO_3^- ion in sodium nitrate and lithium nitrate may be expected due to the stronger polarising effect of the Li+ ion. These effects are, however, found to be too small to be detected experimentally by X-ray analysis But the ionic deformations may be expected to affect their anisotropy, whether magnetic or optical, markedly

Although deformations of the ions in crystal lattices exist, they do not appear to have any profound influence on the ionic diamagnetic *susceptibilities* It has been found that in the case of most simple ions having electronic configurations of the rare-gas type, the calculated and experimental values obtained for solid salts do not differ from each other to any great extent, thus indicating that the additive law is approximately valid Careful measurements of the diamagnetic susceptibilities have been made by Brindley and Hoare[16] (1935) and Kido[12] (1932) for the alkali halides, and by comparing the experimental values of ionic diamagnetic susceptibilities, with the theoretical values deduced by various workers, it has been found that large deviations occur only in one or two cases

But although the influence of neighbouring ions, in crystals, on ionic diamagnetic *susceptibility* may be of the order of a few per cent only at the most, the influence on diamagnetic *anisotropy* can be considerable Considering the case of the (CO_3) group, we note in the first place that the anisotropy is only about one tenth of the mean susceptibility In calcite, the (CO_3) group is surrounded by six Ca++ ions, arranged about it in an approximately octahedral fashion. The influence of these six cations will produce a deformation of a certain character depending upon the symmetry of their arrangement Now, if the arrangement of the cations relative to the anion is changed, the character of the deformation of the anion also undergoes a corresponding change. Such a change may be expected to produce no appreciable change in the total susceptibility of the group, but if the change of deformation is of a highly anisotropic character, a significant difference of diamagnetic anisotropy may be expected Compared to the total susceptibility, the change may be small, but compared to the feeble anisotropy, it will be quite large In fact, by the delicate methods now available for determining feeble diamagnetic anisotropies, we can easily detect these differences and study the influence of environment on the diamagnetic anisotropy of (CO_3) and similar groups

In aragonite, there is a staggering of the (CO_3) groups to one side in the (100) plane (Bragg[17], 1937), as a result of which, the (CO_3) groups are nearer to one set of calcium atoms than another This should produce a deformation of the (CO_3) group sufficient to alter its diamagnetic anisotropy considerably Experimentally, we find that, the anisotropy is increased The asymmetric character of the new arrangement of the cations also, presumably, accounts for the slight anisotropy of the crystal in (001) plane which, in fact, is to be attributed to the (CO_3) group itself losing its trigonal symmetry owing to change of environment Evidence for such distortion is available from infra-red analysis of molecular structure also (Rawlins and Rideal[18], 1927) where the doubling of the reflection maxima due to (CO_3) group has been attributed to a distortion of the group in its own plane

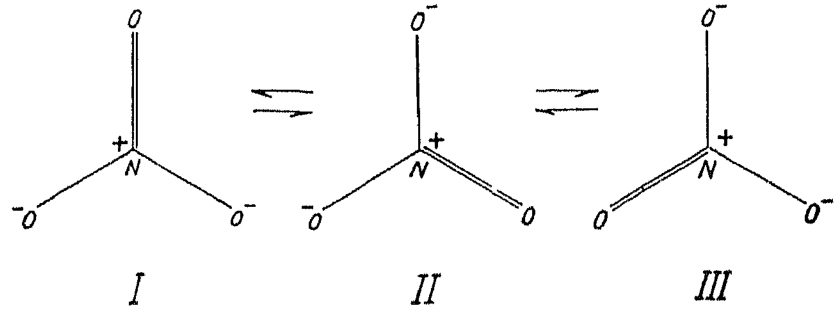
Thus the altered character of the environment of the (CO_3) group in aragonite, in the first place, affects the anisotropy (K_1–K_3) of the ion and secondly introduces a slight anisotropy in its own plane such that $K_1 \neq K_2$ (K_1, K_2 being as usual, susceptibilities in the plane, and K_3 that perpendicular to the plane of the ion) A similar behaviour of the (NO_3) group is observed in sodium and potassium nitrates, respectively In general, we see that the anisotropy of the (CO_3) and (NO_3) groups in the aragonite type of structure is greater than that in the calcite type

6. *Comparison between the Diamagnetic Anisotropy of (NO_3) and (CO_3) Groups*

The remarkable difference in the diamagnetic anisotropy of nitrate and carbonate groups is noteworthy. The $(NO_3)^-$ and $(CO_3)^{--}$ ions are very similar in structure, each consisting of 24 valence electrons The C–O distance of (CO_3), in calcite, is 1 31 A°, whereas the N–O distance of (NO_3) is 1.21 A° in sodium nitrate. Thus the

(NO$_3$) group, in sodium nitrate, is actually smaller than the (CO$_3$ group in calcite On the other hand, the diamagnetic anisotropy o (NO$_3$) is seen to be nearly one and half times that of (CO$_3$) Th reason for this has to be sought for, either in the intrinsic structure o the ion itself or in the influence of the environment

The structure of (NO$_3$) and (CO$_3$) groups are now fairly wel established (Bragg[21], 1937) Each group consists of a central nitroge or carbon atom as the case may be, with three oxygen atoms at th corners of an equilateral triangle, all the atoms lying in the sam plane The nature of the bonds in such structures has been th subject of much discussion by Slater, Pauling and others It is no generally accepted that these ions belong to the class of conjugate structures like the aromatic ring-shaped organic molecules in whic there is 'resonance' (Sidgwick[19], 1937) Fig 8 shows the (NO structure as understood at present



(The CO$_3$ structure is obtained by substituting C for N+ in the above scheme)
FIG. 8

There is resonance between I, II and III, and the diamagneti anisotropy is due to the conjugation of these structures (Lonsdale 1938) The only difference that we can notice in the structures that, whereas there is one co-ordinate bond in (NO$_3$)$^-$, the bonds (CO$_3$)$^{--}$ are all of the covalent type It is not immediately obvio how this can give rise to the observed enhanced diamagnetic anisotropy Bragg[21] (1924) has explained the greater birefringence of th (NO$_3$)$^-$ ion as compared to that of the (CO$_3$)$^{--}$ ion, as being due to th closer proximity of the oxygen atoms in the former, due to which, th mutual actions of the induced electric dipoles are stronger A similar argument does not seem to hold good in the magnetic case since the induced magnetisation is extremely feeble in diamagnetics N Elliot[22] (1937) has pointed out that the smaller N–O distance in (NO_3) is most probably due to the fact that the central nitrogen atom is positively charged and hence, owing to the strong attraction between the positive and negative changes, the atoms are drawn closer together It is possible that the electronic configuration of the (NO_3) ion, has a flatter shape than in (CO_3), on account of the presence of the positive charge This can partly account for the enhanced diamagnetic anisotropy since, if the electronic configuration assumes a flatter shape, the difference between its projected mean square radius on two planes, parallel and prependicular to the plane of the ion respectively, will be greater, and hence the diamagnetic anisotropy also will be correspondingly great

There is possibly also the influence of the environment as a contributing factor The sodium ions surrounding the (NO_3) group in sodium nitrate are singly charged, whereas the calcium ions surrounding (CO_3) in calcite are doubly charged The deformations produced on the ions may, therefore, be expected to be quite different in the two cases The distortion produced on the (CO_3) group should be sufficiently great to decrease its anisotropy considerably But although this effect might be a contributing factor, the character of the valency bonds in (NO_3) being different to some extent from those in (CO_3), it is most likely that the intrinsic diamagnetic anisotropy of the (NO_3) group is higher than that of the (CO_3) group

7. Calculation of Diamagnetic Anisotropy of the (NO_3) Group

So far, no quantitative theoretical computations of the diamagnetic anisotropy of carbonate and nitrate groups have been attempted, in view of the complexity of the problem

The large molecular diamagnetic anisotropy of the aromatic ring-shaped organic compounds like benzene and napthalene, to which attention was first drawn from investigations on light scattering and magnetic double-refraction by Raman and Krishnan[23] (1927) have been quantitatively explained recently by Pauling[24] (1936), Lonsdale[25] (1937) and London[26] (1937) independently. Pauling's theory is based on semi-classical considerations, while the more complete theory of London is developed from the standpoint of quantum mechanics. According to Pauling, the diamagnetic anisotropy of benzene is due to six L-electrons which describe large orbits along the circumference of the ring in a magnetic field. These electrons are assumed to contribute to the diamagnetic susceptibility perpendicular to the plane of the molecule only, and make no contribution parallel to the plane. Hence the large anisotropy. The author has here attempted to calculate the diamagnetic anisotropy of the (NO_3) group on similar lines.

The problem in the case of the nitrate ion is more complicated. Of the 24 valence electrons in the ion (the K electrons being left out of account since their contribution to the susceptibility, is comparatively negligible) a certain number may be assumed to make a normal contribution to the susceptibility, (corresponding to orbital wave functions symmetrical with respect to reflections in the plane of the ion) and the rest to contribute to the susceptibility perpendicular to the plane of the ion only, having antisymmetric orbital wave functions. The latter may be regarded as being common to the whole ion just as six L-electrons in benzene can be regarded as being common to the whole molecule. In order to understand the character of the orbits which these electrons describe in a magnetic field, it is necessary to know their probability distribution function. It may be postulated for purposes of calculation that the probability distribution function has got a large value only in two regions, more or less disc-shaped, one above and one below the plane of the ion. In these regions the potential function representing the interaction of an electron with the rest of the ion, should be such that the electron can easily and freely pass from the field of one atom to that of another. Assuming an electronic configuration for the (NO_3) ion described above, the ctrons responsible for the anisotropy may be regarded as being ead over two disc-shaped regions of radii equal to the N-O tance If n is the number of these electrons, then according to the ih expression we have,

$$\chi_{elec} = -\frac{Ne^2}{4mc^2}\,\overline{\rho^2}$$

$$\text{Hence } (\Delta\chi)_{NO_3} = -\frac{nNe}{4mc^2}\int_0^a 2\pi\sigma\rho^3 d\rho$$

ere 'a' is the distance from N–O and σ is the density of electron tribution in the disc-shaped region such that $\pi a^2\sigma = c$, assuming a form distribution On integrating, we get

$$(\Delta\chi)_{NO_3} = -\frac{nNe^2}{4mc^2}\,\frac{a^2}{2}$$

ien $n = 2$, we get $(\Delta\chi)_{NO_3} = 6\ 24 \times 10^{-6}$, on substituting the numerical ues of the various constants in the expression ($a = 1\ 21$ A°U) This ems to agree very well with the experimental value $6\ 15 \times 10^{-6}$ per im ion of (NO_3) That the probable value of n should be 2 is also ggested by the structure of the ion shown in Fig 8 as well as by alogy with the case of benzene, in which there are three double nds whereas there is only one in the nitrate ion

The above calculations are only tentative, but they are instruc-e in so far as they give an idea of the probable number of sonance' electrons in the (NO_3) group and the general character of eir distribution

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CHAPTER III

MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES

Introduction

We have seen that magne-crystallic action provides a useful method of determining the orientations of the molecules in diamagnetic crystals, especially in crystals of organic aromatic benzene derivatives Just as a crystal is an aggregate of ions or molecules regularly arranged in the crystal lattice, there are naturally occurring substances which are known to be aggregates of minute crystals in a more or less regular sort of arrangement If the individual crystals are themselves anisotropic, one should also expect the aggregate to show magnetic anisotropy, the magnitude of which will depend upon the orientation of the crystallites in the substance In a series of investigations, the author has studied the magnetic anisotropy of several naturally occurring substances, with a view to establish a method of finding crystallite orientations by magnecrystallic action Mother-of-pearl, was examined first, and the orientations of the aragonite crystals could be determined very easily, and the results were found to agree quite satisfactorily with those of X-ray and optical investigations Several molluscan shells, egg-shells, and wood, have been next examined and interesting results have been obtained as will be seen later, regarding their structural peculiarities

Diamagnetic Anisotropy of naturally occurring substances in relation to their structure

If, in a naturally occurring substance, there is perfect arrangement of the crystallites just as the units in a crystal lattice, the magnetic anisotropy of the substance will exactly correspond to that of the individual crystals (Here we can ignore the mutual interactions of induced magnetic moments, since, in diamagnetics, these will be negligibly small) Many mineral crystals have got a mosaic structure, as has been inferred from X-ray analysis, and the approach to a perfect arrangement is attained only in such The diamagnetic anisotropy of the mosaic will, in general, be indistinguishable from that of the single crystal Such ideal perfection is, as a rule, never found in built-up aggregates like mother-of-pearl, bone, teeth, wood or egg-shells, produced by living organisms, and there is considerable error of orientation The effect of this will be to minimise the diamagnetic anisotropy of the substance Usually, the crystallites may be arranged in any one of the following ways —

(a) Regular arrangement, with only a slight error of orientation of the three crystallographic axes The magnetic anisotropy of the substance here approximates to that of the single crystal.

(b) One of the crystallographic axes of the crystallites more or less parallel, the other two having random orientations For instance, the '*c*'–axes of the crystallites might have a definite parallel orientation, while the '*a*' and '*b*' axes may have random orientations in the aggregate As a result, there will be no diamagnetic anisotropy of the substance in the plane perpendicular to the '*c*'–axis of the crystallites

(c) Completely random orientation of all the axes of the crystallites In this case, the substance will be isotropic, although the individual crystallites may be highly anisotropic magnetically

(d) There are special cases of crossed alignment of the crystals in alternate layers This is found in some shells In one layer, the crystal might be pointing all in one direction, while in the next, the crystals may have a different orientation. Such cases can be investigated only with the help of the polarising microscope, although the magnetic data might give a general idea of the character of the crystal orientations

Since the shells of molluscs afforded a convenient material for study to test the validity of the magnetic method, they were examined first The measurements have been later extended to egg-shells The magnetic data obtained from wood and wood-cellulose have then been employed to determine the directional magnetic properties of cellulose.

1. MOTHER OF PEARL

Mother of pearl is the nacreous substance which forms the ide layer of the iridescent shells of molluscs It consists essen- lly of aragonite (calcium carbonate) crystals which are held together an organic substance known as conchyolin, and which form iodic stratifications giving rise to the characteristic property of descence Optical and X-ray investigations have indicated that the ystals of aragonite are arranged more or less regularly so as to ild up the laminated structure A detailed examination of the cre of iridescent shells under the polarising microscope has been rried out by Schmidt[1] (1924) The structural peculiarities of shells ve also been described in detail by Boggild[2] (1930) in his important moir on the structure and optical properties of molluscan shells

The nacreous layer in the shell is found in the three principal isses of molluscs, namely, the Bivalves, the Gastropods and the phalopods The magnetic studies have been carried out on the creous layer of the shells of some typical members of these isses

From among the Bivalves, the nacre of the shells of *Aviculi- e*, *Pinnidæ*, *Vulsellidæ*, and *Mytilidæ* have been taken up for amination The family of *Aviculidæ* includes the Pearl-oyster argaratifera) and the Hammer-oyster The Pearl-oyster is common the seas near Ceylon, where pearl fisheries are carried on In dian waters, *Pinna bicolor*, belonging to the family of *Pinnidæ*, also very common *Vulsella rugosa*, an oblong shell without ears, the most common member of *Vulsellidæ* in the Indian ocean *ytilus Viridis* is also abundantly found in the Indian coast and is cognised by its striking iridescence

The Gastropods comprise the following families, which yield other-of-pearl *Pleurotomariidæ*, *Haliotidæ*, *Stomatidæ*, *Turbidæ*, *Delphinulidæ*, *Trochidæ*, *Umboniidæ* Of these, *Haliotis*, *urbo* and *Trochus* were available for examination These are com- on in India, especially, *Haliotis varia* The Californian specimen iown as *Abalone* is remarkable for its vivid iridescence. The *Turbo* and *Trochus* are some of the commonest shells to be met with in South India and the coastline abounds in these

Of the Cephalopods, *Nautilus pompilius* is very well-known The nacre of the shell is rather thin and brittle but highly iridescent t contains a higher percentage of conchyolin than the nacre of other shells

A detailed structural examination of the shells under the polarising microscope has been made by W J Schmidt[1] (1924) and by Boggild[2] (1930), and a summary of Schmidt's work is available in the book by F Haas[3] (1931) on the Bivalves According to Boggild, the nacreous structure is only one of a variety of other forms, such as the homogeneous ', ' the prismatic ', and ' the crossed lamellar ' The oliated structure characteristic of *Placuna placenta* or the window pane Oyster, consists of calcite instead of aragonite crystals

The molluscan shell consists essentially of three layers, the outer-most being the periostracum, consisting of conchyolin The econd layer is in most shells ' prismatic ' and in *Haliotis* ' grained ' The third and final layer is mother-of-pearl, which may be easily eparated from the others by either mechanical means or by using hydrochloric acid to dissolve off the outer layers

As Schmidt has shown, mother-of-pearl consists of microscopically small, tablet-shaped crystals of aragonite which are regularly rranged in layers parallel to the surface of the shell, and are cemented together by conchyolin The platelets, so held together, form lementary laminæ and these are superposed on one another The ndividual platelets of aragonite are about 10 μ in diameter and about μ thick They are sometimes rounded in shape and sometimes bounded by straight edges The aragonite crystals are generally orientated with the '*c*'-axes normal to the elementary laminæ

Recently from a study of the optical properties of nacre, Raman[4] (1935) has drawn attention to the structural differences in the hells of the three classes of molluscs S Ramaswamy[5] (1935) has also made an X-ray analysis of nacre in order to determine crystal-ite orientations

Nacken and Jager[6] (1926) and Michel and Riedl[7] (1926) have ved the diamagnetic anisotropy of nacre qualitatively, in con- on with the study of the differences between real and 'cultured' s The latter contain a small sperical inner core of mother-of- (F Haas[8], 1931) and as a consequence, take up a definite tation in a magnetic field unlike real pearls which do not show preferred orientation The individual aragonite crystals of er-of-pearl are themselves anisotropic, as shown by Voigt and hita[9] (1907), and since X-ray and optical investigations have led regularity of arrangement of the crystallites in nacre, the vations of Nacken and Jager may be readily understood

ermination of the Diamagnetic Anisotropy of Nacre

his was done by the method of oscillations The details have given earlier For purposes of investigation, the nacre of the was carefully removed and some good specimens free from ts and discolourations were selected The pieces were further ically tested and found to be free from paramagnetic impurities were also cleaned beforehand with dilute acid to remove e impurities

The important directions in nacre are (1) the direction of the of growth and (2) the normal to the laminar plane When pre- g the specimens of rectangular shape, the planes of the pieces ground parallel to the laminar plane, and the length of the igle made parallel to the lines of growth In this way the ation of the crystallites with respect to the lines of growth and minar plane could be determined

nitially, the nacreous substance was tested in the magnetic field ound to be diamagnetic in all cases Further, the direction ximum diamagnetic susceptibility was found to be perpendi- to the plane of the laminæ

Evidently, this direction coincides with one of the principal otibilities of the substance, the other two being in the laminar The anisotropy was determined for three modes of suspension

First of all, the plane of the laminae was kept horizontal and the orientation of the specimen as well as the magnitude of the anisotropy determined. The direction of greatest diamagnetic susceptibility in the plane will set itself perpendicular to the field and that of least, will be parallel to the field. These two mutually perpendicular directions were noted and the specimen was suspended with these directions vertical respectively.

The absolute susceptibilities were determined by Rabi's (1927) null method, using a saturated solution of potassium iodide. Although the diamagnetic susceptibility of pure aragonite is too high to be determined in this way, in the case of the shells, the diamagnetic susceptibilities were found to be sufficiently low. The volume susceptibilities of the solutions were found by Quincke's U-tube method in each case. The concentrations of the patassium iodide solutions were also incidentally determined in order to find out whether saturation point was reached in any case.

Results

The following notation has been adopted. χ_1', χ_2' denote the principal susceptibilities in the laminar plane ($\chi_1' > \chi_2'$ algebraically) and χ_3' denotes that perpendicular to the laminar plane. The orientation of the plane of the nacreous layer in the magnetic field is with respect to the direction of the lines of growth. In Table I, the observed values for the nacre of *Margaratifera margaratifera*, *Turbo*, *Haliotis*, *Mytilus viridis*, *Nautilus pombilius*, *Pinna bicolor*, and *Vulsella rugosa* are given. The values represent the mean of several determinations with different specimens.

TABLE I

Class	Shell	Mode of Suspension	Orientation in the field	Specific diamagnetic anisotropy × 10^8	Remarks
Gastropod	*Turbo*	Laminar plane horizontal	Lines of growth had no definite orientation in the field for various specimens	$\chi_1'-\chi_2'=0.0_5$	Orientation of the axes of the crystallites in the laminar plane indefinite
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=5.6$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1'-\chi_3'=5.7$	
	Haliotis	Laminar plane horizontal	Orientation of the lines of growth indefinite for various specimens	$\chi_1'-\chi_2'=0.0_7$	Random orientation of the axes of crystals in the laminar plane
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=6.0$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1'-\chi_3'=6.1$	

Class	Shell	Mode of Suspension	Orientation in the field	Specific diamagnetic anisotropy × 10^8	Remarks
Bivalve	*M. Margaritifera*	Laminar plane horizontal	Lines of growth nearly perpendicular to the field in all specimens	$\chi_1'-\chi_2'=0.21$	
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=5.6$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1'-\chi_3'=5.7$	
	Mytilus Viridis	Laminar plane horizontal	Lines of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0.16$	
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=5.7$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1'-\chi_3'=5.8$	
	Pinna bicolor	Laminar plane horizontal	Lines of growth parallel to the field	$\chi_1'-\chi_2'=0.3$	
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=7.0$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1'-\chi_3'=7.2$	

Class	Shell	Mode of Suspension	Orientation in the field	Specific diamagnetic anistropy × 10^8	Remarks
Bivalve	*Vulsella rugosa*	Laminar plane horizontal	Orientation of lines of growth indefinite	$\chi_1' - \chi_2' = 0\ 1$	
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi_3' = 7\ 2$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 7\ 4$	
Cephalopod	*Nautilus pompilius*	Laminar plane horizontal	Lines of growth nearly perpendicular to the field	$\chi_1' - \chi_2' = 0\ 5$	
		Plane vertical and χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi_3' = 6\ 1$	
		Plane vertical and χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 6\ 4$	

TABLE II

Absolute Susceptibilities of nacre

Shell	χ_1' $-\times 10^6$ *(observed)*	χ_2' $-\times 10^6$ *(calculated)*	χ_3' $-\times 1$ *(calculat*
Turbo	0.29	0.29_1	0.35
Haliotis	0.28	0.28_1	0.34
M. Margaritifera	0.29	0.29_2	0.35
Mytilus viridis	0.29	0.29_2	0.35
Pinna bicolor	0.28	0.28_3	0.35
Vulsella rugosa	0.30	0.30_1	0.37
Nautilus pompilius	0.26	0.26_6	0.32

Density of Nacre

Shell	Density in gm/cm^3
Turbo	2.77
Haliotis	2.73
M. Margaritifera	2.78
Mytilus viridis	2.80
Pinna bicolor	2.82
Vulsella rugosa	2.75
Nautilus pompilius	2.62

Discussion

The results definitely show that in all cases the 'c' axes of the aragonite crystallites are orientated perpendicular to the elementary laminæ. For, we know that the direction of maximum diamagnetic susceptibility for aragonite is along the '*c*'–axis, which is also an axis of approximate magnetic symmetry. But although the orientation of the '*c*' axis is easily inferred, the orientations of the '*a*' and '*b*' axes are difficult to determine, since $\chi_b - \chi_a$ in aragonite is small. Besides, there are a few complications such as (1) differences in the curvatures of the elementary lamanæ in different directions, (2) the possibility of the laminar plane being not exactly parallel to the plane of the specimens and (3) natural irregularities in the elementary laminæ such as pits and elevations. We can, however, tentatively draw the following conclusions.

In *Turbo* and *Haliotis,* the '*a*' and '*b*' axes are orientated more or less at random in the laminar plane, so that the anisotropy is negligible. This result is verified by the X-ray analysis made by Ramaswamy (1935). The preferred orientation which he has found for *Haliotis* could not, however, be detected by the magnetic method, owing to the very large error in the orientations of the '*a*' and '*b*' axis which he has reported. In *M margaratifera* and *Mytilus viridis*, we find that, when the laminar plane is horizontal, the lines of growth are nearly perpendicular to the field. This should correspond to an alignment of the '*a*' axis of the aragonite crystals parallel to the lines of growth. In the case of *Pinna bicolor*, however, the '*a*' axes of the crystallites are orientated perpendicular to the lines of growth. The diamagnetic anisotropy of the nacre of *Nautilus pompilius*, in the laminar plane, is comparatively large. This may be due to a preferred tilting of the '*c*'–axis of the aragonite crystals in the direction of the lines of growth.

It will be noticed that the diamagnetic anisotropy of nacre is, in general, larger than that of pure aragonite. This may be due to an intrinsic anisotropy of conchyolin itself. Conchyolin belongs to the class of sklero-proteins with empirical formula $C_{30}H_{48}N_9O_{11}$. Recent work on the ring structure of proteins by Langmuir and others (1939) suggests that the conchyolin molecule may have a large diamagnetic anisotropy, just like benzene and its derivatives The regular arrangement of conchyolin molecules, in between aragonite crystals, in a quasi-crystalline manner, might well give rise to diamagnetic anisotropy. This hypothesis could not be tested out experimentally since, it was found to be very difficult to isolate conchyolin from nacre without disturbing its structure

2. *MOLLUSCAN SHELLS*

The success of the previous experiments with mother-of-pearl encouraged the author to investigate further the general structure of molluscan shells The magnetic measurements were extended to the shells of *Placuna placenta, Pinna bicolor, Meretrix casta, Mactra lurida, Mactra hebbalensis, Vulsella rugosa* and *Turbinella pyrum,* some of which are purely calcitic, while others consist of both calcitic and aragonitic layers

Placuna placenta is the well known species of window-pane oyster found in the Indian ocean The shell possesses a pearly lustre, is faintly iridescent, and consists of calcite only It has got a 'foliated' structure and cleaves into thin plates like mica When examined under the microscope, numerous fine lines (*streifen*) can be seen on the foliae, parallel to one another, the surface resembling a fibre-mat The leaves easily break into small strips parallel to these lines By examination under the polarising microscope, W J Schmidt[1] (1924) has found that the thin laminae show extinction in the direction of the fine lines. Conoscopically examined, they always gave a negative uniaxial eccentric interference pattern This indicates that the optic axes of the elementary crystals are inclined to the plane of the laminæ Schmidt has also found that the smallest elements of the shell are extremely thin leaf-like structures, about 1μ thick, 5μ wide and 100μ long They are arranged with their lengths parallel to the fine lines on the laminæ Their accurate crystallographic determination was not, however, found to be possible Boggild[2] also s mentioned the inclination of the optic axes of the crystals to the minar plane

The shell of *Pinna bicolor* consists of two layers, an upper smatic calcitic layer and a lower aragonite nacreous one The creous layer, which shows bright iridescent colours, can be easily pped off, and is usually very thin. Schmidt has isolated the tiny sms of calcite in the upper layer and has found that the optic axis ncides with the prism axis Each prism is a single crystal of lcite arranged in the shell with its axis normal to the shell surface. has also been found that there is very little difference in optical aracteristics among the different species of *Pinna.*

The common feature of the shells of the *Mactra* species cording to Boggild, is the crossed lamellar concentric layer This , however, in many cases irregular *Mactra lurida* is a white ragonite shell with a violet coloured patch in the middle The lowest orcellanous layer was taken for examination, from both the white as ell as the coloured portions The shell of *Mactra hebbalensis* is ark in colour and very brittle.

Vulsella rugosa has got a very thin and fragile shell It onsists of an upper prismatic calcitic layer and an extremely thin acreous layer below The shell of *Meretrix casta* is hard and orcellanous in appearance The "Chank" is very well known in outh India[10] The shell is white and chalky in appearance, and onsists of several calcitic layers These were found to break easily long a particular direction in a somewhat similar manner as the leaving of crystals Only the lowest layer which appeared to be ranslucent was taken up for examination

Determination of the Diamagnetic Anisotropy

The shell specimens were prepared exactly as in the case of mother-of-pearl, similar precautions being taken By employing fine quartz fibres, very small bits of the shell a few milligrams in weight could be used.

The anisotropy was determined as usual for three modes of suspension First with the plane horizontal, and then with the χ_1'– and χ_2'– directions vertical respectively

Case of Inclined Orientation

An unusual feature was exhibited by the shell of *Placuna placenta* Here we have a case of inclined orientation, the trigonal axes of the calcite crystals making a definite angle with the plane of the foliae The angle of orientation may be easily deduced from the magnetic measurements, as the following considerations will indicate

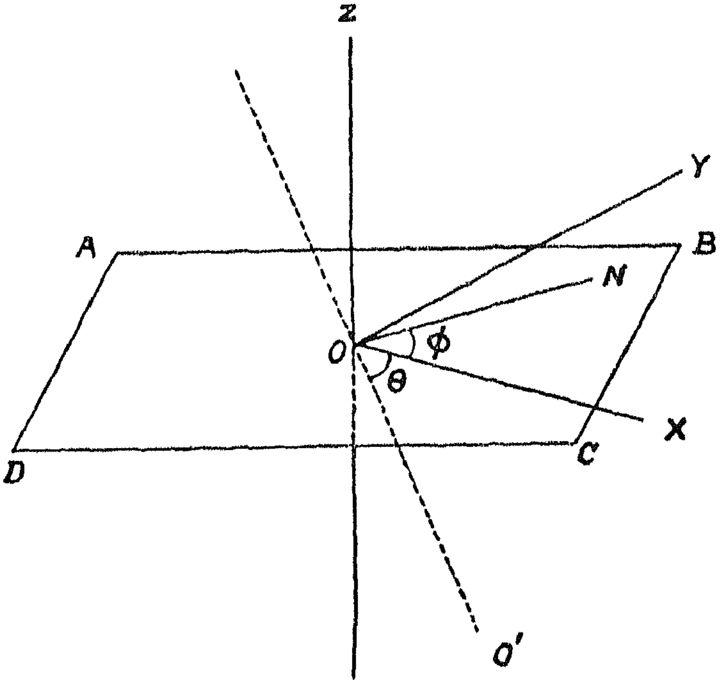


Fig 9

Let ABCD (Fig 9) represent the plane of the foliae and let OO′ be the direction of the trigonal axis of the calcite crystals inclined at an angle θ to the plane. Let a rectangular co-ordinate system be chosen such that the direction of the projection of OO′ on the plane is the X-axis OY in the plane represents the Y-axis If K_1 and K_2 are the magnetic susceptibilities along and perpendicular to the trigonal axis of calcite respectively* and if ON is any arbitrary direction in the plane, making an angle ϕ with OX,

$$\chi_{ON} = K_1 \cos^2 \theta \cos^2\phi + K_2 (\sin^2\theta \cos^2 \phi + \sin^2\phi)$$

$$\frac{d\chi}{d\phi} = (K_2 - K_1) \sin 2\phi \cos^2\theta$$

This will be zero when $\phi = 0$ or 90°

It is maximum numerically when $\phi = 0$

and is equal to $K_1 \cos^2 \theta + K_2 \sin^2\theta$

The minimum value of $\chi = K_2$

when $\phi = 90^\circ$.

OX and OY are thus the directions of maximum and minimum diamagnetic susceptibility in the plane The magnetic anisotropy in the plane

$$(\Delta\chi) = (K_1 - K_2) \cos^2\theta$$

The directions OX and OY can be easily located by suspending the shell with the plane horizontal in a uniform magnetic field and observing the orientation When the piece of shell is suspended with the OX-direction vertical, the orientation will be with the plane parallel to the field

$$\text{and } (\Delta\chi) = (K_1 - K_2) \sin^2\theta$$

When, however, it is suspended with the OY direction vertical, the plane will make an angle $(90^\circ - \theta)$ with the field

Hence, θ can be known

and $(\Delta\chi)$ will be $= (K_1 - K_2)$ in this case

The directions of OX, OY will correspond to χ_2' and χ_1' in our notation Hence, when the specimen is suspended with the χ_1'-direction vertical, the diamagnetic anisotropy will correspond to that of a single crystal of calcite

The results are shown in Table I

All the shells were found to be diamagnetic

---

*$K_1 > K_2$ in calcite, numerically

TABLE I

$\chi_1' > \chi_2' > \chi_3'$, *Algebraically*

Shell	Class	Mode of suspension	Orientation	Specific anisotropy ×10⁶ E M U	Remarks
Placuna placenta	Bivalve	(A) Plane of the shell-folia horizontal	Direction of the fine lines perpendicular to the field	$\chi_1' - \chi_2' = 0\ 8$	The optic axes of the crystals make an angle of 64° with the laminar plane and are inclined in the direction of the fine *streifen*
		(B) χ_1'-axis vertical	Plane made an angle of 26° with the field	$K_2 - K_1 = 5\ 2$	
		(C) χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 4\ 6$	
Pinna bicolor (*calcite layer*)	,,	(A) Plane of the shell folia horizontal	Indefinite	$\chi_1' - \chi_3' = 0\ 0_6$	Optic axis perpendicular to the shell plane
		(B) χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi_3' = 5\ 6$	
		(C) χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 5\ 8$	
Meretrix casta	,,	(A) Plane of the shell-folia horizontal		$\chi_1' - \chi_3' = 0\ 0_5$	Trigonal axis of the crystallites of calcite perpendicular to the shell plane
		(B) χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi' = 5\ 7$	
		(C) λ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \lambda_3' = 5\ 8$	

Mactra lurida	Bivalve	(A) Plane of the shell folia horizontal		$\chi_1' - \chi_2' = 0\ 0$	Trigonal axis of the crystallites perpendicular to the plane
		(B) χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi' = 5\ 7$	
		(C) χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 5\ 7$	
Mactra hebbalensis	Bivalve	(A) Plane of the shell folia horizontal	Line of growth nearly parallel to the field	$\chi_1' - \chi_2' = 1\ 7$	The values obtained with different specimens differed considerably. Those given are only approximate
		(B) χ_1'-axis vertical	Plane made an angle of about 15° with field	* $\chi_2'' - \chi_3'' = 6\ 2$	
		(C) χ_2'-axis vertical	Plane nearly parallel to the field	$\chi_1' - \chi_3' = 5\ 0$	
Vulsella rugosa (calcitic layer)		(A) Plane of the shell folia horizontal		$\chi_1' - \chi_2' = 0\ 1$	Trigonal axis of the crystals perpendicular to the shell plane
		(B) χ_1'-axis vertical	Plane parallel to the field	$\chi_2' - \chi_3' = 6\ 2$	
		(C) χ_2'-axis vertical	Plane parallel to the field	$\chi_1' - \chi_3' = 6\ 4$	
Turbinella pirum	Gastropod	(A) Plane of the shell folia horizontal	Line of cleavage parallel to the field	$\chi_1' - \chi_2' = 0\ 4$	Here also the values for different specimens differed by more than 15% and the orientation by about 10°
		(B) χ_1'-axis vertical	Plane made an angle of about 20° with field	$\chi_2'' - \chi_3'' = 5\ 3$	
		(C) χ_2'-axis vertical	Plane nearly parallel to the field	$\chi_1' - \chi_3' = 4\ 7$	

---

* χ_2'', χ_3'' refer to the directions of maximum and minimum susceptibility (algebraically) in the horizontal plane when the χ_1'-axis is vertical

4. Discussion

It is evident from the results that the shell elements are crystalline and regularly arranged to a greater or less extent.

In the case of *Placuna placenta* significant conclusions can be drawn since consistent results were obtained with several specimens. The optic axes of the small crystals are inclined to the laminar plane at an angle of 64°, and the inclination is in the direction of the fine lines seen on the thin foliæ A simple calculation shows that the trigonal axis in a single crystal of calcite makes almost the same angle (63°, 48′) with faces of the form [110] This evidently means that the long leaf-like elementary crystals of calcite have the direction of one of the three crystal axes, (which may be denoted as 'a_1', 'a_2' and 'a_3'–axes) lying along their lengths, the (110) planes being parallel to the laminar plane These crystals themselves are arranged with their lengths parallel to the direction of the fine lines on the foliæ

It is very likely, in view of the extreme thinness of the elements, that the (110) and ($\bar{1}\bar{1}0$) faces are well-developed in them and this peculiar crystal *habit* then accounts for the foliated structure of the shell also

We know that the prisms of calcite are orientated in the upper layer of *Pinna* with the prism-axis normal to the shell surface The anisotropy determinations show that the trigonal axes of the crystals are normal to the shell surface which means, that the optic-axes of the prisms coincide with the prism axes This agrees with the observations of Boggild

With *Mactra hebbalensis,* no consistent results could be obtained This is most probably due to considerable irregularity of structure The 'c'–axes of the aragonite crystals, in this case, seem to be inclined to the shell surface In *Mactra lurida,* the probable orientation of the aragonite crystals is with the 'c'–axes normal to the shell surface No great difference was found in the anisotropies of the white and coloured portions of this shell.

In the calcitic layers of the shells of *Meretrix casta* and *Vulsella rugosa,* the crystals are evidently orientated with the optic-axes more or less normal to the shell plane. In '*Chank*' however, an inclined orientation is present.

It may be noted that in the case of the calcitic layers of all the shells investigated, the values of the magnetic anisotropy are nearly the same as that of calcite. But in view of the irregularity in the arrangement of the crystals, which we should expect, the values ought to be lower, but actually they are some 20% higher. It is probable that here also, the cementing medium makes a contribution to the anisotropy due to a quasi-crystalline structure, as suggested earlier.

3. EGG SHELLS

The common egg-shell is a crystalline aggregate, consisting mostly of calcite prisms and the crystals in this case also are more or less regularly arranged, just as in the case of molluscan shells. Hence, it offers a substance well-suited for an investigation of its structure by magnetic methods.

Structure of Egg Shells

According to Stewart[11] egg-shell consists essentially of (1) a thin outer layer made of protein, (2) middle layer which constitutes 80% of the thickness of the shell of calcite crystals, with protein in the form of interlacing fibres, and of a small quantity of crystalline calcium phosphate, and (3) small knob-like formations of calcite and calcium phosphate constituting the inner 'mamillary' layer. Langworthy[12] gives the percentage composition of the shell as follows —

	Organic matter	Calcite	Magnesium carbonate	Calcium phosphate
Hen's egg ...	4.2	93.7	1.3	0.8
Duck's egg ..	4.3	94.4	0.5	0.8

Magnetic Anisotropy

Only the middle layer consisting almost entirely of calcite wa taken up for examination The specimens were cleaned with ver dilute HCl followed by distilled water and alcohol The result representing the mean of several determinations carried out with fou specimens of hen's egg and two of duck's, are given in table I Th specific anisotropy refers to the difference in the susceptibilitie parallel and perpendicular to the shell surface in the case of eg shells, and parallel and perpendicular to the optic axis in the case calcite The mean susceptibilities were measured by means of th torsion balance

It is seen that while the susceptibilities of the shells are almo the same as that of calcite, the values of the magnetic anisotropy ar found to be much lower These results are significant in the light the optical examination of egg shells under the polarising micros cope[3] It has been found that calcite is present in the form columnar prisms in the middle layer, and examination unde convergent polarised light of a tangential section of the shell, ha revealed that the optic axes of the prisms are inclined to the she surface Further, with parallel polarised light it has been found tha the extinction directions for the different prisms are differen indicating a random orientation in *azimuth* of the optic axe of the prisms relative to the shell-surface The magnetic measurements fit in very well with these findings

If the trigonal axes of the calcite crystals are inclined to th shell surface, and at the same time randomly orientated in *azimut* relative to the shell surface, we should, in the first place, expect comparatively smaller anisotropy in egg-shells relative to that o calcite, and besides, due to the randomness of orientation in azimut there should also be no anisotropy in the shell-plane The experimental facts are in full accord with these considerations An interesting feature of the results is that the anisotropy of hen's egg i definitely lower than that of duck's egg This would indicate tha

TABLE I

Units—c g s E M

Specimen	Specific Magnetic anisotropy $\chi_{\perp r} - \chi_{\parallel l} \times 10^8$	Mean susceptibility $- \times 10^6$	Remarks
Hen's egg ...	1 2 (1 0–1 4)	0 35	The anisotropy in the plane of the shells is practically negligible
Duck's egg	1 6 (1 4–1 9)	0 36	
Calcite	3 89	0 358	

The calcite crystals in the latter are orientated with their optic axes more nearly normal to the shell surface than in the former

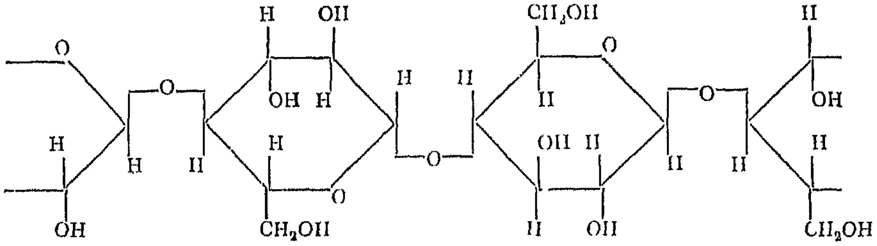
4. *WOOD AND ITS CONSTITUENTS*

In the light of the knowledge that we already possess concerning its structure and constitution, an extension of the magnetic studies to the case of wood should be expected to give results of considerable interest A knowledge of the magnetic properties of a universal substance like cellulose is still lacking, although many of its other physical properties such as double-refraction, fluorescence, specific heat, hygroscopicity, thermal conductivity, elasticity, etc, have been investigated in greater or less detail Wood-cellulose, in view of the fact that it can be isolated from wood without serious damage to its intrinsic structure, is particularly suitable for the study of magnetic anisotropy The author has studied the absolute diamagnetic susceptibility and anisotropy of wood and its major constituents, with a view to gain additional information regarding their physical structure, and to find out their directional magnetic properties

The Structure and Constitution of Wood

A knowledge of the structure of wood and its chemical constitution is essential for the interpretation of the magnetic data The relevant facts are briefly mentioned in the following pages[13] —

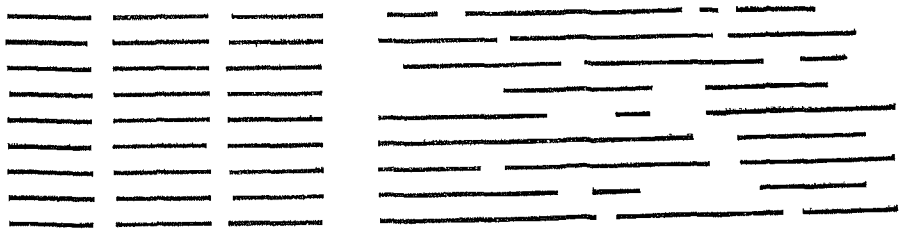
The major constituents of wood are cellulose, lignin and the hemicelluloses It is now known that cellulose is an ortho-glucosan, i e, glucose anhydride Its empirical formula is $(C_6H_{10}O_5)_n$ The molecule is made up of a chain of glucose residues linked by primary valence forces according to the following scheme (Fig 10)



Fragment of Cellulose Chain
Fig 10

Actually, the unit in the cellulose-chain is the cellobiose residue, as will be seen from the arrangement of the glucose residues in the chain It has been shown that all plant celluloses, regardless of their source, are identical The cellulose in wood is found in the cell-wall of the tracheid, and is 'crystalline' With the fibre-axis placed perpendicular to a beam of monochromatic X-rays, wood gives a fibre pattern characteristic of cellulose An examination of teakwood by X-rays has been made by the author[14] (1937) and reported in a communication in which details regarding the character of the patterns, and the information they yield about the structure of wood-cellulose are given The 'crystal structure' of plant cellulose has been the subject of extensive investigations by Polanyi, Herzog, Sponsler and Dore, Astbury, Andress, Meyer and Mark, E Sauter, Meyer and Misch and Clark[15]. There is still considerable difference of opinion as regards the dimensions of the unit cell and atomic positions, although the recent work of Gross and Clark[16] seems to support the original structure proposed by Meyer and Mark. But there is general agreement regarding the parallel orientation of the long chain molecules more or less in the direction of the fibre-axis Without laying special emphasis, in the present uncertain character of the X-ray analysis, on the cell dimensions or the crystal parameters, we can definitely say that the length of the cellulose chain is parallel to the '*b*' axis of the 'crystallites' which possess monoclinic symmetry and are arranged spirally on the cell-wall (the spirals being steep enough to be almost straight in fibres like ramie and comparatively flat in cotton, wood, etc) with their '*b*'-crystallographic axes orientated more or less along the spiral

The character of the submicroscopic crystalline elements in cellulose is still in the course of being elucidated Meyer and Mark at first came to the conclusion from a critical examination of the available X-ray data, that these were discrete micelles of dimensions 600×50 A° approximately But it was shown later on that X-ray analysis can give no decisive answer to the question On the basis of their physico-chemical investigations, Staudinger and his collaborators[17] have favoured the view that the submicroscopic unit is the macro-molecule and not the micelle A parallel arrangement of the macro-molecules, bound together by secondary valence forces to form a bundle, constitutes the cellulose lattice The actual difference between the macro-molecular and micellar schemes, is brought out in the figure shown below (Fig. 11)



Molecular Lattice Macro-molecular Lattice

FIG 11

But neither the macro-molecular nor the micellar theory has been able to account for the various physical and physicochemical properties of cellulose satisfactorily. Recently, Frey-Wyssling[18], Sauter[15], Kratky and Mark[19] and others have attempted to arrive at a more rational hypothesis Without entering into a detailed discussion of the various theories, it may be said that the following, incorporating the ideas of Frey-Wyssling is a fairly satisfactory picture of the internal architecture of the cell-wall in cellulose fibres In the first place, we have the fibrils, running more or less along the fibre-axis, which can be made visible under the microscope[20] These consist of a parallel arrangement of the long-chain molecules of cellulose so placed, that there are localised regions of perfect orientation, (Kratky and Mark, 1937) which may be said to correspond to the crystalline micelles of the old theory, the forces between the molecules being of the Van der Vaals type in these regions The dimensions of these micellar regions may be variable over a wide range, sometimes comprising the whole fibril. These 'crystallised' regions are interspaced by either air cavities or by cementing matter like the pectins and the hemicelluloses. *The important fact to be noticed is that the regularity of arrangement of the cellulose chains in the fibre with their lengths parallel to the fibre-axis, should give rise to magnetic anisotropy if the individual molecules are themselves anisotropic and vice versa, the study of the magnetic anisotropy of wood-cellulose should lead to a knowledge of the directional magnetic properties of the cellulose molecule* It should be pointed out, however, that from a study of the diamagnetic anisotropy of wood, as such, it will not be possible to determine the two principal susceptibilities of the cellulose molecule perpendicular to its length, since, there is a random orientation of these in azimuth in the wood fibre.

Lignin is present mostly in the primary layer of the cell-wall of the wood-fibre known as the middle lamella The constitution and the morphology of lignin have been the subjects of extensive investigations[21] Examination by physical methods like microscopy, X-ray analysis and polarisation-optics, suggests that lignin is amorphous in tructure. Various hypotheses have been put forward regarding the manner of combination of cellulose and lignin. One view is that they re chemically combined with each other, but the idea that lignin is dsorbed on cellulose seems to be more plausible in the light of the nvestigations by the physical methods mentioned above.

The hemi-celluloses[22] are the anhydrides of hexose and penose sugars: xylan, araban, mannan and galactan give on hydrolysis ylose, arabinose, mannose and galactose respectively. Not much s known concerning their physical structure and manner of combinaion with cellulose and lignin.

Experimental Details

The Experiments were all confined to teakwood, the structure of which had been previously examined by the author by X-ray analysis. The wood specimens were subjected to extractions with various solvents and subsequent chemical treatment, in order to solate the major constituents. The X-ray analysis was made incidentally to discover whether any radical structural changes had occurred during the extractions and chlorination. It was found that specimens taken from the less compact layers were subject to hanges, while those from the most compact layers were practically unaffected. The anisotropy measurements were, therefore, made on specimens obtained from the most compact dark-brown layer of the annual rings. The specimens were prepared for examination as described below :—

(1) *Raw wood*.—Washed clean with 5 per cent HCl and warm water to remove surface impurities, and dried at 102–104° C for 6 hours.

(2) Extracted with alcohol-benzene mixture for 24 hours and hen with boiling water for 6 hours and finally dried for 12 hours at 102–104°C.

(3) Wood extracted as in (2) was treated with 5 per cent solution of NaOH in the cold for 48 hours. Washed several times

with dilute acetic acid and then warm water and finally dried for 12 hours at 102-104°C.

(4) Treated with 72 per cent sulphuric acid in the usual way for 36 hours to obtain lignin, which retained the shape and continuous structure of the original sample of wood.

(5) Wood, after extraction with alcohol-benzene was chlorinated by the Cross-and-Bevan method to obtain wood-cellulose. The apparatus employed was similar to the one used by Sieber and Walter with a few minor modifications. The procedure described by Dore[23] (1920) was adopted with all the necessary precautions. Particular care was taken to see that the samples did not get distorted in shape during chlorination. The prepared samples were also subjected to X-ray analysis. Two samples of wood-cellulose were prepared, one by partial, and the other by complete chlorination. The specimens were dried in the oven for 12 hours at 102-104°C.

(6) Wood-cellulose was treated with 17.5 per cent NaOH in order to get α-cellulose according to the procedure described by Schorger[24].

Sampling of wood for magnetic measurements—The wood samples were taken in the form of shavings about 0.5 mm thick, from which pieces 5 × 3 mm were cut out for the anisotropy measurements. For measurements of absolute susceptibility, the samples were taken in the form of powder.

Proximate Analysis of Wood

The wood samples, prepared as described before, were all analysed for the determination of their cellulose and lignin contents. The hemi-celluloses and the rest were only indirectly estimated.

It must be stated beforehand that, of all the various methods which have been suggested for the determination of the major constituents and groupings in wood, there is scarcely one which can be said to be entirely satisfactory. This, no doubt, is due to the inherent difficulties involved in dealing with a highly complicated substance like wood The older methods for the determinations of cellulose, lignin and the hemi-celluloses have been continually refined, modified and standardised However, for purposes of the magnetic investigation a high order of accuracy in analysis is not necessary, especially in view of the fact that the samples have to be taken in the form of shavings about 0 5 mm thick for the anisotropy measurements, whereas the standard procedure in wood analysis is to start with saw-dust which passes through 80 but not 100 mesh Therefore, the recent refinements and improvements in the estimation of lignin, etc, have not been adopted The analytical procedure is outlined below and the results should be sufficiently accurate for interpreting the magnetic data

Lignin—The lignin content in the various samples was estimated by treatment with 72 per cent sulphuric acid in the usual way[21]

Cellulose—Cellulose in wood was determined according to the analytical procedure described by Dore and already referred to earlier

α-Cellulose in wood-cellulose was also determined by treatment with cold 17 5 per cent NaOH as described by Schorger

Hemi-Celluloses—A direct determination of the hemi-cellulose content was not attempted These were grouped with small quantities of the other miscellaneous substances present and the whole indirectly estimated

Determination of Magnetic Anisotropy

The anisotropy of wood is comparatively feeble and the technique has to be made specially sensitive. The torsional method was employed using very fine and fairly long (20–30 cm) quartz fibres Only $\chi_{\perp r}-\chi_{\parallel l}$ was found, since, in the case of wood, the anisotropy in the plane of the cross-section of the fibre, is negligible in all cases and of no special significance ($\chi_{\parallel l}$ is the diamagnetic susceptibility along the fibre-axis, and $\chi_\perp$ is that perpendicular to the fibre axis)

The average dimensions of the specimens employed were 5 × 3 × 0 5 mm

Absolute Susceptibilities

The absolute mass susceptibilities were determined by the torsion balance The wood samples were all used in the form of fine powder dried at 102 104° C for 12 hrs, and the susceptibilities compared with that of pure water

Results

Raw wood gave somewhat inconsistent values of anisotropy probably due to occluded impurities After extraction with alcohol-benzene and boiling water, consistent values were obtained, the maximum discrepancy noticed being 11 per cent In all cases, at least 10 independent determinations were made and the mean value taken The results of the magnetic anisotropy measurements are given in Table I Table II gives the values of absolute susceptibilities and Table III the results of the proximate analysis A summary of results is given in Table IV

Discussion of Results

An examination of Table IV shows that the anisotropy is more or less proportional to the cellulose content of the specimens It apparently does not depend on the amount of lignin present α–Cellulose has the maximum specific anisotropy whereas lignin isolated by treatment with 72 per cent sulphuric acid does not show any. The 'crystalline' element responsible for the magnetic anisotropy appears to be cellulose only

The magnetic measurements, however, do not rule out the possibility of lignin being present as crystallites which are randomly orientated But X-ray analysis shows that isolated lignin gives only a 'liquid' pattern characteristic of an amorphous substance.[25]

TABLE I

Specific Magnetic Anisotropy in C G S—E M Units

Specimen of wood	Mode of Suspension	Orientation in the field	Specific magnetic anisotropy $(\Delta\chi)=\chi_{\perp r}-\chi_{\parallel l}\times 10^{8}$
(1) Extracted with alcohol, benzene and boiling water	Fibre-axis horizontal	Fibre-axis perpendicular to the field direction	0 39
(2) After treatment with 5 per cent NaOH	,,	,,	0 40
(3) Lignin prepared by treatment with 72% sulphuric acid	,,	Nil	0 00
(4) (a) after partial chlorination	,,	Fibre-axis perpendicular to the field direction	0 68
(b) after complete chlorination	,,	,,	0 84
(5) α-Cellulose	,,	,,	0 92

TABLE II

Absolute Mass Susceptibilities

(C G S—E M Units)

		Wood specimen	$\chi_{(\text{mean})}$ $- \times 10^{6}$
(1)	Teakwood	Most compact layer of annual ring	0.44
(2)	Teakwood	Least compact layer of annual ring	0.43
(3)	Teakwood	After extraction with alcohol-benzene and boiling water	0.47
(4)	Teakwood	After treatment with 5 per cent NaOH	0.45
(5)	Teakwood	Lignin prepared by treatment with 72 per cent sulphuric acid	0.42
(6)	Teakwood	After partial chlorination	0.48
(7)	Teakwood	After complete chlorination—Cross and Bevan cellulose	0.503
(8)	Teakwood	α-Cellulose	0.506

The diamagnetic susceptibility of pure double distilled water was taken as -0.720×10^{-6}

TABLE III

Proximate Analysis of Teakwood

(Figures refer to percentage of oven-dry specimen taken)

Specimen	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-cellulose, *etc*, indirectly estimated %
(1) Teakwood extracted with alcohol-benzene and water	54 1	39 9	33 5	12 4
(2) Treated with 5 per cent NaOH	50 9	40 1	44 8	4 3
(3) After partial chlorination	82 8	59 3	14 7	2 5
(4) After complete chlorination Cross and Bevan cellulose		72 9		

TABLE IV

Summary of Results

Wood specimen	Absolute Susceptibility $-\times 10^6$	Specific Magnetic anisotropy $\chi_{\perp r}-\chi_{\parallel l}$ $-\times 10^8$	Cellulose %	α-Cellulose %	Lignin %	Remaining hemi-celluloses, etc , %	$\frac{(\Delta X)\times 100}{\%\text{ of total Cellulose}}$ $\times 10^8$	$\frac{(\Delta X)\times 100}{\%\text{ of }\alpha\text{-cellulose}}$ $\times 10^8$
After extraction with alcohol - benzene and boiling water	0 47	0 39	54	37	33	13	0 72	1 05
After extraction with 5 per cent NaOH	0 45	0 40	51	40	45	4	0 78	1 00
Lignin prepared by treatment with 72 per cent sulphuric acid	0 42	.	.		100			
After partial chlorination	0 48	0 68	83	59	15	2	0 82	1 15
After complete chlorination Cross and Bevan cellulose	0 503	0 84	100	73		.	0 84	1 16
α-Cellulose	0 508	0 92		100			..	0 92

There is also nothing indicative of 'crystalline' lignin in the X-ray patterns of wood obtained Examination of lignin under the microscope has not revealed any property characteristic of crystals Taken together, the X-ray, optical and magnetic investigations lead o the conclusion that lignin in its natural state has an amorphous structure

Ordinary wood-cellulose obtained by chlorination, is really a complex substance, and consists of what are known as the α, β and γ celluloses, distinguished from one another by their solubility in 17 5 per cent NaOH solution From Table IV we can see that the magnetic anisotropy of wood is essentially due to the α–cellulose in it It is also seen that treatment with 5 per cent NaOH, which removes a good part of the hemi-celluloses, leads to an increase in the value of $\frac{(\Delta \chi)\times 100}{\%\text{ of total cellulose}}$ The initial removal of the hemi-celluloses naturally means a decrease in the total cellulose, for wood-cellulose (prepared without pre-treatment with NaOH) contains as much as 20 per cent of the hemi-celluloses We may conclude from this that the hemi-celluloses like lignin do not contribute to the magnetic anisotropy In view of their gummy texture it is most probable that they are amorphous in structure

We also notice that the value of $\frac{(\Delta \chi)\times 100}{\%\text{ of }\alpha\text{-cellulose}}$ is less for α–cellulose than for Cross and Bevan cellulose This will mean that $(\Delta \chi)$ is greater for Cross and Bevan cellulose than can be accounted for by the presence of α–cellulose alone in it The inference is that the β and γ celluloses are also anisotropic just like α–cellulose and most probably possess the same 'crystalline' structure.

Magnetic Properties of the cellulose molecule—The diamagnetic anisotropy of cellulose in wood leads to important conclusions regarding the directional magnetic properties of the cellulose molecule The diamagnetic susceptibility in the direction of the fibre axis is seen to be maximum Since the cellulose chains are orientated with their lengths more or less parallel to the fibre-axis it follows that the *direction maximum diamagnetic susceptibility is along the chain-length* The values of $\chi_{\parallel r}$ and $\chi_{\perp r}$ can be easily calculated from χ and $(\Delta\chi)$ We have, $\chi_{\parallel r} = -0.514 \times 10^{-6}$, and $\chi_{\perp r} = -0.505 \times 10^{-6}$, for *α*-cellulose

Now, it is known from the data of refraction of cellulose[26] that the direction of maximum optical polarisability of the cellulose molecule is also along the length of the chain The directions of maximum optical polarisability and diamagnetic susceptibility, therefore, coincide This property is in fact suggested by the investigations of Ramanadham[27] and Scherer[28] on the magnetic double-refraction of saturated long-chain aliphatic hydro-carbons of the type C_nH_{2n+2} These compounds have been found to exhibit negative magnetic double-refraction and according to the orientation theory of Langevin and Born, this property implies that the directions of maximum optical polarisability and diamagnetic susceptibility coincide in the molecule By analogy, the conclusion may be drawn that a solution of native cellulose in neutral solvent will exhibit negative magnetic double-refraction From available experimental evidence, we may also draw the general inference, that the direction of maximum diamagnetic susceptibility in saturated long-chain aliphatic compounds (in which there are no double bonds in the chain) will be along the length of the chain

Since the above investigation was carried out by the author (1937), Lonsdale[29] has determined the diamagnetic anisotropy of crystals of several long-chain aliphatic compounds She has found that in $C_{29}H_{60}$ and several fatty acids, the direction of maximum diamagnetic susceptibility is nearly parallel to the '*c*'-crystallographic axis This direction is, in fact, also that of largest refractivity The molecules in all these crystals are arranged more or less parallel to the '*c*'-axis These results indicate that the directions of maximum diamagnetic susceptibility and maximum optical polarisability coincide in the long-chain compounds as suggested already by the experiments of Ramanadham on magnetic double-refraction and are in agreement with the conclusions of the author The author's work on cellulose is the first direct experimental investigation of the character of the diamagnetic properties of aliphatic long-chain compounds

* *Note added :*

Recently H Kiessig[30] has made a critical examination of all the available literature on the structure determination of native cellulose by X-ray analysis He has pointed out that while the model suggested by Sauter is far from satisfactory, that of Meyer and Mark has also got its draw-backs Further experimental work in the field appears to be necessary and the actual crystal structure of cellulose has yet to be discovered

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CHAPTER IV

THE MAGNETIC ANISOTROPY OF RHOMBIC SULPHUR

1. *Introduction*

The structure of rhombic sulphur has been recently investigated by Warren and Burwell[1] by the method of X-ray analysis They found that their results could be satisfactorily interpreted by assuming a symmetrical puckered ring-shaped molecule, consisting of eight atoms with a bond angle of 105° and an S-S distance of 2 12 A° From intensity considerations, they deduced the orientation of the molecules in the crystal, and found that the plane of the ring is parallel to the '*c*' crystallographic axis and makes an angle of about 50° with the '*a*' axis

The magnetic anisotropy of rhombic sulphur has been studied by Krishnan, Guha and Banerjee[2]. At the time of their investigation, however, the necessary data concerning the molecular structure and arrangement were not available for any interpretation of the results to be possible (For chemical evidence, see Ephraim, " Anorganische Chemie ", Dresden and Leipzig, 1934) But in the light of the recently proposed model, the magne-crystallic data assume considerable importance We can test the general validity of the X-ray analysis by examining whether the results obtained from the magnetic experiments fit in with the suggested scheme of molecular arrangement and structure. And if so, we should also be in a position to get valuable information regarding the magnetic properties of the S_8 molecule

2. *Experimental*

The magnetic anisotropy of the crystal was determined by the torsional method Since the crystal system is orthorhombic, the orientation in the field could be conveniently observed by noting the setting of the crystal edges Fine quartz fibres were used in view of the comparatively feeble anisotropy of sulphur Employing a field of 8000 Oersteds and crystals weighing 20 to 30 milligrams, the critical angle of rotation of the torsion-head was found to be large enough to justify the use of the approximate formula $(\Delta X) = 2 \left(\alpha_0 - \frac{\pi}{4}\right) \frac{CM}{mH^2}$.

Special care was taken to prepare sulphur crystals free from impurities. A saturated solution of recrystallised sulphur in Kahlbaum's pure carbon disulphide was allowed to evaporate slowly inside a large bell-jar. Beautiful crystals with well developed (111) faces were obtained. Experiments were performed on six different crystals.

3. *Results*

The results are shown in Table I below. The mean values of the specific anisotropy, as well as the gram molecular anisotropy for the S_8 molecule are given. The usual notation has been adopted χ_a, χ_b, χ_c standing for the specific susceptibilities along the respective axes. The susceptibilities along the different axes have been computed from a knowledge of the mean susceptibility of rhombic sulphur with the help of the anisotropy data. The calculated values are presented in Table II.

TABLE I

Mode of suspension	Orientation	Specific Anisotropy × 10^8	Gram molecular Anisotropy (S_8) × 10^6
'*a*' axis vertical	'*c*' axis along the field	$\chi_c - \chi_b = 0.31$	=0.79
'*b*' ” ”	'*c*' ” ”	$\chi_c - \chi_a = 2.56$	=6.57
'*c*' ” ”	'*b*' ” ”	$\chi_b - \chi_a = 2.27$	=5.82

TABLE II

Specific susceptibility × 10^6	Gram molecular susceptibility (S_8) × 10^6
$\chi_a = 0{\cdot}500$	128·2
$\chi_b = 0{\cdot}477$	122·4
$\chi_c = 0{\cdot}474$	121·6

Mean susceptibility of rhombic sulphur[3] $= -0{\cdot}484 \times 10^{-6}$

4. *Discussion*

The results obtained are found to disagree with those of Krishnan, Guha and Banerjee. According to them, $\chi_b - \chi_c = 0{\cdot}22$, $\chi_c - \chi_a = 0{\cdot}78$ and $\chi_b - \chi_a = 0{\cdot}94$ (unit 10^{-8}) which gives $\chi_b > \chi_c > \chi_a$ numerically. But actually we find that $\chi_a > \chi_b > \chi_c$. The author's results have been confirmed later by Prof. K. S. Krishnan (private communication).

The feeble anisotropy of the sulphur crystal indicates that presumably, the individual molecules are themselves only slightly anisotropic. Herein, sulphur differs from the aromatic ring-shaped molecules which possess a very large anisotropy. The shape of the molecule suggests that we may reasonably assume the principal susceptibilities parallel to the plane of the molecule to be the same. Hence if K_1, K_2, K_3 are the principal molecular susceptibilities (referred to a gram molecule), $|K_1| = |K_2|$ and K_3, perpendicular to the plane, will be either greater or less than K_1 or K_2. According to the X-ray analysis of Warren and Burwell, the plane of the S_8 molecule coincides with the '*c*' crystallographic axis and makes an angle of 50° 53′ with the '*a*' axis. We have the following relations between the principal susceptibilities of the crystal and those of the S_8 molecule

$$\chi_{c_M} = K_1 \qquad (1)$$

$$\chi_{b_M} = K_1 \sin^2\theta + K_3 \cos^2\theta \qquad (2)$$

$$\chi_{a_M} = K_1 \cos^2\theta + K_3 \sin^2\theta \qquad (3)$$

where θ is the angle which the plane of the molecule makes with the '*a*' axis.

Now equations (1) and (2) are sufficient to determine K_1 and K_1, putting $\theta = 50^\circ 53'$ as given by X-ray analysis These values can be checked up by applying them in equation (3) From (1) and (2) we get

$$K_1 \quad K_2 = -121\ 6 \times 10^{-6}$$
$$K_1 = -123\ 7 \times 10^{-6}$$

Applying this value in (3), we get $\chi_{aM} = -122\ 8 \times 10^{-6}$ This value differs considerably from the experimentally determined value -128.2×10^{-6}

If on the other hand, we calculate the value of the angle from the known values of χ_{bM} and χ_{aM}, it comes out to be about 71° instead of 50°–53′ We thus find that there is no exact agreement between the values obtained by X-ray analysis and by the magnetic method

An apparently approximate agreement is found in the general character of the results, if instead of 50°-53′, we use 71° in the formulæ (2) and (3), but then it is found to be impossible to explain the X-ray intensities according to the scheme adopted (Private communication from Dr B E Warren).

Now the magnetic method would be a very good test of any structure proposed by X-ray analysis In the first place, the anisotropies can be determined easily with a high degree of accuracy, especially the ratio of $\chi_c - \chi_b \quad \chi_c - \chi_a \quad \chi_b - \chi_a$ Now these ratios are the most important quantities in structure determination by the magnetic method, and even if the accuracy of determination of the absolute values of $\chi_c - \chi_b$ etc, is not high, if their relative values are found correctly, the orientations can be obtained accurately With suitably fine quartz fibres we can find out the ratios with an accuracy of 0 5 per cent. and the experiments with six different crystals gave identical values Since all the assumptions made in the calculations are quite justifiable and the specific diamagnetic anisotropy of rhombic sulphur, although feeble, is more than half that of calcite, the magnetic method should be a decisive check on any structure suggested by X-ray analysis.

It would, therefore, appear that the structure proposed by Warren and Burwell is in need of revision It can be easily understood that the structure determination of a complicated crystal like sulphur is extremely difficult, containing as it does, 128 atoms in the unit cell, and a complete X-ray examination of the crystals on the lines of J M Robertson's analysis of organic crystals (recent papers in Proceedings of the Royal Society, London) is desirable

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CHAPTER V

TEMPERATURE VARIATION OF THE DIAMAGNETIC ANISOTROPY OF CRYSTALS

No serious attempt has been made so far to study the temperature variation of the diamagnetic anisotropy of inorganic and organic compounds The temperature dependence of diamagnetism observed in metals and semi-conductors is essentially connected with problems of the metallic state and the properties of the conduction electrons In crystals of organic and inorganic compounds, although no profound changes of the mean diamagnetic susceptibility are to be expected with rise of temperature, the anisotropy may be expected to exhibit very significant variations The author has, in this connection, examined several inorganic crystals and organic crystals of aromatic ring-shaped compounds which are known to exhibit marked diamagnetic anisotropy The results of these investigations are presented in this chapter

In general, we may distinguish between two types of changes occurring in crystals when the temperature is raised Considering only crystals containing anisotropic groups as being of interest in our investigations, changes of crystal anisotropy may be caused by the intrinsic change of anisotropy of the molecules or ions in the crystal, secondly, there will be the changes due to alterations in the character of the lattice due to polymorphism, presence of impurities and rotations or oscillations of molecules or ions in the lattice

In organic crystals of low melting point, we may safely regard the intrinsic molecular anisotropy to remain unaffected by either the direct influence of temperature, or by any structural changes within the crystal But in the case of inorganic crystals like carbonates and nitrates, we have seen that the diamagnetic anisotropy of the (CO_3) and (NO_3) groups, which is comparatively feeble, is sensibly affected by the character of the environment Hence, a change of structure in these crystals will affect the crystalline anisotropy in two ways Firstly due to alteration of the intrinsic anisotropy of the groups and secondly by the change of their relative positions and orientations in the lattice

The present investigation clearly shows that a careful study of the temperature variation of the diamagnetic anisotropy of crystals is able to reveal various aspects of the transformations taking place in solids in a graphic manner In view of the delicacy of the methods developed even feeble changes can be detected

Among inorganic crystals the nitrates are very remarkable for the variety of phenomena they exhibit on being heated It is very well-known that as a class they are subject to polymorphic inversions Ammonium nitrate is unique in that it exists in six different forms and the changes occurring to the substance when it is heated up or cooled down are very striking Sodium nitrate is remarkable for a gradual transition that it exhibits in the temperature range 185°–275°, and this change has been studied by various physical methods by many experimenters The corresponding changes of the magnetic properties of the crystal should be very useful in understanding these changes better Faraday, as early as 1855, had examined the effect of temperature on calcite and observed that there was practically no change of anisotropy, even when the crystal was raised to the temperature of red-heat The author has studied the temperature variation of diamagnetic anisotropy of calcite by the more delicate methods now available Rhombic sulphur is subject to a polymorphic transformation at 95 5° into the monoclinic form and the corresponding change of diamagnetic anisotropy should be of interest

Among organic crystals some typical aromatic ring-shaped compounds have been chosen—e g , resorcinol, azobenzene, benzophenone and naphthalene The behaviour of other organic crystals may be expected to be similar to one or the other among these

1. SODIUM NITRATE

Experiments with sodium nitrate at various temperatures have revealed changes of diamagnetic anistropy which appear to be of significance in the understanding of the nature of the solid state. In the present investigation, the temperature variation of both magnetic as well as optical properties have been studied In this connection the work of Kracek and his co-workers[2] " (1931) on gradual transition in sodium nitrate is of great interest and an attempt has been made to correlate the various phenomena Although the magnetic properties have been the main consideration, the variation of the birefringence of the crystal with temperature was also examined quantitatively for a clearer understanding of the changes taking place As has been pointed out by *Bragg[1] (1924), the birefringence of the crystal* is also due to the intrinsic optical anisotropy of the (NO_3) groups, the polarisability parallel to the plane of the ion being greater than that perpendicular to the plane Hence a close correspondence may be expected to exist between the magnetic and optical changes

CRYSTAL DATA

Sodium nitrate $NaNO_3$, Gm Mol Wt = 85 01, density = 2 265 Gm/cc, melting point – 309 5°C, trigonal rhombohedral, space group D^6_{3d}, Z = 2, dimensions of the unit cell, a -- 6 32 A° U and $\alpha = 47°–15'$ (Bragg[3])

Refractive index in sodium light

$$n_o = 1.5852$$

$$n_o = 1\ 3348$$

(From Groth's—Chemische Kristallographie)

Temperature Variation of Magnetic Properties

Magnetic Anisotropy · Krishnan's torsional method has been adopted to determine the diamagnetic *anisotropy* *The experimental* conditions were so adjusted that the simple formula,

$$(\Delta X) = 2\left(\alpha_0 - \frac{\pi}{4}\right)\frac{CM}{mH^2}$$

could be employed, several rotations of the torsion-head being necessary to reach the critical position The crystals were prepared with great care *to eliminate impurities which might vitiate the results* *In* fact, the presence of impurities has a marked influence on the temperature variation of diamagnetic anisotropy near abouts the melting point, as the author's investigations on azobenzene crystals of different grades of purity (described later) have clearly brought out

The experiments were done on three crystals of masses 28 2, 39 5 and 55 8 m gms respectively A modified technique was adopted in order to determine the temperature variation of the magnetic anisotropy One of the chief difficulties was in suspending the crystal We cannot use shellac or canada balsam

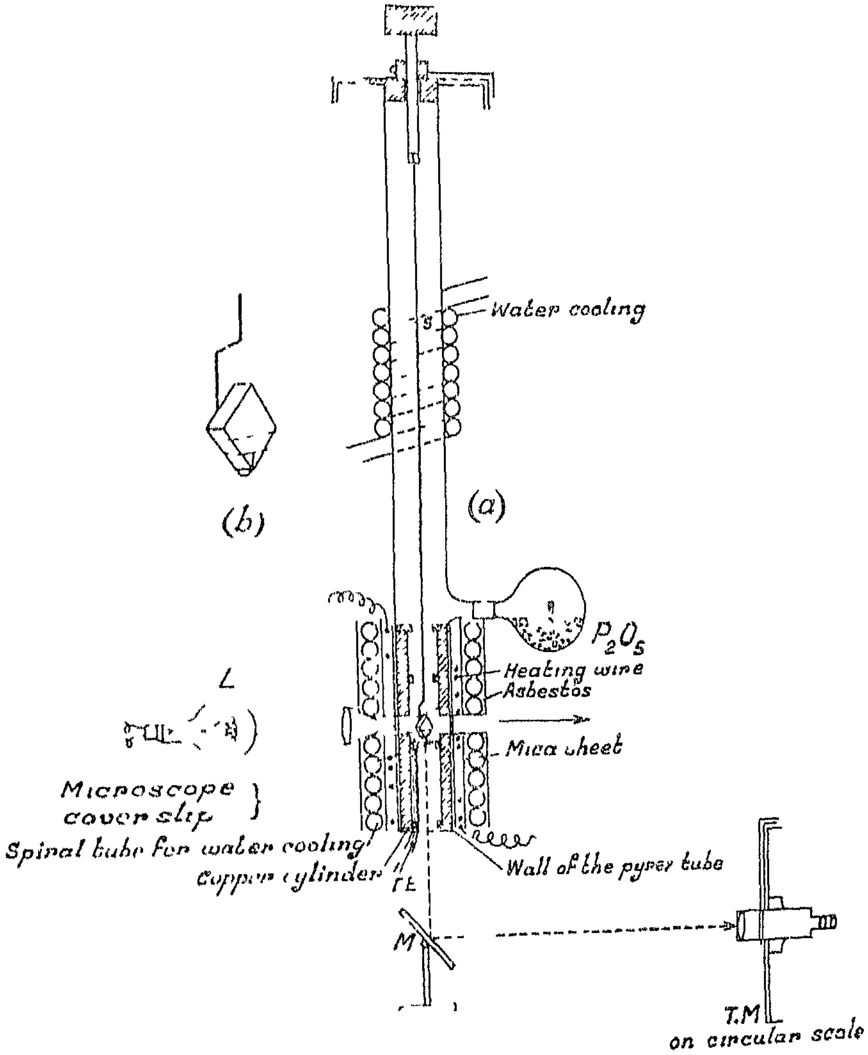

FIG 12

for fixing the crystal to the end of the fibre since they would melt at the higher temperatures. Hence, a crystal holder of delicate pyrex glass fibre was made, in which the crystal could be fixed in the desired manner. The crystal holder was fused on to a straight glass fibre about 20 cm. long, to the other end of which was attached the quartz fibre by means of shellac far above the heating oven (Fig. 12). It is important to level the suspended system so that it rotates freely when the torsion-head is rotated. This could be accomplished by softening the straight glass fibre at various points carefully by means of a *ruby* flame until the crystal showed no tendency to take up any preferred orientation. Initially the crystal holder alone was tested in the magnetic field in order to make sure that no spurious effects were caused by it. It should rotate freely in the magnetic field and should exhibit no tendency for preferred orientation. The couple acting on the holder in any position was ascertained to be negligible. Fig. 12 shows the heating arrangement. The heating was done electrically by passing steady current from a battery, through chromel wire (which was found to be only feebly magnetic) uniformly wound non-inductively round the pyrex tube. It is important that the introduction of the heating arrangement should not produce spurious magnetic effects. This was carefully tested in some preliminary experiments and the observed changes were found to be less than 0.5%. A copper cylinder inside the pyrex tube ensured uniformity of temperature in the region surrounding the crystal. The temperature was measured by means of a silver-constantan thermocouple, the hot junction being placed very near the crystal. The calibration was done directly with reference to a standard thermometer whose bulb was placed in the position usually occupied by the crystal. The temperature could be kept at various values by adjusting the heating current by a system of rheostats. Measurements were taken after the temperature had attained a steady value in each case. For avoiding fluctuations of temperature, a further precaution was taken by constantly maintaining a steady current of water at room temperature in the coil tubing wound round the oven outside. The temperature could be maintained steady correct to 1°C. It was found that t higher temperatures convection currents were set up inside the ven and for eliminating these, a thin microscope cover-slip was laced just below the crystal to act as a screen and it was found that he disturbing effects could be satisfactorily eliminated. The crystal as illuminated from the side by means of a lamp, the light entering hrough a hole in the copper tube (Fig. 12), and the position of the rystal relative to the field could be observed by means of the mirror M kept at an inclination of 45° and the telemicroscope mounted on a ircular scale.

The variation of the magnetic anisotropy of the crystal with emperature was determined by observing the value of the critical ngle of rotation of the torsion-head at the various temperatures.

TABLE I

(The values refer to a gm. mol.)

Substance	Diamagnetic Anisotropy $(\chi_{\perp r} - \chi_{\parallel r}) \times 10^6$	Mean susceptibility (Kido) $- \times 10^6$
Sodium Nitrate $NaNO_3$	6.15	25.6

Temperature °C	Susceptibility $- \times 10^6$
24°	$\chi_{\parallel r} = 29.7$ $\chi_{\perp r} = 23.5_5$
292°	$\chi_{\parallel r} = 29.3$ $\chi_{\perp r} = 24.2$

The quartz fibre was throughout at room temperature and hence, C remains unchanged In order to avoid any possibility of the shellac at S from softening, a copper spiral was wound round the pyrex glass tube surrounding the region and a current of cold water passed through it constantly (Fig 12)

Absolute Susceptibilities A modified form of magnetic balance of the Curie-Wilson type, constructed by the author (Fig 13), was employed for determining the temperature variation of the absolute susceptibility of sodium nitrate both in the form of powder as well as single crystal The balance beam and arms were of diamagnetic glass and glass parts were used wherever possible Measurements were made by the null method The experiment essentially consisted in measuring the variation of the force acting on the specimen placed in a non-uniform field, when the temperature was raised from 25°C to 300°C No absolute measurements were made, since, only relative values are required The following procedure was adopted Two phials (Fig. 13_a) were made out of extremely thin-walled glass tubing of uniform bore such that the dimensions of the phials were exactly the same After careful cleaning, one of the tubes was evacuated completely and sealed off at the constriction Q A glass rod P of thickness 1 mm and length 20 cm was fused on to the phial at Q, the other end of the rod being ground to a conical shape and made to fit correctly into a ground socket at S (Fig 13) In this way the phial could be rigidly fixed to the arm of the balance Dry, finely powdered sodium nitrate was introduced into the other phial and compressed up to suitable mark on the phial The second phial was also evacuated and sealed off in the same manner and the glass rod attached to it similarly Under identical experimental conditions, the variations of the force acting on the phials respectively when the temperature was raise from 25°–300°C were measured by means of the magnetic balance using the null method The zero-position of the phial in the fiel could be accurately fixed with the help of mirror M and a telescop and-scale arrangement, and the phial was brought back always to th

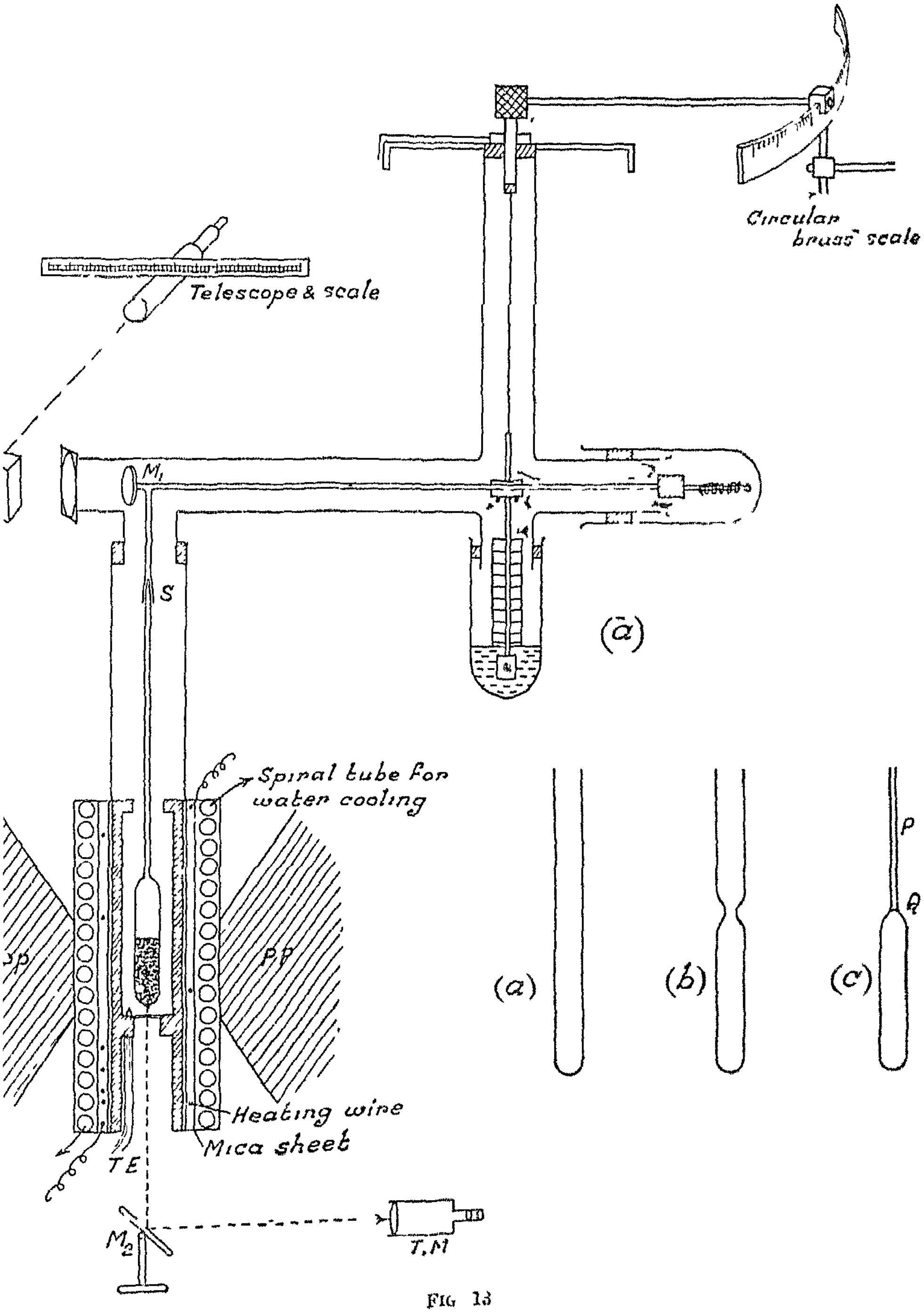
Circular
brass scale
Telescope & scale
M₁
S
(a)
Spiral tube for
water cooling
PP
Heating wire
Mica sheet
TE
M₂
T.M
(a)
(b)
(c)
P
Q

FIG 13

same position by suitably rotating the torsion-head The heating arrangement was similar to the one described before and the temperature was measured by means of a silver-constantan thermo couple The angle of rotation of the torsion-head was accurately measured correct to a minute of arc by attaching to it a long brass rod, to the end of which was fixed a brass slider which moved over a brass scale bent into an arc of radius of about 50 cm (Fig 13)

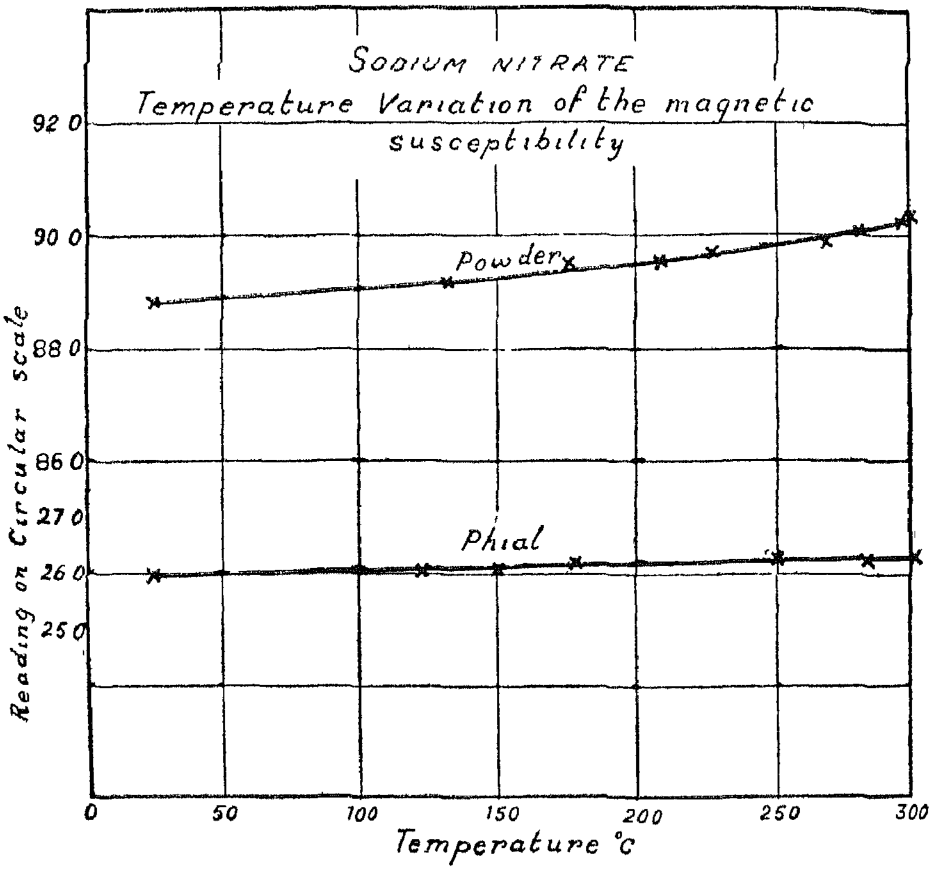

Fig 14

The determination of the actual variation of the susceptibility of the specimen with temperature involves the elimination of the effects due to the heating of the container and the surrounding air, besides the complications introduced by change of volume of the substance on heating The readings taken with the empty phial (Fig 14) enable us to get rid of the first two, since, the phial.

are of the same material and dimensions Small differences in the dimensions of the phials will not affect the results, since, we are concerned only with the *changes* of susceptibility and not the absolute values Since sodium nitrate expands by about 5% between 25° and 300°C, it is necessary to get an idea of the order of magnitude of the effect of this expansion on the measurements This was estimated as follows —A phial with a stopper was prepared out of the same thin-walled glass tubing and a mark made on it at the same distance from the bottom as in the case of the other phials, mentioned before A second mark was made just above this, so that the distance between the marks was one twentieth of the distance of the lower mark from the bottom of the tube Just enough sodium nitrate powder was introduced such that, when partially compressed, it came up to the upper mark The force acting on the phial in the magnetic field was now determined in the usual way by suspending it from the arm of the balance The phial was now removed and the powder fully compressed until it came up to the lower mark The force in the magnetic field was again measured under identical conditions The difference in the forces in the two cases was 0 3%, which is comparatively less than the observed temperature variations and a correction for this was made in the observed values

The experiments were also repeated with a single crystal* of sodium nitrate prepared from the melt in exactly the same way as in the case of the powder, using similar glass phials By preparing the single crystal in a container of exactly the same dimensions as the phials employed in the magnetic balance, it was possible to get it of such shape and length that it occupied the same volume in the phial as in the experiments with the powder It was found that the optic axis of the crystal coincided with the axis of the cylinder to within 5°, and hence, the results gave practically, the variation of the susceptibility perpendicular to the trigonal axis of the crystal. The experimental conditions were kept the same as in the experiments

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*My thanks are due to Mr T M K Nedungadi for kindly preparing the single crystal for me with the powder The crystal was not altogether free from flaws, an there were slight cracks which showed a tendency to widen on bein heated But the damage was not serious as could be checked u experimentally The observed changes were quite small but fe definitely outside the limits of experimental error It will be obviou however, that in view of some unavoidable sources of error an complications, a high percentage of accuracy cannot be claimed i such determinations but the results indicate clearly the direction an order of magnitude of the changes involved

Results

Fig 15 shows the variation of $\chi_{\perp r} - \chi_{\| l}$ with rise of temper ture graphically The crosses indicate the course of the curve a

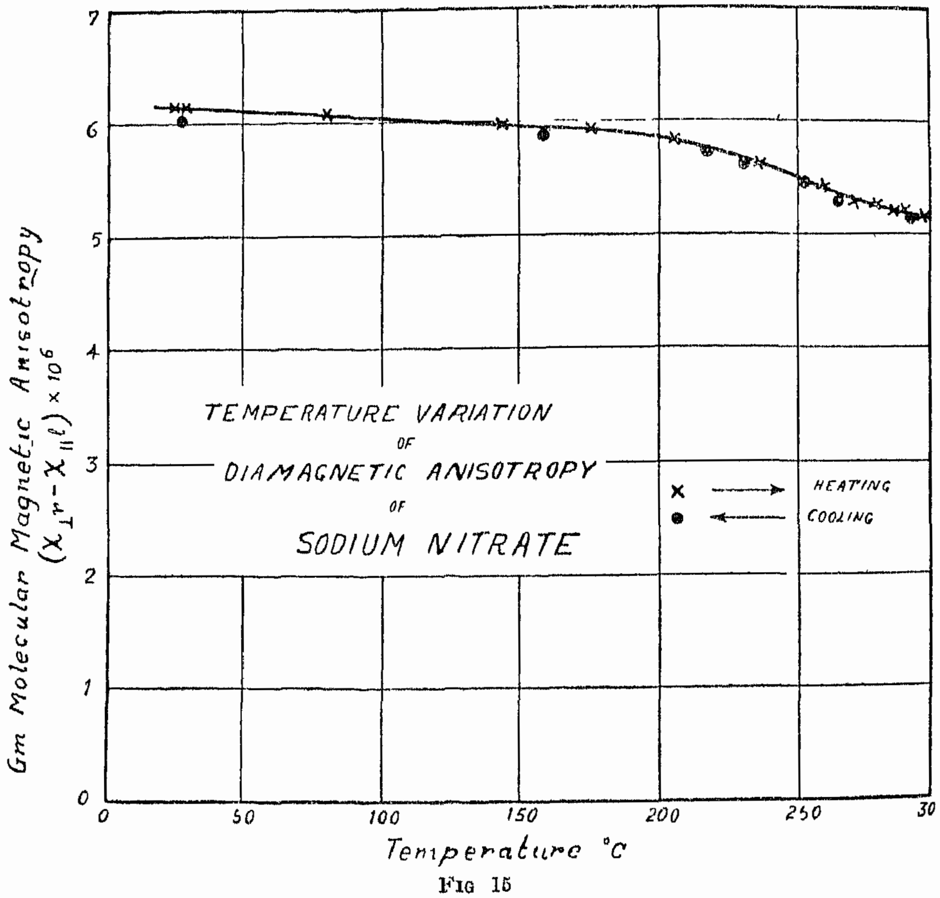


Fig 15

e crystal is heated from 25° to 300°C, while the dots represent the alues as the crystal is cooled down It is seen that the initial value f the anisotropy is practically restored, and hence, the changes are ot due to any accidental causes The experiment was repeated with hree crystals to confirm the results The course of the aniso- opy-temperature curve is very significant Up to about 185°C, the iamagnetic anisotropy diminishes but very slightly with rise of emperature From 185°C onwards, the decrease of anisotropy is ery pronounced At 280°C a slight inflexion in the curve can be oticed, corresponding to a diminished rate of change of anisotropy ith temperature The changes occurring above 300°C were difficult follow, although a rapid diminution was observed a few degrees elow the melting point

Fig 16 shows the variation of the susceptibility of the powder d that of the single crystal, respectively, with rise of temperature he changes are seen to be comparatively very small The diamag-

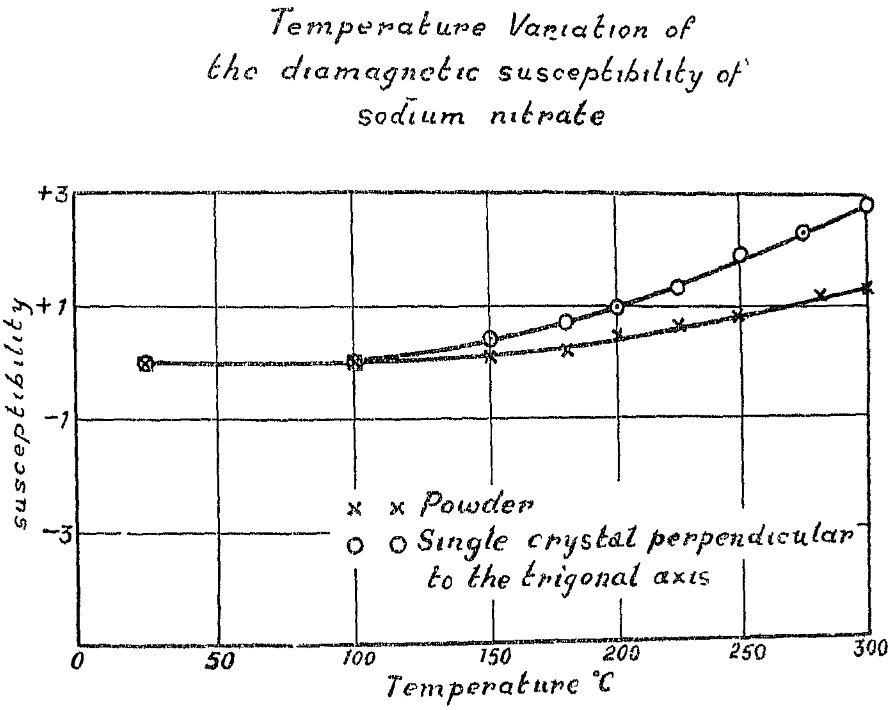


FIG 16

netic susceptibility is seen to increase with rise of temperature in cases

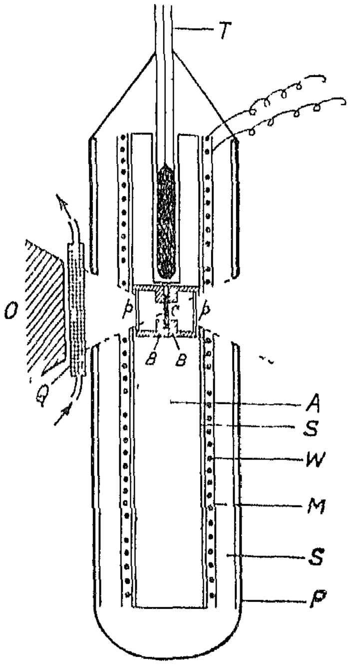
The increase in the diamagnetic susceptibility of the crystal, direction perpendicular to the trigonal axis, is found to be greater than the increase in the mean susceptibility of the powde simple calculation shows that this would imply a diminution o diamagnetic susceptibility parallel to the trigonal axis of the cr From the data in table II, we have, $\chi_{\parallel r} = -29\ 7 \times 10^{-6}$, and $-23\ 55 \times 10^{-6}$, referred to a gram molecule of sodium nitrate, at temperature At 292°C, the values are, $\chi_{\parallel r} = -29\ 3 \times 10^{-6}$, $\chi_{\perp r} = -24\ 2 \times 10^{-6}$ These figures would indicate that the ch in the magnetic properties of the (NO_3) group takes place both in perpendicular to its plane, assuming that these changes of susce lity are entirely due to the (NO_3) group The diamagnetic susce lity in a direction perpendicular to the plane of the ion decr while the susceptibility parallel to the plane increases

Optical Properties

The influence of temperature on the birefringence of so nitrate has been qualitatively investigated by Kracek[1] (1931) found that there is no sudden change of birefringence on heating dicating that there is no sudden change of phase during the gr transition observed by him in the crystal from 185°–275°C uniaxial character of the crystal persists up to its melting point

The temperature variation of the birefringence of so nitrate crystal has been quantitatively studied by the autho measurements made on the birefringence pattern obtained whe crystal is examined under monochromatic convergent polarised between crossed nicols, the crystal plate being cut with the optic perpendicular to its plane

The arrangement for obtaining the birefringence patte rings and brushes with monochromatic convergent light transm through a plane parallel plate of a double-refracting crystal p between crossed nicols is too well-known to need any descri ere But the heating device employed by the author, embodying ome new features, will be described briefly A crystal holder B of rass (Fig 17) in which the crystal plate could be fixed conveniently, ts exactly into a hole bored in a copper rod A of diameter about 2



O—Microscope objective
Q—Flat cell through which cold water is circulated
pp—Pyrex end plates
C—Crystal plate
BB—Crystal holder
A—Copper rod
S—Asbestos
W—Heating Wire
M—Mica sheet
P—Pyrex holder tube
T—Thermometer

Fig 17

The copper rod is covered with a thin layer of asbestos over ich chromel wire is wound for electrically heating the rod The ole rod is then covered with asbestos for insulating it, leaving only two openings for light to pass through the crystal A thermomet reading up to 300°C fits into a hole at the top of the copper rod, t bulb being kept quite near the crystal The arrangement w supported in a wide pyrex tube which could be clamped vertically a stand Initially the crystal in the holder was kept inside desiccator for 24 hours in order that it may be quite dry The e plates *p.p* were fixed to the crystal holder so that no moisture fr outside might affect the crystal in the course of the experiment

The interference pattern thrown on a ground-glass screen v found to remain more or less unchanged in character on heating fr 25°–300°C indicating that no sudden changes take place when temperature is raised The diameter of the first dark ring obtain with 5461 A U radiation of the mercury arc was measured by me of a Zeiss glass scale The change in the dimensions of the ring v also recorded photographically with 4046 A U radiation (Fig Plate III) The ring was found to have increased in diameter 3 6% in the range of temperature 25°–292°C The table be gives the mean diameters of the ring at the various temperatur measured on the photographic plate by means of the travell microscope

TABLE III

Temperature °C	Diameter of ring in Cm λ = 4046 A U
25	1 65
100	1 65
185	1 65
220	1 66
250	1 67
275	1 69
292	1 71

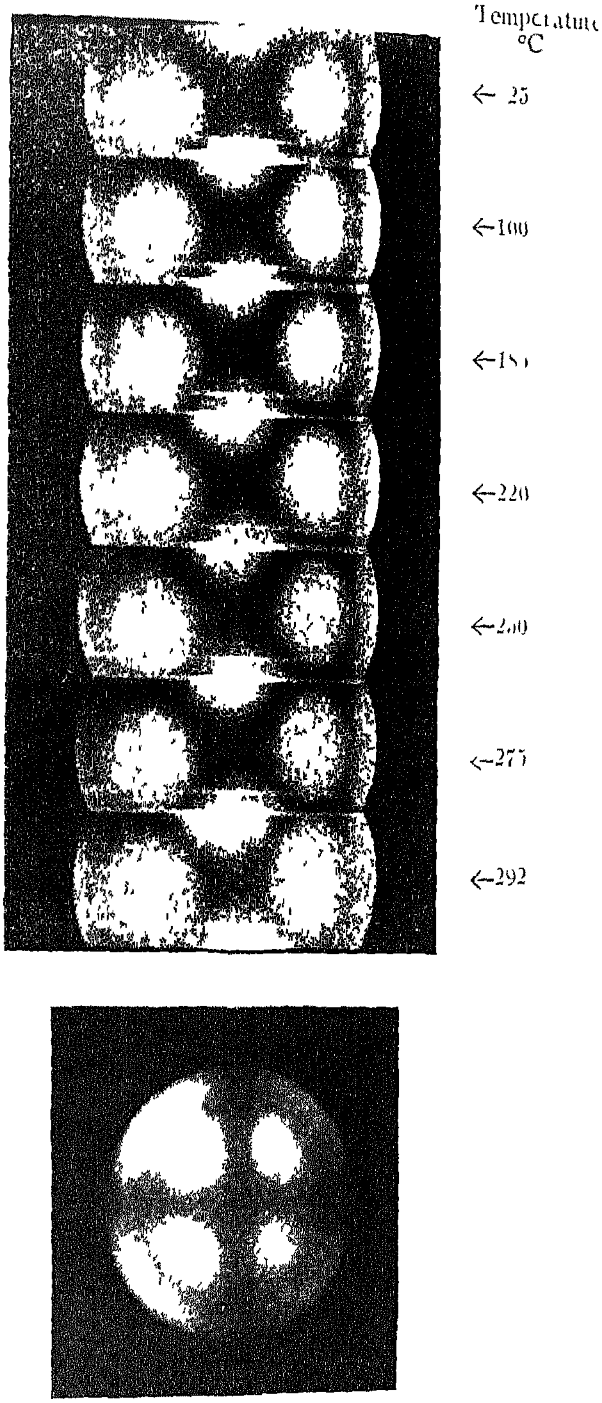


Fig 16

The theory of the method is developed below

Let a monochromatic plane-polarised wave be incident obli-
on the plate of sodium nitrate crystal (Fig 19) OP denotes
irection of the incident wave-normal and PQ, PR, the directions
ordinary and extraordinary rays within the crystal The phase
ence of the emergent rays is then given by the expression
zels, "Kristalloptik", Leipzig, 1906)

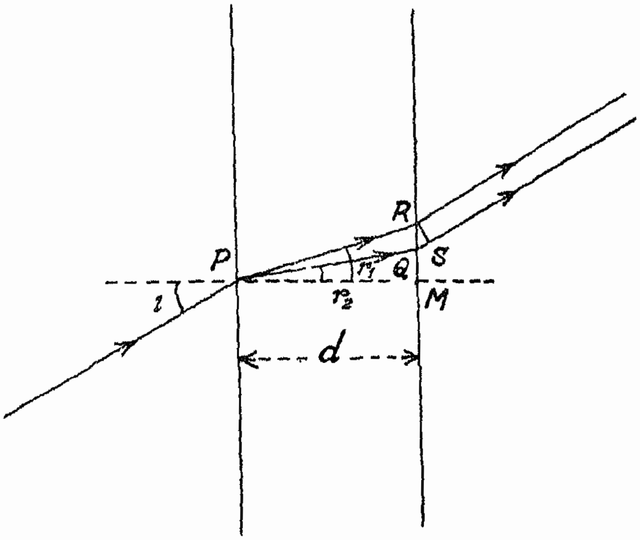


FIG 19

$$\Delta = 2\pi \left\{ \frac{d}{\lambda_2 \cos r_2} - \frac{d}{\lambda_1 \cos r_1} + \frac{d(\tan r_1 - \tan r_2)\sin i}{\lambda_0} \right\}$$

$$= 2\pi d \left\{ \frac{\cos r_2}{\lambda_2} - \frac{\cos r_1}{\lambda_1} \right\}$$

$$= 2\pi d \sin i \quad \frac{\sin (r_1 - r_2)}{\sin r_1 \sin r_2}$$

e λ_0, λ_1, λ_2, represent the wavelengths in vacuum and within the
l respectively.

If we put

$$\sin r_m = \frac{n_0 \sin i}{\sqrt{n_1 n_2}}$$

e r_m denotes the mean angle of refraction and n_0, n_1, n_2, the refractive indices corresponding to λ_0, λ_1, λ_2 $\left(n_1 = \frac{\lambda_0}{\lambda_1},\ n_2 = \frac{\lambda_0}{\lambda_2},\ n_0 = 1\right)$ we get by substitution,

$$\Delta = \frac{2\pi d(n_2 - n_1)}{\lambda_0 \cos r_m}$$

This relation is strictly applicable only in the case of weakly birefringent crystals but is approximately valid in the present case when r_1 and r_2 are very small If n_o and n_e are the principal refractive indices of the crystal, we have

$$n_2 - n_1 = (n_o - n_e) \sin^2 r_m$$

and therefore,

$$\Delta = \frac{2\pi d}{\lambda_0} \; \frac{(n_o - n_e) \sin^2 r_m}{\cos r_m} \text{ approximately}$$

From this we get for the first dark ring, between crossed nicols, the following relation, on equating the phase difference to 2π

$$\sin r_{m_1} = \left\{ \frac{\lambda_0 \cos r_{m_1}}{d\,(n_o - n_e)} \right\}^{\frac{1}{2}}$$

Since the angles of refraction are small, $\sqrt{\cos r_{m_1}}$ may be taken as unity, and r_{m_1} can be evaluated from the known values of λ_0, d, n_o and n_e. This was found to be 2 8° in the actual experiment when $d = 0\ 580$ mm and $\lambda_0 = 4046$ A U It is evident that since r_{m_1} is very small, we are quite justified in assuming $\sqrt{\cos r_{m_1}} = 1$ nearly

Now $\frac{2\pi d\,(n_o - n_e) \sin^2 r_{m_1}}{\lambda_0 \cos r_{m_1}}$ is constant, being the phase difference corresponding to the first dark ring Hence, for any variation in the value of $\frac{d \sin^2 r_{m_1}}{\cos r_{m_1}}$ with temperature, there must be a corresponding change in the value of $n_o - n_e$ in the opposite direction The change in the value of d is known from the data of thermal expansion of the crystal and that of $\sin^2 r_{m_1}$ can also be calculated from measurements of the diameter of the first dark ring as follows

Let the radius of the ring change by $\delta\rho$ If ρ is the radius and d the thickness of the plate initially, then,

$\tan r_{m_1,t_1} = \frac{\rho}{d}$ and similarly $\tan r_{m_1,t_2} = \frac{\rho + \delta\rho}{d + \delta d}$ where t_1 and t_2 are the l and final temperatures and δd is the change in the thick- of d' at t_2

$$\frac{\tan^2 r_{m_1,t_2}}{\tan^2 r_{m_1,t_1}} = \left\{ \frac{1+\frac{\delta\rho}{\rho}}{1+\frac{\delta d}{d}} \right\}^2 = \frac{\sin^2 r_{m_1,t_2}}{\sin^2 r_{m_1,t_1}},$$

angles being small. Hence since $\cos r_{m_1}$ may be assumed to inity,

$$\frac{(d+\delta d)\sin^2 r_{m_1,t_2}}{\cos r_{m_1,t_2}} \qquad \frac{d\sin^2 r_{m_1,t_1}}{\cos r_{m_1,t_1}} = \frac{\left(1+\frac{\delta\rho}{\rho}\right)^2}{1+\frac{\delta d}{d}}$$

$$\therefore \quad \frac{(n_o-n_e)_{t_2}}{(n_o-n_e)_{t_1}} = \frac{1+\frac{\delta d}{d}}{\left(1+\frac{\delta\rho}{\rho}\right)^2}$$

Thus from the data of thermal expansion of the crystal and surements of the diameter of the rings at various temperatures, possible to get an estimate of the corresponding change of fringence Sodium nitrate expands by 4 7% along the trigonal when heated up to 290°C Hence

$$\frac{1+\frac{\delta d}{d}}{\left(1+\frac{\delta\rho}{\rho}\right)^2} = \frac{1\ 047}{(1\ 036)^2} = 0\ 976$$

the birefringence decreases by 2.4% when the crystal is heated 25°–290°C

Now temperature can affect the refractive index of an aniso- ic crystal in two ways : (1) the thermal expansion of the crystal bring about a variation of the principal refractive indices which be, in general, different for the three directions, (2) there will be ntrinsic change in the value of the refractive indices due to rise emperature Hence the experimentally-observed values of the nge of refractive index will essentially consist of two parts If n_b

denotes one of the principal refractive indices (h = 1, 2, 3) and t the temperature, we have the following relation

$$\frac{dn_h}{dt} = \left(\frac{dn_h}{dt}\right) + \frac{\partial n_h}{\partial t}$$

where $\left(\frac{dn_h}{dt}\right)$ is the part due to thermal expansion and $\frac{\partial n_h}{\partial t}$ the true temperature coefficient of refractive index. The birefringence $\Delta n_h \left[\text{i.e.,}\ (n_1 - n_2),\ (n_2 - n_3) \text{ and } (n_3 - n_1) \right]$ will thus depend upon temperature in a complicated way, and to establish the true variation of the birefringence of the crystal as distinct from that due to the thermal expansion only, it is necessary to know the data of thermal expansion of the crystal as also its elasto-optical constants (Pockels, Kristalloptik, 1906). Unfortunately, the elasto-optical data for sodium nitrate are not known at present. Simple considerations indicate that $\left(\frac{d\Delta_n}{dt}\right)$ due to the thermal expansion of the crystal will be positive, since the expansion parallel to the trigonal axis is large while that perpendicular to the axis is comparatively very small. $\frac{d\Delta_n}{dt}$, the observed change, is negative, and therefore, $\frac{\partial \Delta_n}{\partial t}$ will also be negative, i.e., the intrinsic birefringence due to the (NO_3) group decreases with temperature.

Discussion

The observed decrease in the diamagnetic anisotropy of sodium nitrate with rise of temperature can be due to any of the following causes :—(1) change in the relative orientations of the (NO_3) ions in the crystal lattice, (2) large amplitude swinging oscillations of the (NO_3) groups perpendicular to their planes which are excited at higher temperatures, (3) change in the intrinsic anisotropy of the (NO_3) ion with rise of temperature due to deformations produced on it or other causes.

X-ray analysis has shown that there is no change of crystal structure up to 300°C. The (NO_3) ions continue to remain with their planes parallel to each other and perpendicular to the trigonal axis of crystal and therefore, the change of anisotropy cannot be attribut-to change in the relative orientations of the (NO_3) groups Swing-oscillations of large amplitude also do not appear to be the cause he change of anisotropy Although it is evident that if the ions in to swing with large amplitudes about their plane, a diminution he diamagnetic anisotropy will occur, a simple calculation indicates to account for the observed magnitude of the effect, amplitudes he order of 20° on either side of the equilibrium position will be essary If the amplitude of oscillation is denoted by θ_0 at any ant, the angular position θ of the plane of the ion with respect to equilibrium position will be given by $\theta=\theta_0 \sin\left(\frac{2\pi}{T}t\right)$ The con-ution of the ion to the susceptibilities of the crystal parallel and pendicular to the trigonal axis, are then given by the following tions (referred to gm ion)

$$\chi_{\parallel}' = K_{\parallel} \cos^2\theta + K_{\perp} \sin^2\theta$$

$$\chi_{\perp}' = K_{\parallel} \sin^2\theta + K_{\perp} \cos^2\theta$$

$$\chi_{\perp}' - \chi_{\parallel}' = (K_{\perp} - K_{\parallel}) \cos 2\theta$$

value of $(K_{\parallel} - K_{\perp})$ is, therefore, diminished by a factor Now θ ially varies from $-\theta_0$, to $+\theta_0$ and we have to take the time aver-of the effect The mean value of θ is given by

$$\theta_{mean} = \frac{2}{T}\int_0^{\frac{T}{2}} \theta_0 \sin\left(\frac{2\pi}{T}t\right)dt$$

$$= \frac{2}{\pi}\theta_0 = 0.636\ \theta_0$$

For values of $\theta_0 = 5°, 10°, 15°$ and $20°$, we have $\cos 2\theta_{mean}$ 4 = 0.975, 0.944 and 0.848, respectively Calculations of the plitude of swinging oscillations based on the data of light scattering cate that this is comparatively small Using the relation,

$$\theta_0^2 = \frac{h}{2\pi^2\nu I}$$

ived by Raman and Nedungadi (1939), the amplitude of the tilting illation for $\nu = 185$ cm^{-1} comes out to be 5.8° This can produce ecrease of magnetic anisotropy of the order of 1% only on the rage.

The work of Kracek and his collaborators on the gradual transition in sodium nitrate when the crystal is heated up to 300° has an intimate bearing on the change of diamagnetic anisotropy observed by the author, for it is only natural that all these phenomena should be inter-related These authors have studied the heat capacity, thermal expansion, solubility etc , of sodium nitrate from room temperature up to about 300°C and have observed a gradual transition in these properties, whose characteristics were found to differ from those of normal polymorphic inversion in that there is no finite discontinuity during the transition To explain the observed changes, they have postulated that the (NO_3) groups begin to rotate freely *in their plane* at high temperatures The transition from oscillation to rotation of the ions commences at about 185°C and as the temperature is increased further, more and more of the ions begin to rotate until at 275°C all of them are rotating The anomalous increase in the specific heat of the substance in the temperature range 185°–275°C has been explained by them on this hypothesis Austin and Pierce[5] (1933) have studied the linear thermal expansion of sodium nitrate in great detail and they have also observed an anomalous increase in the coefficient of thermal expansion parallel to the trigonal axis of the crystal between 150° and 280°C They have tried to explain their observations also with the help of the rotation hypothesis, although in this case some points are not quite clear They assume that the increasing amplitudes of oscillation of the (NO_3) ions *in their own plane* cause a marked separation of the planes of the nitrate ions and metal ions without any abnormal increase of dimensions in the plane of the group, or in other words, the intermolecular forces which are affected by such oscillations and rotations are assumed to be those acting between alternate layers of nitrate and metal ions It is not immediately obvious why this should be so If on the other hand, we assume rotations to exist side by side with lateral swinging oscillations of the (NO_3) ions perpendicular to their planes the large thermal expansion in the direction of the trigonal axis may be qualitatively explained.

The rotations of the $(NO_3)^-$ ions *in their own plane* cannot
unt for the change of diamagnetic anisotropy If we regard
(NO$_3$) group as a rigid structure, whether it is stationary
tating in its own plane, its contribution to the anisotropy of the
tal will be the same

From the above considerations we are led to conclude that
e is most probably an intrinsic change of the diamagnetic aniso-
y of the (NO$_3$) group with rise of temperature

The recent work of Frenkel and Saveliev[6] (1937) on the
erature variation of the diamagnetic anisotropy of ring-shaped
ecules is noteworthy in this connection They have been able to
w that the diamagnetic susceptibility of electrons in rings should
inish with rise of temperature, as for instance, in the case of
hite (Krishnan and Ganguli[7], 1937) They differentiate between
cases, the case of interacting and non-interacting electrons A
erature-dependence of diamagnetic susceptibility and anisotropy
be expected only in the latter case, as in graphite In the case
enzene and similar conjugated structures, they have pointed out
whether the 'resonance electrons' are of the interacting type or
interacting type can only be decided by experiment The fact
the diamagnetic susceptibility of sodium nitrate actually increases
itly with temperature would indicate that the 'resonance elec-
s' are of the interacting type in the (NO$_3$) group, and therefore
tically unaffected by temperature in the manner considered by
nkel and Saveliev and the theory as applied to graphite does not
n to be valid here

The observed changes can be satisfactorily explained as being
to the change of structure of the sodium nitrate lattice caused by
gradual transition In fact, this inference is suggested by the
e correspondence between the specific heat and thermal expan-
changes, and the change of diamagnetic anisotropy The main
ures in the observed changes are, a comparatively small decrease
o about 180°C, a pronounced variation between 180° and 280°C
a less pronounced decrease between 280° and 300°C. Schulze[8]

(1938) has investigated the change of diamagnetic susceptibility with change of temperature of several inorganic crystals and has observed changes of susceptibility of the order of 2–4% when polymorphic transitions took place These changes were attributed to deformations produced on the ions due the altered character of their environment with change of crystal structure A similar behaviour may be expected in sodium nitrate due to its anisotropic expansion, and although there is no polymorphic inversion, the relative positions of the ions are altered to a considerable extent by the expansion at high temperatures This may be sufficient to bring about a change in the diamagnetic anisotropy of the (NO_3) group, of the observed order of magnitude Since the diamagnetic anisotropy of sodium nitrate is comparatively small it will be easily seen that a change in the principal susceptibilities of the order of 3% can cause a large percentage change of the anisotropy The sodium ions are arranged about the (NO_3) group in an approximately octahedral fashion, and when the crystals expands the layers of oxygen atoms move farther apart The crystalline fields acting on the (NO_3) groups, therefore, also change in character, and ultimately the deformation of the (NO_3) ion will depend upon the nature of these fields The problem of rigorously calculating the influence of the lattice on diamagnetic anisotropy is being considered

The optical studies clearly indicate that the uniaxial character of the crystal remains unchanged on increasing the temperature The birefringence decreases by about 2 4 per cent of its room temperature value at 292°C We have seen that this corresponds to a decrease in the intrinsic optical anisotropy of the (NO_3) group itself Since the observed changes are quite small, the method adopted for studying the changes in the character of the birefringence pattern cannot be very accurate, especially since the rings are rather diffuse, and an actual determination of the changes in the refractive indices n_0 and n_e is necessary for strict quantitative determination This is being attempted employing a prism of sodium nitrate cut with its optic axis parallel to the edge of the prism, measurements being made

a spectrometer But the fact that the optical anisotropy of the
) group itself decreases at high temperatures supports the
ts of the magnetic measurements

The results of this investigations may now be briefly sum-
sed We find that there is a decrease in the diamagnetic
otropy of sodium nitrate which commences at about 185°C An
xion in the $\Delta X - T$ curve is also observed at about 280°C The
rved changes of diamagnetic anisotropy are found to be intimately
ected with the anomalous changes of specific heat and thermal
nsion observed in the substance between 185°–275°C The
ge in the mean susceptibility of sodium nitrate powder and that
ie susceptibility perpendicular to the trigonal axis of a single
al with rise of temperature (25 to 300°C) has been determined
observed changes are comparatively small It has been deduced
the susceptibility parallel to the trigonal axis diminishes with
erature while that perpendicular to the axis increases with tem-
ture The changes in the magnetic properties of the substance
been attributed to a change in the deformation of the (NO_3)
p brought about by the anisotropic expansion of the lattice with
of temperature, as a consequence of which, the relative positions
e ions are altered The optical anisotropy of the (NO_3) group is
found to have decreased slightly The results lead to the
lusion that the anisotropy of radicals like the (NO_3) group is
ted to a considerable extent by changes in the relative positions
ie ions in the crystal lattice and that the disposition of the
unding ions is an important factor governing the magnitude of
nisotropy of the group, and hence that of the crystal as a whole

2. *CALCITE*

As mentioned earlier, Faraday[9] could not find any difference
e diamagnetic anisotropy of calcite even when it was raised to
ieat Since the diamagnetic anisotropy of calcite is compara-
y feeble, with the methods at his disposal at that time Faraday
l not have detected small changes,

The author employed a crystal weighing 49 2 m gm which was suspended as usual at the end of the quartz fibre with the trigonal axis horizontal The same technique as in the case of sodium nitrate was followed It was found that the anisotropy $\chi_{\perp r}-\chi_{\parallel}$ remained practically unchanged from 25°-300°C The observed changes (decrease of the anisotropy) did not exceed 2 per cent A feeble change of this order may be expected on account of the anisotropic expansion of calcite, the coefficient of thermal expansion is much greater parallel to the trigonal axis than that of perpendicular to the axis But there is no anomalous expansion as in the case of sodium nitrate in which the lattice expands by about 5% along the trigonal axis in the range 25°–300°C The change in the diamagnetic anisotropy of the (CO_3) group due to these small structural changes may be expected to be very small, as observed experimentally

3. AMMONIUM NITRATE

The behaviour of ammonium nitrate is typical of many other nitrates which undergo polymorphic transitions with change of temperature *Ammonium nitrate has five low pressure modifications* and one high pressure modification, and the polymorphic inversions have been extensively studied by optical, thermal and dilatometric methods, and recently by X-ray analysis also, by many workers[10].

When the molten salt freezes at about 168°C, it forms, first cubic crystals of I-ammonium nitrate At about 125°C, we get the tetragonal form first discovered by Wallerant, II-ammonium nitrate At 84°C again, III-ammonium nitrate is formed, which is now known to be orthorhombic, although monoclinic symmetry was at first assigned to this form The best representative value of this transition temperature is given by Early and Lowry as 84 2°C At about 32°C, there is a third transition to IV-ammonium nitrate, which is the usua rhombic room-temperature modification Below 18°C, a tetragona or pseudo-hexagonal form has been found to be stable.

The most probable values of the temperatures of transition are narised in the table below

Phase	Temp °C
I ⇌ II	125.2
II ⇌ III	84.2
III ⇌ IV	32.3
IV ⇌ V	−18.0

The X-ray analysis of Hendricks, Posnjak and Kracek shows each of these transitions, as may be naturally expected, is charac- ed by altered relative positions and orientations of the $(NO_3)^-$ $(NH_4)^+$ ions in the lattice In the cubic form, evidence has been l for the existence of actual rotations of the (NO_3) groups in the e The structural characteristics of the other modifications found iem are

Tetragonal (*II-ammonium nitrate*) (125.2°–84.2°C), $a=b=$ A°U, $c=5.00$A, 2 NH_4NO_3 in the unit cell Plane of the (NO_3) ps parallel to the 'c'-axis and inclined at 45° to the 'a' and 'b'-axes

Orthorhombic (*III-ammonium nitrate*) (84.2°–32.3°C) $a=$ A°, $b=7.66$A°, $c=5.80$A° 4 NH_4NO_3 in the unit of structure es of the (NO_3) groups parallel to the 'c'-axis and inclined at an e of nearly 26° to the 'b'-axis of the crystal

Orthorhombic (*IV-ammonium nitrate*) (32.3° to −18°C) Sp p V_h^{13}, $a=5.75$A°, $b=5.45$A°, $c=4.96$A°, (the 'a' and 'c' crystal- phic axes have been interchanged in the X-ray measurements) 2 NH_4NO_3 in the unit cell Planes of the (NO_3) groups perpendi- to the 'b'-crystallographic axis

V-ammonium nitrate. stable below −18°C Hexagonal, $a=$ A°, $c=15.9$A°, with 6NH_4NO_3 in the unit cell. The true lattice be pseudo-hexagonal

C D West[11] in his X-ray analysis of the room temperature fication retains the crystallographic axial ratios a b $c=0.909$ · 1.0553, whereas Hendricks, Posnjak and Kracek have found it ssary to interchange 'a' and 'c', so that they get c b a as) . 1 . 1.0553.

Magnetic Anisotropy and Crystal Polymorphism

Crystal polymorphism has so far been studied mainly b optical, thermal and dilatometric methods, taking advantage of th fact that polymorphic inversions are characterised by more or le abrupt changes in the physical properties of crystals such as refractiv index and birefringence, specific heat, volume, thermal expansio coefficient etc Since the advent of X-ray analysis the actual change of structure can now be studied in close detail, as has been accom plished in the case of ammonium nitrate Now, when a cryst like ammonium nitrate changes its structure, we have seen that i each transition the relative orientations of the (NO_3) groups ar altered We have already seen that the (NO_3) group possesse diamagnetic anisotropy and that the diamagnetic anisotropy of nor isotropic crystalline nitrates is essentially due to the intrinsi anisotropy of the (NO_3) ions The magnitude of the cryst anisotropy will thus depend upon the orientation of the (NO ions in the lattice It may be easily inferred that the absolute valu of the diamagnetic anisotropy of the high temperature modification of ammonium nitrate will be all different Hence, the polymorphi changes are capable of being studied by magne-crystallic actio The present investigation was undertaken to explore the possibilities and the limitations of this new method of detecting and studyin crystal polymorphism The experiments on sodium nitrate, described before, seem to indicate that the diamagnetic anisotropy of th (NO_3) group itself might undergo a change when the characte of the environment of the group also changes Hence, over an above the change of crystalline diamagnetic anisotropy due to th altered positions and orientations of the ions in a polymorphic change there is also the additional effect of a small intrinsic change of diamagnetic anisotropy of the ion which, however, may be comparativel small

The fact that the magnetic studies require single crystals, leads to many complications which should not be overlooked Although we start with a single crystal at room temperature, it is

y that the crystal remains intact over the whole range of tem-
ure studied and transforms to *single* crystals of the other modi-
ons Ammonium nitrate itself is a typical case for examining
aspect When the room temperature modification is heated
ually beyond 32°, it transforms to III-ammonium nitrate The
l mechanism of the change seems to be the formation of centres
ansformation all over the crystal at first the transformation
ading out from each centre in all directions We have to consider,
efore, a number of important points when carrying out the mag-
studies namely, (1) the exact nature of the crystal-structure-
sformation, whether a mosaic crystal or a polycrystalline aggre-
has been formed, and in the latter case, the character of the
itations of the crystallites formed, (2) the duration of the
morphic change, whether it is sudden or gradual, and the optimum
itions at which the change takes place with maximum speed
se points will be discussed in detail later

When making a general survey of the various transformations
he method of magne-crystallic action, it is sufficient to choose a
convenient temperatures and determine in each case the diamag-
anisotropy of the crystal when it has reached a steady value
en the temperature is well above a transition point, in general,
transition takes place quickly in most substances, except a few,
which several days are required for the complete reaction to take
e, as for instance the transition, monoclinic → Rhombic sulphur
ie case of ammonium nitrate, the time-lag is very little, except
ie case of IV $\rightleftharpoons$ III inversion where the temperature has to be
ed well beyond the transition point for the transition to take place
kly At temperatures one or two degrees above the transition
erature (32 3°), the reaction is comparatively slow, taking a few
s Early and Lowry (1919) have shown that in contrast to the
sition at 32 3°, the velocities of the transitions at higher tempera-
s are fast enough to give sharply defined breaks in the heating and
ing curves It is important to note, however, that the actual tem-
ture of the crystal is the most important factor governing the velo-

city of transition, and the rate of transformation increases in mor or less direct proportion to the difference between the temperatur at which transition takes place and the true transition temperature

Experimental

Single crystals free from streaks and defects could be prepare from aqueous solution of recrystallised 'Kahlbaum' ammonium nitrat which had been carefully filtered beforehand The crystals wer grown by slow evaporation inside a desiccator They were furthe kept in a perfectly dry state for several days before the experimen in a desiccator containing P_2O_5 Ammonium nitrate is very hygroscopic and the polymorphic changes are very sensitive to the presenc of moisture which can cause anomalous results Therefore, moistur has to be carefully excluded Coating the crystal with a thin layer diamagnetic shellac might protect the crystal from moisture, but it wa found that there was always a tendency of the crystal to break up du to polycrystal formation, if this was done Hence, it was foun advantageous to keep the tube in which the crystal is suspende perfectly dry by means of P_2O_5

The technique adopted for high temperature measurement was exactly the same as described before in the case of sodiu nitrate A suitable crystal holder of sufficiently thick glass fibre wa made to hold the ammonium nitrate crystal rigidly Experiment were made with the '*c*'- axis of the crystal kept vertical The suspended crystal was kept inside the experimental tube for a day in th presence of P_2O_5, so that no trace of moisture might be present

The experimental procedure was as follows the critical angl of rotation of the torsion-head was found at room temperature wit the field on Now the temperature was gradually raised by a fe degrees, and when equilibrium conditions had been attained, th critical angle of rotation of the torsion-head was again found Thi was done for a few temperatures up to the first transition point of th crystal i.e , 32 3°C The next range of temperature employed wa between 32 3°C and 84 2°C The diamagnetic anisotropy of the al at temperatures 47°, 59° and 78°C. in this range was found investigated the range 84 2°–125 2°C and finally 125 2°– C The results obtained in an experiment with a crystal of mass mgm are shown graphically in Fig 20

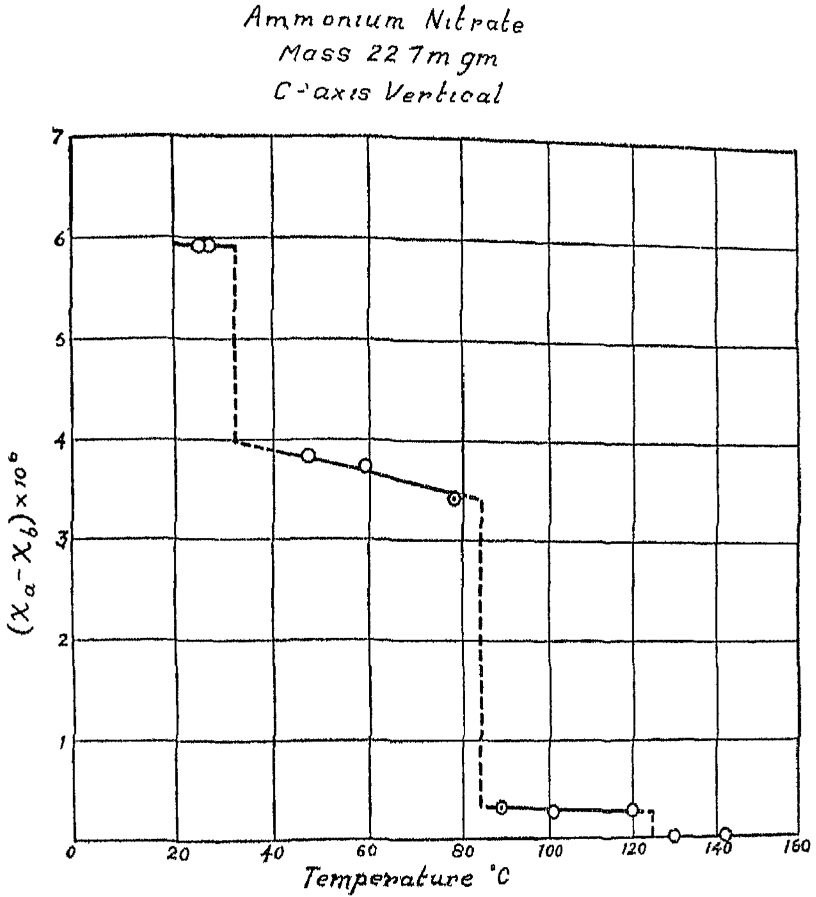


FIG 20

There are complications during the high temperature transi- due to the sublimation and breaking up of the crystal Owing us and various other causes inherent in polymorphic changes, the e could not be retraced on cooling But it was found that the tal regained a large part of its anisotropy on cooling down to room perature, although it was no longer a single crystal When heat- above 84 2°C, the crystals usually developed opacity and were ently polycrystalline aggregates

The transition at 32 3°C was studied in some detail and the changes are represented graphically in Fig 21 It is found that the changes commence only after the transition point is passed The curve shows definitely that at temperatures just above the transition point, the velocity of reaction is slow and increases as the temperature is raised further The crystal was allowed to remain at each temperature for about fifteen minutes In fact, the time taken to measure the critical angle of rotation of the torsion-head three times at each temperature was fifteen minutes on the average A curve of this character gives only a general idea of the velocity of reaction a various temperatures For more accurate determination we have to keep different crystals at various temperatures just above the transition point and study the change of diamagnetic anisotropy with time in each case This was done for three temperatures, 32 8°C, 34 2°C and 36 0°C At 36°C, it was found that the velocity of reaction is high enough to be considered abrupt Fig 22 shows the curves obtained ΔX being plotted against time

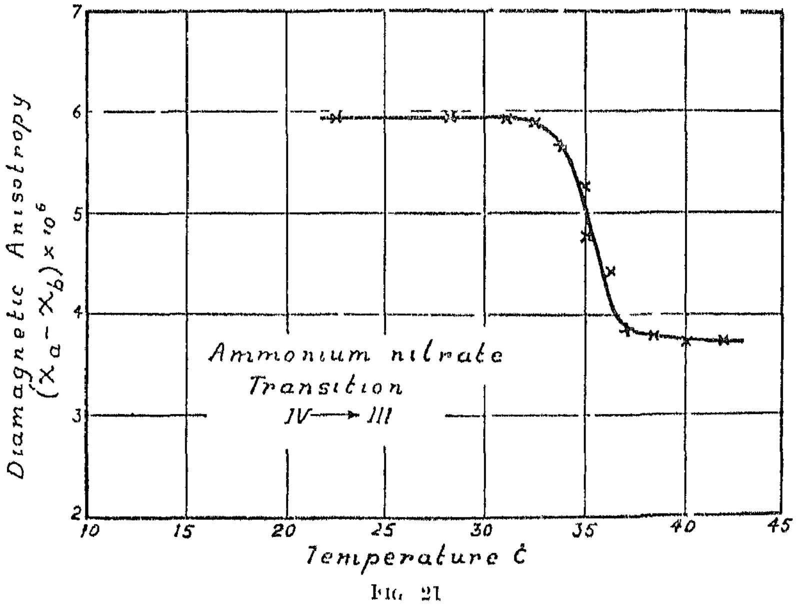


FIG 21

Experiments with a Crystal which was heated and ooled about the transition point 32.3° several times

In such a case, it was found that there is practically no re ation of the polymorphic transition If the temperature is kept tle higher than 32 3°C, the diamagnetic anisotropy falls to a low e and does not change preceptibly with time If, however, the tal is brought to a temperature lower than the transition tempera-, the anisotropy assumes a higher value It was noticed that, alternate heating and cooling destroyed the homogeneity of the tal and there were considerable variations in the actual values of diamagnetic anisotropy obtained The original room temperature e of the single crystal could not be reached in any case although es very near to it were obtained in one or two instances

When a crystal of IV-ammonium nitrate, after transformation I-ammonium nitrate by being kept at a temperature of 60°C for w hours, was gradually cooled down to room temperature, it was rved that at about 27°C the diamagnetic anisotropy did not show perceptible increase The velocity of reaction III→IV was d to be rather very slow under the conditions of the experiment urther cooling to 20°C the diamagnetic anisotropy was found to increased considerably to very nearly the original value for IV-onium nitrate crystal indicating reconversion to IV-ammonium te

The transition at 84 2°C was observed to be comparatively k but was not investigated in great detail

Diamagnetic Anisotropy in relation to Polymorphism in Ammonium Nitrate

The most significant feature of the results in the more or less ipt changes of the values of the diamagnetic anisotropy of the tal corresponding to the occurrence of the various polymorphic ifications It is quite clear that in favourable cases as in ammo- n nitrate, we can easily detect polymorphism by magne-crystallic action It is also evident that a detailed study of a polymorphic transition is possible by this method and considerable information may be gained regarding the velocity of transition at various temperatures

Now it must be emphasised that there are limitations to this method Recent X-ray work by Leonhardt and Borchert[10] and Tiemeyer[10] indicates that, in general, during a polymorphic transition the single crystal of one modification gets transformed into a polycrystalline aggregate of the second modification Tiemeyer has examined the various transitions in ammonium nitrate by X-ray analysis He finds that III–ammonium nitrate formed from IV consists of minute crystals which, however, are not very markedly separated from each other so that it approximates to a mosaic crystal The orientations of these crystallites are more or less of a regular character, although there is some departure from perfect regularity of arrangement Cooling the III-ammonium nitrate thus formed below 32 3°C, produced polycrystalline IV-ammonium nitrate

The magnetic measurements also indicate that there is regularity in the arrangement of the crystallites in III-ammonium nitrate formed from IV. It is found that the diamagnetic anisotropy of III ammonium nitrate (Fig 20) is approximately what should be expected if the '*c*'-axis of the original room temperature modification corresponds to the '*c*'-axis of the III-ammonium nitrate crystal (from the standpoint of the magnetic measurements, it makes little difference whether the III-form is a single crystal or a polycrystalline aggregate the crystallites of which are arranged regularly with similar axes pointing in the same direction) According to the X-ray analysis of Hendricks and others the planes of the nitrate ions are inclined to the crystallographic '*b*'-axis at an angle of 26° and they are also parallel to the '*c*'-axis The inclination of the planes of the ions accounts for the lower value of the diamagnetic anisotropy of the III modification, experimentally observed If we tentatively assume that the '*c*'-axis of the III-form is in the same direction as the '*c*'-axis of the

n temperature modification, and calculate the angle of inclination
ie plane of the (NO$_3$)$^-$ ion from the observed diamagnetic anisotropy
ie crystal, it comes out to be 25° nearly From this it appears to
ustifiable to draw the important conclusion that when a polymorphic
sition takes place in a single crystal, there is usually a definite
tion between the orientation of the crystallographic axes in the
forms Several independent experiments gave more or less
lar values for the change of diamagnetic anisotropy indicating
eby that the coincidence is not purely fortuitous

As regards transitions at 84 2°C and 125 2°C, there is consider-
difficulty on account of the lack of homogeneity of the crystal
igh temperatures Beyond about 100°C the crystal becomes
te and opaque, evidently due to its polycrystalline character But
ertheless, the changes of diamagnetic anisotropy are very charac-
stic Above 84 2°C the anisotropy falls to a low but definite value
mmonium nitrate has a tetragonal form according to X-ray
lysis and it will have no anisotropy in a plane perpendicular to the

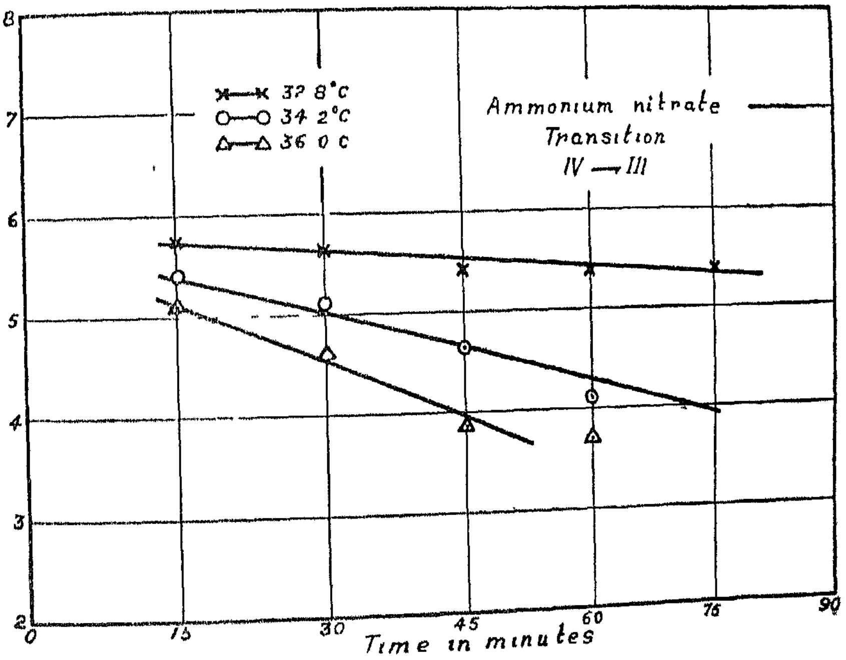


FIG. 22

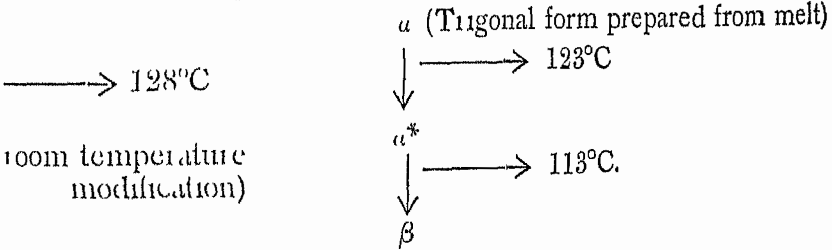
tetragonal axis. But there will be anisotropy in other planes. The results clearly show that the tetragonal axes of the crystallites formed are probably inclined to the vertical, thus accounting for the small anisotropy observed in the crystal.

The cubic form will naturally exhibit no magnetic anisotropy on account of its symmetry. In this particular case, as suggested by Hendricks and others from X-ray analysis, the nitrate ions are actually freely rotating the lattice. The diamagnetic anisotropy of the crystal will disappear in the case of free rotation of the (NO_3) group. Cubic symmetry in a crystal is achieved either by a suitable arrangement of anisotropic ions or molecules in the unit cell, or in case there is only one anisotropic group in the unit cell, by a free rotation of this group which will introduce spherical symmetry for the group. Cubic ammonium nitrate is remarkable in belonging to the latter class of crystals.

Fig. 22 shows that the rate of the reaction IV→III is greater if the temperature of the crystal is much higher than the transition temperature. The observation that the rate of reaction IV→III is accelerated when the temperature at which the transition takes place is much higher than the transition point, is in agreement with the observations of Pershke and Popov[10]. The fact that alternate heating and cooling accelerates the change at the transition point 32.3°C may be due to the presence of both modifications together simultaneously. Cohen and Lieshout have noticed that if the substance is alternately heated and cooled several times about the transition temperature there is practically no lag in the transformation. If on the other hand, III-ammonium nitrate is kept for a long time well above the transition temperature 32.3°C, we have seen that on cooling down the crystal there is hysteresis in the III→IV transformation.

4. *POTASSIUM NITRATE*

Just like ammonium nitrate, potassium nitrate also exhibits polymorphism. But only two forms are known. M. L. Frankenheim[12] first discovered the existence of the two forms. The transition perature was later investigated by E Mallard[13] who fixed it at ut 300°C But G Foussereau[14] was able to arrive at the more urate value of 130°C by experiments on the electrical conductivity the substance On careful investigation M Bellati and R nanese[15] found that there is considerable lag in the transition, nges occurring at 129°C on heating up and 122°C on cooling down ectively From optical investigations W Schwarz[16] could arrive omewhat similar conclusions The change of double-refraction found to take place at 129 5°C The experiments of F Wallerant[17] icate that the transition takes place at 126°C On cooling, however, llerant did not observe any transition till at about 114°C, when a lden increase of birefringence was observed due to the occurrence a third 'trigonal' modification This on further cooling became noclinic later The last transition has not been confirmed by later rkers The effect of pressure on the polymorphic transformation KNO$_3$ has been extensively investigated by P W Bridgman[18] Cohen and H L Bredee[19] also report the occurrence of a 'third dification' below 127°C which, however, soon transforms to the al form. More recently W Borchert[20] has investigated the polyrphism of potassium nitrate in great detail by means of X-rays. finds that the rhombic low-temperature modification (β) of the gonite type is transformed to the high-temperature modification of calcite type (α) at 128°C The change $\alpha \rightarrow \beta$ occurs in a comcated way On cooling, the trigonal modification assumes a mosaic racter at 123°C This has been called the α^*-modification by rchert The α^* crystal changes to β at 113°C, the β-modification formed consisting of very fine crystallites (Fig 23)



Scheme of Polymorphic transitions in Potassium Nitrate

FIG 23

Now the trigonal modification called α_0 obtained by the transformation of the β-form at 128°C has been found to differ from the α crystal prepared from the melt, in that on cooling down the β-modification occurs at 128°C without any lag The β-modification thus obtained retains more or less the character of a single crystal, in general, but it was found that the individual "Gitter blocke" exhibit an error of orientation of the 'c'-axis

If, however, the α_0-modification is kept at a high temperature, (about 195°C) then, on cooling, it behaves like the α-modification prepared from the melt, the transition to the β-form occurring at 113°C only

It will be evident from the above that the observed changes are rather complicated The author has investigated the corresponding changes of the diamagnetic anisotropy of the crystal under various experimental conditions and the results obtained are presented and discussed in relation to the earlier X-ray work.

The crystals of potassium nitrate were prepared from a saturated solution of the substance (Kahlbaum's purest) in dilute nitric acid. The crystal was suspended from the quartz fibre with the 'c'-axis horizontal and the 'a'-axis vertical The value of $X_b - X_a$ determined at room temperature, has been given earlier ($X_b - X_a = 6\ 98 \times 10^{-6}$) and the changes in this quantity with rise of temperature were investigated

It was found that the diamagnetic anisotropy changed at 127°C more or less abruptly (Fig 24), and no lag in the transition could be found, as far as could be made out from the magnetic measurements The measurements were taken after the temperature had reached a steady value in each case The observed change apparently corresponds to the transition of the crystal from the aragonite type of structure to the calcite type Heating of the crystal above 127°C had practically no further effect on the diamagnetic anisotropy

The changes on cooling down the crystal from 150°C were not equally striking At 124°C. an increase in the diamagnetic anisotropy could be observed (Fig 21) This should correspond to the change to the β-modification

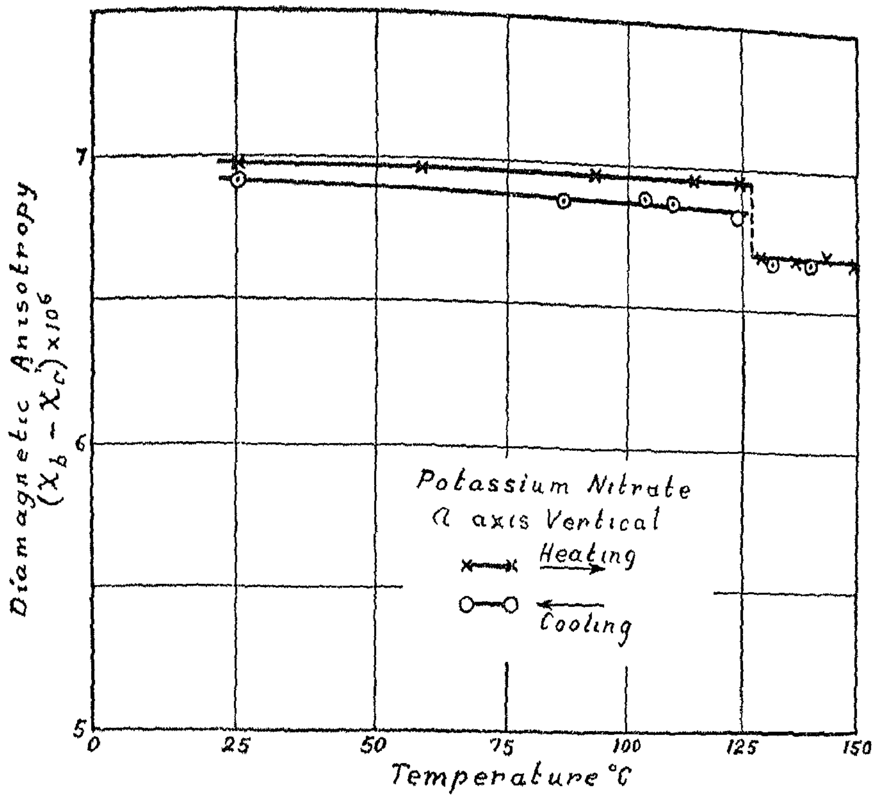


FIG 21

The remarkable fact in these experiments is that the orientation of the 'c'-axis of the crystals relative to the field is not affected to any great extent during the transition The maximum deviation found was only about 1° This would indicate that when the polymorphic transition takes place, the trigonal axis of the α-modification corresponds more or less to the 'c'-axis of the original β-modification The planes of the (NO_3) groups are perpendicular to the 'c'-crystallographic axis in the β-modification and perpendicular to the trigonal axis in the α-modification"[1] Hence, when polymorphic changes take place there appears to be a definite geometrical relation between the crystallographic axes of the two modifications involved in the change in the case of some crystals. Attention has been drawn to this aspect of crystal polymorphism by Borchert also as mentioned earlier. The author has pointed out before that in the case of ammonium nitrate also such a relationship seems to exist, the crystallographic axes of the two forms having definite orientations relative to each other. A detailed investigation of these relationships is possible by X-ray analysis only.

In one experiment the β-modification was heated up to 200°C and then cooled down in order to discover whether there is a lag in the $\alpha \rightarrow \beta$ transition. It was observed that the increase in the diamagnetic anisotropy occurred considerably below 127°C. A gradual increase was noticed at 110°C. but the original value of the anisotropy of the β crystal was not attained. The crystal was definitely found to have a polycrystalline structure and had become opaque. The results indicate considerable hysteresis in the $\alpha \rightarrow \beta$ transformation.

5. SULPHUR

The diamagnetic anisotropy of rhombic sulphur at room temperature has been studied by the author as described earlier. Above about 96°C rhombic sulphur (α) transforms into a monoclinic form (β). This transformation was observed by Mitcherlich in 1823 and has been extensively studied by various workers[22]. P. Duhem[23] has found that the rate of reaction depends upon the proportion of soluble to insoluble sulphur present, besides various other physical conditions. Gernez[24] has found that the rate of transformation is very much dependant upon the temperature. The higher the temperature of the crystal above the transition temperature the quicker is the transition $\alpha \rightarrow \beta$. The reaction $\beta \rightarrow \alpha$ has been shown by P. Duhem[23] and H. R. Kruyt[25] to be very slow. The actual temperature of transition $\alpha \rightleftharpoons \beta$ has now been accepted as 95.5°C[26].

Employing the technique previously described, the author has tried to investigate the course of the reaction, rhombic to monoclinic sulphur. A big regular crystal of rhombic sulphur grown from a solution in carbon disulphide was suspended in the magnetic field with the 'c'-crystallographic axis vertical. The change of diamagnetic anisotropy $\chi_b - \chi_a$ was investigated at various temperatures, taking measurements at intervals of half an hour over the range 25°-107°C Practically no sudden change of diamagnetic anisotropy could be observed even at the temperatures, 98°, 105° and 107°C The crystal was then kept at 100°C for two hours A very slight decrease in the diamagnetic anisotropy could be observed which was less than 5 per cent of the total anisotropy After three hours, the decrease of diamagnetic anisotropy amounted to about 7 per cent of the initial anisotropy It was evident that the changes are not of a striking character They seem to indicate, however, a slow rate of reaction There was no serious loss of weight of the crystal due to volatilization In view of the fact that the crystal structure of sulphur is not definitely known still further investigations were not continued.

General Remarks on the Temperature Variation of the Diamagnetic Anisotropy of Inorganic Crystals

The most striking changes of diamagnetic anisotropy are observed in the case of polymorphic inversions At fairly low temperatures it is possible to study polymorphism in detail by the method of magne-crystallic action We note that much valuable information regarding the velocity of polymorphic inversion, the dependence of this velocity on the actual temperature at which the change takes place, hysteresis phenomena, and the relative orientations of the crystallographic axes of the various modifications as they are formed one from the other, can be obtained Changes of a different nature are observed in a crystal like sodium nitrate Here, the decrease of diamagnetic anisotropy of the crystal is associated with the anomalous expansion of the lattice and consequent change of the intrinsic diamagnetic anisotropy of the (NO_3) group When rotations or oscillations of anisotropic groups in crystals set in at high temperatures, they can also be easily detected by magne-crystallic action. A freely rotating group even if it is anisotropic will acquire spherical symmetry, and it will not contribute to the anisotropy of the crystal In cubic ammonium nitrate the (NO_3) groups are supposed to be freely rotating, and that is the reason why the crystal is isotropic although there is only one (NO_3) group in the unit cell The measurements cannot prove that any rotation exists in cul since, rotation or no rotation, a cubic crystal will not usually anisotropy But if in a non-cubic crystal rotation of anisotrop were to set in, it can be easily detected by determinati change of diamagnetic anisotropy

In general, we notice that in magne-crystallic action useful method of investigating various dynamic phenomen in the solid state, and in favourable cases much new n regarding various aspects of these changes may be obtained

ORGANIC CRYSTALS

Cabrera and Fahlenbrach[27] have shown that the d susceptibilities of organic aromatic compounds are not sensib by a rise of temperature of the order of 100°C Since th temperatures employed by the author in the case of orgar investigated here, did not exceed this, we may justifiabl any change of diamagnetic anisotropy observed in the changes taking place in the lattice, and not to any intrinsic of molecular anisotropy.

Several methods were tried to prevent volatilizat crystals Coating the crystal with some heavy viscous boiling point was not found to be very satisfactory Immer crystals in liquids of high boiling point was also not possible account of the lightness of organic crystals torsional mea could not be made accurately Besides, convection curre liquids are set up at high temperatures which seriously inte the measurements Hence, the method adopted was allowance for the sublimation of the crystal, weighing it l after the experiment, and also at various stages as found c All the manipulations were also carried out as quickly as order to minimise losses due to sublimation, allowing time for the crystal to reach the temperature of the surrounding case of azobenzene and benzophenone, on account of melting points, sublimation was very slight and led to no serious difficulties The chief effects studied were, polymorphism, and the effect of impurity-molecules on the stability of the lattice at temperatures nearabouts the melting point. Crystals of resorcinol, azobenzene, benzophenone and naphthalene were investigated

1. RESORCINOL

The early experiments were made on resorcinol, and the preliminary results obtained have been reported in a note to 'Nature' Kahlbaum's purest substance was used and good crystals could be easily grown from aqueous solution by slow evaporation Crystals weighing 15-30 mgm were used in the experiments Resorcinol crystals have a tendency to become coloured on exposure to light The melting point of the crystals used was 109°-110°C

CRYSTAL DATA

Resorcinol – $C_6H_6O_2$; melting point 110°C, gm molecular weight 110 05,, *a* *b* *c* 0 9105 1 . 0 5404, Orthorhombic, space group C^{9}_{2v}, Four molecules in the unit cell[28]

The technique adopted for determining the diamagnetic anisotropy was the same as described in the case of sodium nitrate The crystal was suspended with the '*c*'-axis vertical and changes in the quantity $(X_a - X_b)$ were observed

The actual experimental procedure was as follows The oven was raised to the desired temperature first of all The crystal suspended from the quartz fibre was then introduced and when it had taken up the temperature of the surroundings (this did not take more than five minutes) the critical angle of rotation of the torsion-head α_0 was measured after the preliminary adjustment of the crystal with the axis of greatest (algebraic) susceptibility in the horizontal plane (i e , with the '*a*'-axis parallel to the field direction After two measurements of α_c to check up the accuracy, the crystal was quickly cooled down to room temperature and the diamagnetic anisotropy at room temperature again measured This process was repeated up to 105°C. During each determination, the crystal was not allowed to remain at the high temperature for more than fifteen r was found that in every case, the initial room temper of the diamagnetic anisotropy was almost restored, exc later stages of the experiment at higher temperatures crystal had been alternately heated and cooled several t loss due to sublimation was estimated by weighing at each stage of the experiment It was found that developed considerable opacity on being heated repeatec polycrystal formation

Fig 25 shows the nature of curve obtained in nary experiments With rise of temperature there is

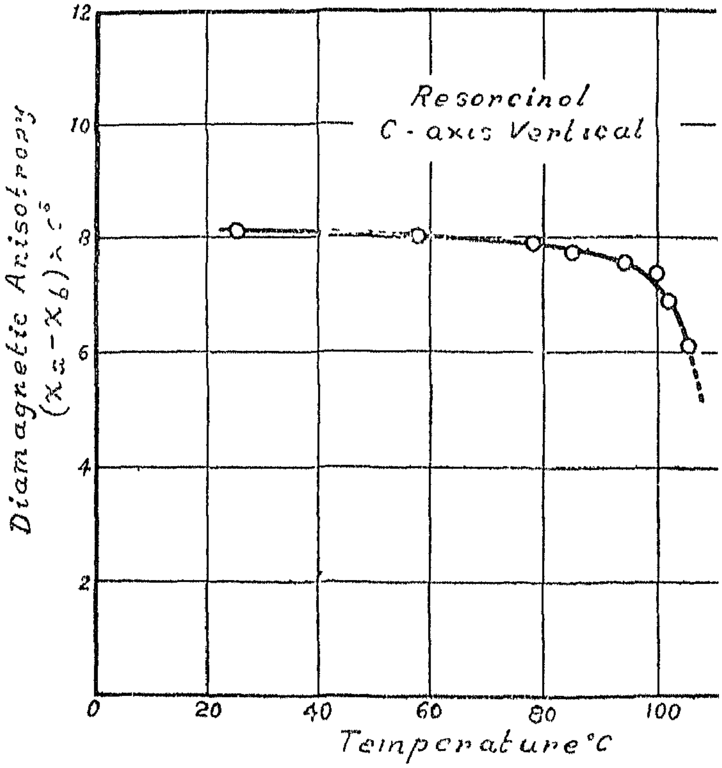


FIG 25

no change of anisotropy up to about 80°C From 8 temperatures near the melting point, the anisotropy rapidly Near the melting point the fall of anisotrop marked. At higher temperatures the orientation of the crystal in the field was observed to have changed by several degrees. This change was rather arbitrary.

The explanation of the changes presented many difficulties. The observed change did not resemble the case of a normal polymorphic inversion in view of the fact that it appeared to be gradual. A polymorphic inversion with considerable hysteresis might give rise to a gradual change in the anisotropy, but in this case, the restoration of the room-temperature value of the anisotropy on cooling requires explanation. While these aspects were being considered, Ubbelohde and Robertson[29] showed that ordinary resorcinol (α) undergoes a transformation into a denser crystalline modification called β-resorcinol at about 74°C of the following characteristics.

β-resorcinol $C_6H_6O_2$, M = 110.05, melting point 109°–110°C, calculated density 1.327 gm/cc, Orthorhombic bipyramidal, space group C_{2v}^{9}, Four molecules in the unit cell[30].

The change from the α to the β-form does not take place at once. Considerable hysteresis in the phenomenon has been observed. The velocity of transformation will be greater the higher the temperature of the crystal above the transition point 74°C. Robertson and Ubbelohde (loc. cit.) have found that it takes nearly an hour for the α-form to get converted into the β-form at 100°C. In the actual experimental technique adopted by the author, there is evidently partial conversion of the α-form to the β-form, which takes place progressively as the crystal is repeatedly heated further and further. It is obvious that this should lead to a change of diamagnetic anisotropy. Since, however, the transition from the β to the α-form takes days, one should in fact expect no restoration of the anisotropy to nearly its initial value on cooling down the crystal again to room temperature as was experimentally observed. This was rather puzzling but could be satisfactorily accounted for in the light of further investigations on azobenzene crystals. The detailed account of these studies will be given later, but we shall here anticipate some of the important results obtained which are relevant here. The azobenzene molecule has two

forms, the *cis* and *trans* Solutions of *trans*-azobenzene
light will contain the *cis*- form also and crystals of *trans*-a
grown under ordinary conditions are likely to contain a sma
age of the *cis*- form molecules which will evidently con
impurity in the lattice

The temperature variation of the diamagnetic anisotrop
azobenzene crystals containing a small percentage of the
molecules was studied and a remarkable diminution of d
anisotropy of the crystal was observed with rise of temper
siderably below the melting point Provided the manipulatio
quickly enough, on cooling down the crystal, there was
complete restoration of the original value of the anisotropy i
stages But if on the other hand, the crystal was kept at a te
of about 60°C for a few hours, these anomalous changes
disappeared and there was practically no temperature depe
the diamagnetic anisotropy except at the vicinity of the me
(regarding which more will be said later) The reason fo
discovered to be the conversion of the *cis* molecules to
form completely at the higher temperatures The anomalou
were all found to be due to the presence of impurity
These bring about an anomalous decrease of diamagnetic
of the crystals If the amount of impurity is small, the c
observed only nearabouts the melting point, and the g
amount of impurity the more striking is the decrease of d
anisotropy and the lower the temperature below the mel
at which it commences

In resorcinol, the changes taking place are now ea
standable. At temperatures above 71°C conversion of α
to β-resorcinol takes place, but owing to the short durat
experiment and the hysteresis of the transformation, o
fraction of the crystal is converted The transformation t
at various points in the crystal lattice, and each minut
formed constitutes, therefore, a defect in the lattice of the
The natural effect of the simultaneous existence of two pha

be cause an anomalous decrease of diamagnetic anisotropy of the the crystal similar to what is observed when impurities are present The anomalous change due to impurities is also more or less reversible is found experimentally in the case of azobenzene and other organic crystals The exact mechanism of the changes brought about by impurities will be discussed later, but it is enough for the present purpose to point out how the formation of the crystallites of β-resorcinol might account for the observed magnetic behaviour of α-resorcinol at high temperatures

When complete transformation to β-resorcinol has taken place, we should not expect any abnormal changes of anisotropy except perhaps very near the melting point, when the presence of the usual impurities found in organic crystals will cause a rapid diminution of the anisotropy This could be tested out by keeping a crystal of α-resorcinol for one hour at 98°C and then studying the temperature variation of the anisotropy in the range 25–105°C It was found that there was practically no change of anisotropy of the crystal with temperature, except what could be explained by the volatilization of the crystal In the following table are given the values of α_0 at various stages

TABLE

α_0 in degrees		Temperature °C	
1085	α- resorcinol	25°	
965	β- ”	↓ 98°–	After being kept for one hour at 98°C
955	”	↓ 25°	
950	”	↓ 90°	
943	”	↓ 105°	
932	”	↓ 25°	

The polymorphism of α-resorcinol was next examined to the volatility of the crystal accurate determination of the taking place was not possible In Fig 26 are shown th curves obtained with two crystals of α–resorcinol The proc this case was as follows. first of all determined the diamagne tropy at room temperature and at several higher temperatu 74°C., then kept the crystal at 78°C *for one hour* and meas diamagnetic anisotropy again, cooled the crystal to room ter and again measured the diamagnetic susceptibility, finally the crystal and determined the extent of volatilization, the

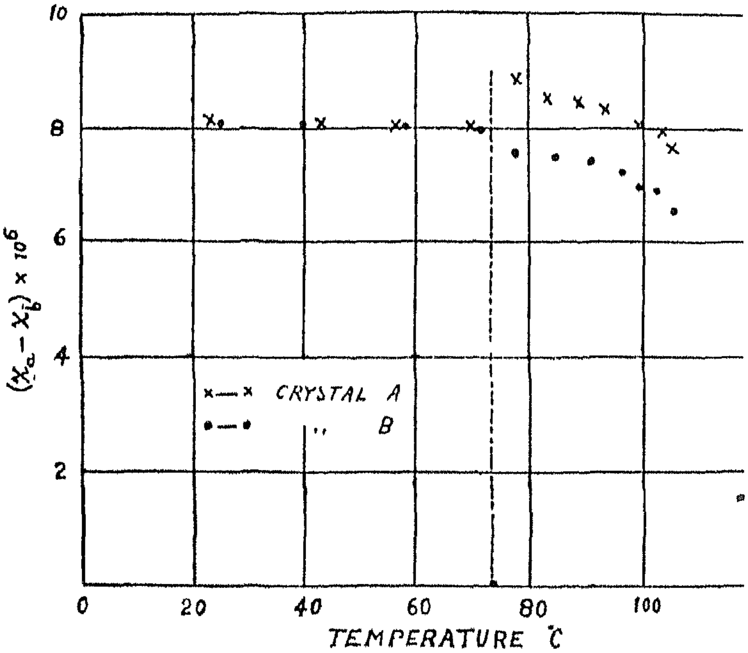


Fig 26

gated the change of diamagnetic anisotropy of the aggrega obtained from 78°C up to the melting point It was foun change at the transition temperature 74°C from the α to th did not always proceed in any definite manner which could b ed as the points in Fig 26 indicate In one case the dia anisotropy of the β–polycrystal is seen to be higher than tl crystal originally taken The orientation of the transformed the magnetic field had also no definite relationship with that of the original α–crystal

It is evident, therefore, that the orientation of the crystallites in the β form obtained from the α-single crystal does not occur in a determinate manner, and the case here is more complicated than in an ionic crystal like KNO_3, in which it was found that the 'c'-axis of the orthorhombic form coincided more or less with the trigonal axis of the rhombohedral high-temperature modification Transition from the β- to the α- form has been studied by Robertson and Ubbelohde (*loc cit*) by X-ray analysis, and they have found that crystallites of the α form are most probably orientated preferentially in certain directions with respect to the original β-crystal Apparently no conclusive evidence for preferential orientation is indicated by the magnetic experiments But it is reasonable to expect the 'c'-axis of the β-crystallites to coincide with the 'c'-axis of the α-crystal, since, the length of the 'c'-axis of the unit cell in both crystals is nearly the same The dimensions of the unit cell are. β-resorcinol; $a = 7\ 91$, $b = 12\ 57$, $c = 5.50$, α-resorcinol, $a = 10\ 53$ $b = 9\ 53$ and $c = 5\ 66$ A° U.

We have seen that in the one case, on undergoing polymorphic transformation, the diamagnetic anisotropy of the crystal suspended with the 'c'-axis vertical has increased while in the other case it has decreased This is evidently due to the peculiarities of orientation of the β-crystals formed. Assuming a preferred orientation of the crystals with respect to the 'c'-axis of the original crystal, we can explain this anomaly in the following manner

Since the planes of the rings are nearly parallel to the 'b'-axis in β-resorcinol unlike in α-resorcinol, where the inclination of the plane of the molecule to the 'a' and 'b' axes is more or less equal, the anisotropy $X_b - X_a$ in β-resorcinol will be much larger than $X_a - X_b$ in α-resorcinol. Hence, a preferred orientation of the β-crystallites, with their 'c'-axes vertical and the 'a' and 'b' axes having definite directions may lead actually to an increase in the anisotropy of the α-crystal on undergoing polymorphic inversion to the β-form In the other case where a diminution in the anisotropy is observ polymorphic inversion, there is probably a partial randomne arrangement of the β-crystals in regard to their '*a*' and '*b*' axes

Room-temperature experiments were made on a single c of α-resorcinol The values obtained were

$$\chi_a - \chi_b = 8.13 \times 10^{-6}$$
$$\chi_c - \chi_b = 13.30 \times 10^{-6}$$
$$\chi_c - \chi_a = 5.22 \times 10^{-6}$$

Assuming Pascal's value, -67.2×10^{-6}, for the mean sus bility, we get

$$\chi_a = -66.1 \times 10^{-6}$$
$$\chi_b = -74.3 \times 10^{-6}$$
$$\chi_c = -61.0 \times 10^{-6}$$

The angles, α, β and γ made by the normal to the plane c ring with the '*a*', '*b*', '*c*' axes can be calculated assuming $|K_1| =$ in the plane of the ring Then $\alpha = 55.9°$, $\beta = -17.0°$ and $\gamma = ($ These results agree with those of Lonsdale[31] More recently Bane has also obtained values which agree with those of the author

2. *TRANS-AZOBENZENE*

We have seen that in the case of resorcinol complication introduced by the tendency of the crystal to sublime at high tem tures The polymorphic inversion also makes it difficult to study aspects such as the influence of impurities *Trans*-azobenzene convenient substance for studying various phenomena associated the variation of diamagnetic anisotropy with temperature It ha a low melting point, does not decompose, it is only slightly volatile it crystallises easily from alcohol There is, however, a *cis*– for azobenzene[33] which may occur as an impurity in *trans*-azobenzene far from being a source of trouble, the existence of the *cis*– form h us to understand better some interesting aspects of the temper variation of diamagnetic anisotropy of crystals

The *cis*– form is present in solutions of *trans*-azoben exposed to light In the crystalline state, the *cis*– form can be indefinitely in the dark On heating *cis*-azobenzene at ordinary p sure, it is converted into *trans*-azobenzene.

CRYSTAL DATA

Trans-*azobenzene* $C_{12}H_{10}N_2$, M = 182, melting point 67.8–68.0°C, density 1.22 gm per cc, monoclinic prismatic, a=12.2, b=5.77 and c=15.1 in A°U, β=111.4°, space group C^5_{2h}, Four molecules in unit cell[11].

Cis-*azobenzene* $C_{12}H_{10}N_2$, M = 182, melting point 71.4°, orthorhombic; a=7.57, b=12.71, c=10.30 in A°U. Four molecules in the unit cell[12].

The crystals were prepared from Kahlbaum's *trans*-azobenzene recrystallised from alcohol. In solutions exposed to light there is the *cis*- form also present, as pointed out by Hartley. *Trans*-azobenzene crystals prepared from alcoholic solution exposed to light will, therefore, contain a small percentage of *cis*-azobenzene molecules as impurities in the lattice. To obtain pure *trans*-azobenzene, crystallisation has to be done in the dark. Large crystals weighing from 15 to 25 mgm could be easily obtained by slow evaporation of the solution inside a bell jar.

The diamagnetic anisotropy of the crystal at room temperature was measured and the values obtained were

$$\chi_1 - \chi_2 = 19.5 \times 10^{-6}$$
$$\chi_1 - \chi_3 = 1.98 \times 10^{-6}$$
$$\psi = 65.6°$$

These agree satisfactorily with the values recently reported by Lonsdale[16] and Banerjee.

The diamagnetic anisotropy of the *cis*– form according to Lonsdale[18]

$$\chi_b - \chi_a = 17.3 \times 10^{-6}$$
$$\chi_c - \chi_a = 82.8 \times 10^{-6}$$
$$\chi_c - \chi_b = 35.1 \times 10^{-6}$$

The crystals of *trans*-azobenzene were suspended with the b'-axis vertical for the measurements at various temperatures. The loss due to volatilization was estimated in all cases by finally weighing the crystal.

Effect of temperature on the Diamagnetic Anisotr of Crystals grown from Alcoholic solution exposed to light

Some remarkable changes were observed in the crystals grown from alcohol in the ordinary way

Fig 27 shows the influence of temperature on the diam anisotropy, (X_1-X_2) There is a marked decrease in the an with rise of temperature on *gradually* heating the crystal changes are observed to begin considerably below the meltin

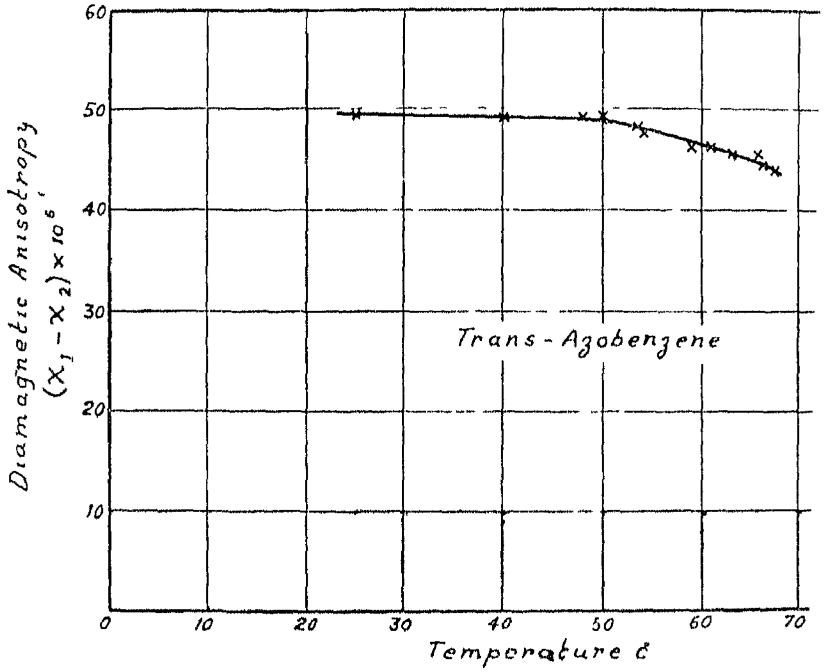


FIG 27

at about 54°C The changes were also found to be rever diamagnetic anisotropy being more or less restored to the value on cooling A more detailed examination, however that the phenomena are more complicated Another cry heated up to 60°C and its diamagnetic anisotropy measur temperature. The crystal was again cooled down to room ture immediately and its anisotropy again measured. At 60 was a remarkable diminution of anisotropy, but the original value was practically restored on cooling down However, it was discovered that on repeatedly heating and cooling the crystal several times in the above manner, the diamagnetic anisotropy assumed a constant value which was afterwards unaffected by temperature, in the range studied. The crystal was not only *not* damaged by this process of alternate heating and cooling, but actually became clearer and more transparent

The results are given in the table below

α_0 in degrees (Initial) Temperature (25°C)		α_0 in degrees (Final) Temperature (60°C)
2520	⟶	2340
	↙	
2500	⟶	2376
	↙	
2460	⟶	2398
	↙	
2412	⟶	2405
	↙	
2400		

The progressive diminution in the room-temperature value of the anisotropy was mostly accounted for by the slight volatilization of the crystal

These changes at first appeared to be difficult to explain But the fact that in pure *trans*-azobenzene crystals no anomalous changes between 23°–60°C were observed at once suggested that they a to the presence of the *cis*– form molecules in the *trans*-azobe On prolonged heating, the *cis*-azobenzene molecules b converted to the *trans*- form and the disappearance of the ano are evidently an indication of the complete transformation

It now remained to elucidate further why the presence azobenzene molecules should cause anomalous changes of diam anisotropy and for this the influence of impurity molecules lattice was studied in detail

Three samples of crystals of different grades of purity prepared from the sample of *trans*-azobenzene available, by re crystallization from alcohol. The purest sample (prepared b sublimation) had a melting point 67 8°–68 0°C, while in the melting was observed to commence at 67 5°–67 7°C and 67 2°C The influence of temperature on the diamagnetic ani $(\chi_1-\chi_2)$ of these crystals was studied after they had all been sub to pre-heating at 60°C for one hour, to convert any *cis*-azoben them to the *trans*- form

Fig 28 shows the nature of the curves obtained In al there is a rapid decrease of diamagnetic anisotropy in the vicinity melting point But the change of diamagnetic anisotropy at a lower temperature for the most impure sample than f purer samples The sharpest curve is obtained in the case purest sample The results clearly demonstrate that the pres impurities is capable of producing striking changes of diam anisotropy near the melting point and in a very impure a large decrease in the anisotropy may occur far below the point The observed changes due to the presence of *cis* molecules can now be readily understood, since these a constitute an impurity in the *trans*-azobenzene lattice

It is well-known that the more impure a substance is, t sharp is its melting point[99] Besides, the melting point is also l by the presence of impurities The determination of the point in fact provides a test for the purity of any sample of an

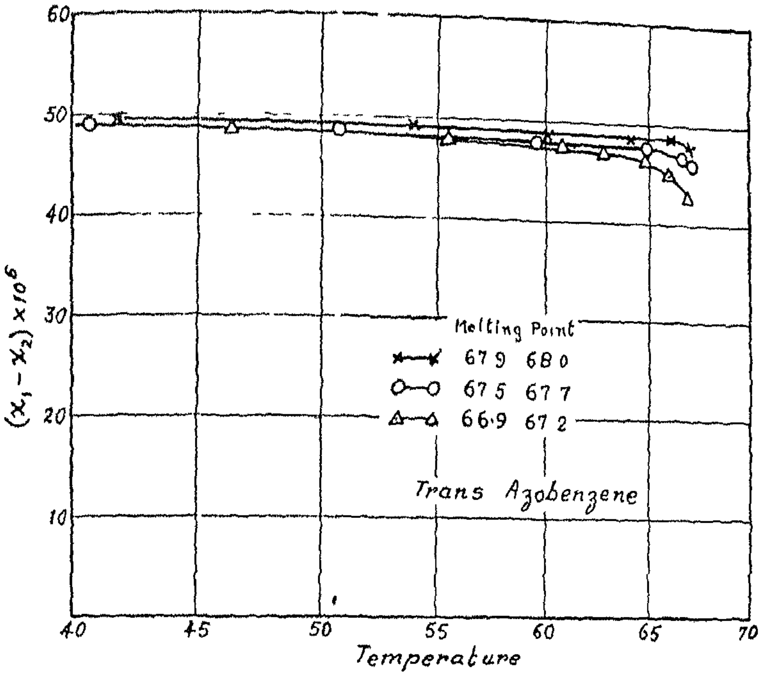


FIG 28

compound Many physical properties of substances are affected by the presence of impurities as the melting point is approached Le Blanc and Mobius[40] have determined the heat capacities of different samples of benzene having impurities $2 9\times10^{-6}$, $5 8\times10^{-\text{[illegible]}}$ and $4 7\times10^{-7}$ molecules per gram at various temperatures between 0°C and 5 5°C They found that the heat capacity curve did not give a sharp break at the melting point as should be expected in an ideally pure substance A smooth curve was obtained in each case, indicating a rapid increase of the heat capacity of the solid as the melting point was approached, the purest sample giving the sharpest curve This phenomenon is universal, and is exhibited by almost all organic crystals as shown by the investigations of Andrews, *Lynn and* Johnston[41] and Parks and his collaborators[42] (Papers in "Journal of the American Chemical Society") on specific heats of organic compounds Fig 29 shows a typical heat capacity curve of an organic compound obtained by Andrews, Lynn and Johnston It *is quite* evident, how in *an impure* sample, *the heat capacity begins* to increase at a lower temperature below the melting point than in the pure sample The rapid increase in the specific heat of the solid as the melting approached has been attributed by Parks to premelting cau impurities The changes of diamagnetic anisotropy and speci are intimately connected and arise from the same cause, viz., conversion from solid to liquid state nearabouts the melting poi

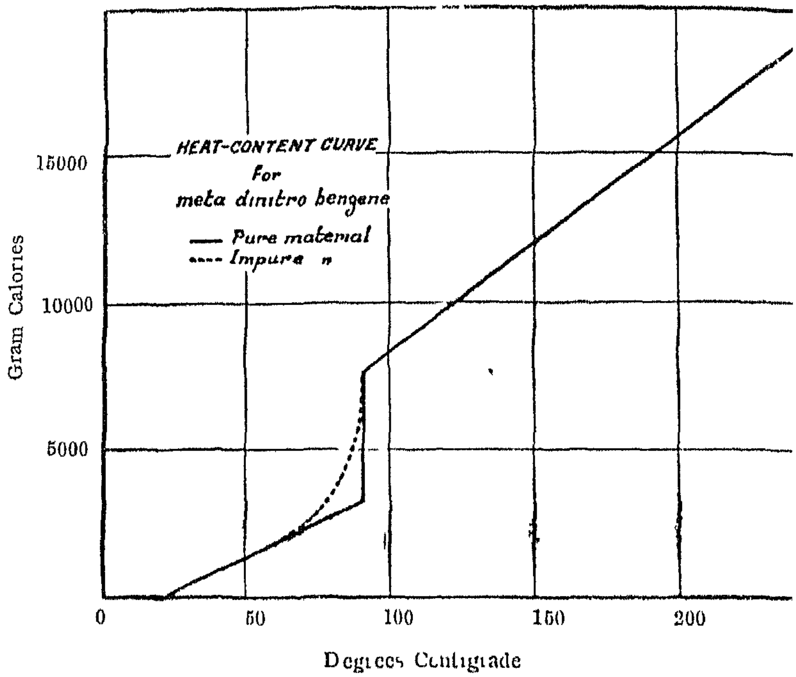


FIG. 29

The magne-crystallic data reveal clearly the mechan these changes We actually see that due to the impuriti sent a partial amorphicization of the lattice develops progr very near the melting point of the crystal, causing a fall in the d netic anisotropy The changes would correspond to a transitio crystal in small localised regions surrounding the impurity mol from the solid to the liquid state, even before the true melting the crystal is reached This naturally accounts also for the ano increase in the specific heat just below the melting point impurity molecule in the crystal introduces a discontinuity in th and acts as a centre for the 'premelting' of the substance in th localised region surrounding it. Due to the presence of the im molecule the surrounding molecules of the substance are in an unstable position and at high temperatures due to the thermal agitation are no longer able to occupy any fixed equilibrium position in the lattice and are consequently thrown into a state of dis-array Their state, therefore, corresponds to that of liquids The greater the number of impurity molecules, the greater will be the number of centres of premelting, and therefore the greater the anomalies in the magne-crystallic and specific heat results Due to the partial amorphicization of the crystal as the melting point is approached, while the heat capacity will *increase*, the diamagnetic anisotropy will naturally *diminish*.

It will be seen from the above that the study diamagnetic anisotropy of organic crystals at temperatures near the melting point is able to throw light on some aspects of fusion of solids The state of purity of a substance is also incidently revealed by the character of the $\Delta\chi-T$ curves. In an ideally pure crystal a sharp disappearance of the diamagnetic anisotropy at the melting point may be expected

3. *a-BENZOPHENONE*

Crystal Data—Benzophenone $(C_6H_5)_2CO$, M=182, Density 1.224 grams per cc , melting point 49 0°C ; Orthorhombic bisphenoidal, Four molecules in the unit cell, $a=10\ 17$, $b=12\ 06$ and $c=7\ 98$ A° U[43] Measurements of the diamagnetic anisotropy of the crystal at room temperature gave

$$\chi_b-\chi_c=71\ 2\times10^{-6}$$
$$\chi_a-\chi_c=71.7\times10^{-6}$$
$$\chi_a-\chi_b=0\ 53\times10^{-6}$$

The recent data of Lonsdale[44] are in good agreement with these results

Big crystals could be easily grown out of alcohol (Melting point, 48–49°C) The temperature variation of the diamagnetic anisotropy of the crystal was very similar to that of pure *trans*-azobenzene Near the melting point $\chi_a-\chi_c$ was found to decrease rapidly (Fig 30) This decrease is evidently due to the presence of a small amount of impurity in the crystal

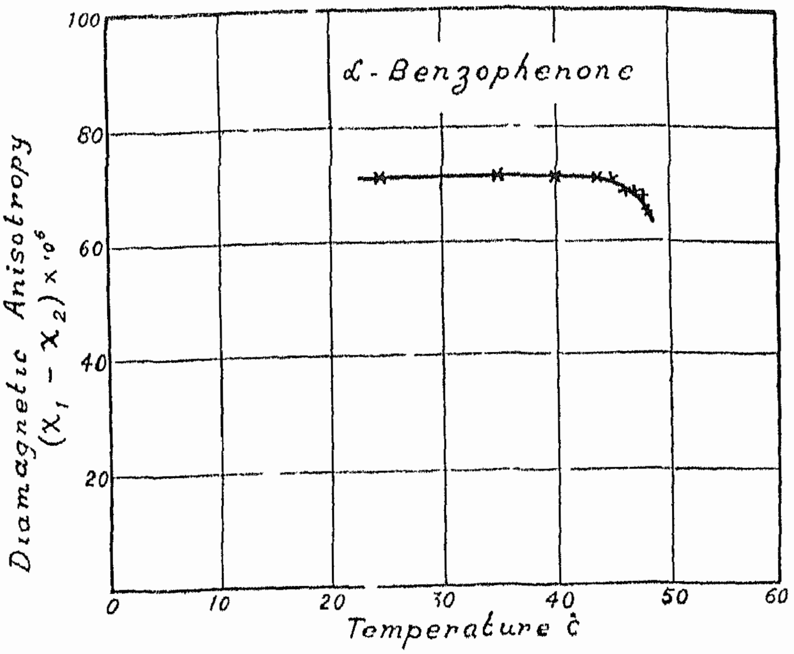


Fig. 30

4. NAPHTHALENE

Crystal data—Naphthalene, $C_{10}H_8$, Melting point 81°C
sity, 1.152, monoclinic prismatic, *a* = 8.29, *b* = 5.97, *c* = 8.68 A°l
$\beta = 122.7°$, Space group C^5_{2h}, Two molecules in the unit
According to Lonsdale and Krishnan[45]

$$\chi_1 - \chi_2 = 90.4 \times 10^{-6}$$
$$\chi_1 - \chi_1 = 20.6 \times 10^{-6}$$
$$\psi = 12°$$

In the case of naphthalene, there is considerable volatil of the crystal especially at high temperatures. The accur measurements is therefore much less. Two samples were av for the experiments, Kahlbaum's analytical reagent (M. P. 8 and also crude naphthalene (M. P. 78 - 80 C.). Large crystals grown out of alcohol. These were suspended with the vertical. Making an allowance for the sublimation of the cryst results clearly showed that $\chi_1 - \chi_2$ in the case of the impure gan to decrease at a much lower temperature than in the pure mple (Fig 31)

The room temperature value of $(\chi_1-\chi_2)$ was found to be .2 × 10^{-6} for the pure crystal, and 87 5 × 10^{-6} for the impure one

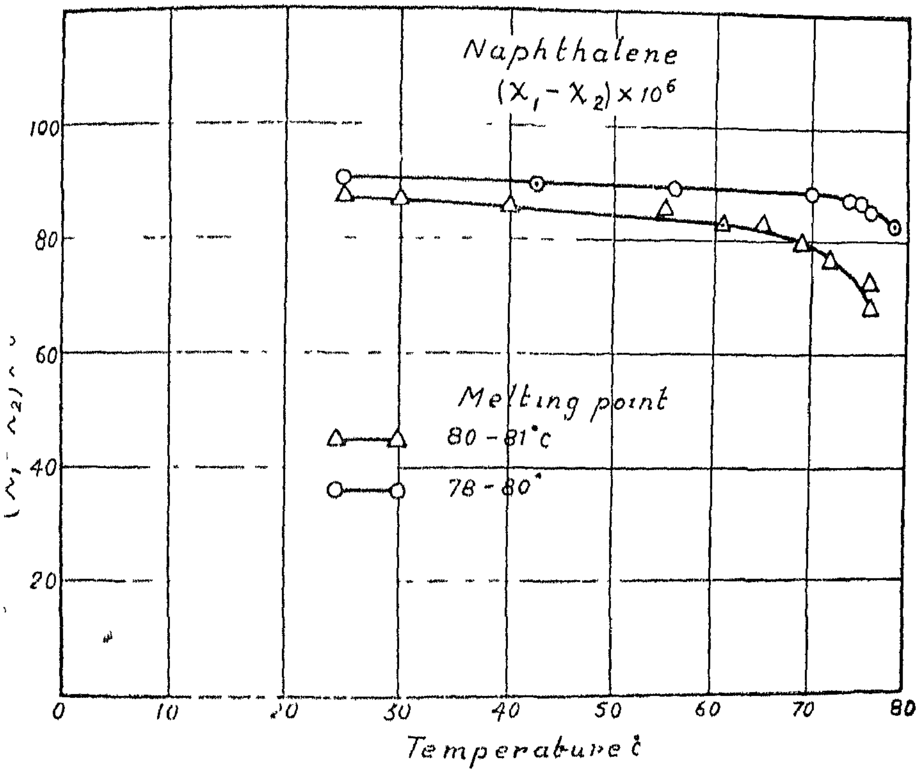


Fig. 31

General Remarks Regarding the Temperature Variation of the Diamagnetic Anisotropy of Aromatic Organic Crystals

Although the investigation of the temperature variation of the diamagnetic anisotropy of organic crystals is complicated by various factors, we see that, in general, much useful information may be gained in regard to the following phenomena (1) crystal polymorphism, (2) the effect of impurities on the melting of crystals and their influence on the lattice at temperatures nearabouts the melting point Polymorphic transitions at fairly low temperatures, at which complications due to volatilization of the crystals do not arise, can be stud conveniently by magne-crystallic action and the general procedure been outlined in the author's typical experiments It should be no that the changes of diamagnetic anisotropy accompanying polymor transitions in organic crystals, appear to be rather arbitrary owin polycrystalline formation of indefinite orientation, and the observati can be of a qualitative nature only In ionic crystals like the nitra there seems to be evidently a geometric relation between the axe the crystallites formed during polymorphic transition and the orig room temperature modification Hence the changes occurring in latter are more or less reproducible while in organic crystals the chan of diamagnetic anisotropy on transition are not always predictable regards the study of the influence of impurities, the magnetic meas ments offer a convenient method of investigation which is at the s time simple It would not be easy to study the phenomena qu tatively by X-rays which will involve careful intensity measureme The specific heat determinations give a general idea of the anoma behaviour of impure substances at the melting point but do not sug clearly the mechanism of the changes occurring in the lattice of crystal The rapid decrease in the diamagnetic anisotropy of im crystals shows strikingly the gradual breaking up of the lattice the melting point. Incidently the close connection between the cha in the specific heat and diamagnetic anisotropy as the melting is approached is also revealed The rapid decrease of diamag anisotropy of an impure crystal as the melting point is approache evidently a universal phenomenon which will be exhibited b impure substances, and the state of purity of the substance determine the temperature at which the anomalous change diamagnetic anisotropy will become prominent

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CHAPTER VI

MAGNETIC ANISOTROPY AND PLEOCHROISM OF MICA

1. *Introduction*

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

The magnetic anisotropy of a large number of varieties of mica has been studied by E Wilson[1] He examined both spotted as well as clear varieties, and in all cases found that the paramagnetic susceptibility parallel to the cleavage plane was much greater than that perpendicular to it The ratio $\frac{\chi_{\parallel r}}{\chi_{\perp r}}$ was very much greater in the spotted varieties It was not clearly stated to which group the specimens belonged Presumably only muscovite was examined It was tentatively suggested that the anisotropy might be due to either an orderly arrangement of the inclusions of magnetite present, or an actual difference in the behaviour of the mica itself in different directions relative to the crystallographic axes. No attempt was made, however, to decide between the two hypotheses The position has now altered considerably Clear inclusion-free specimens of mica containing iron which forms an integral part of the lattice (as in pholgopite and biotite) may well show a genuine crystalline magnetic anisotropy In the light of the X-ray crystallographic data now available[2] and recent developments in the theory of the magnetic anisotropy of paramagnetic solids due to Van Vleck, and Penney and Schlapp[3] a satisfactory interpretation of the magnetic data is now possible In the present investigation the author has determined the susceptibility and magnetic anisotropy of three varieties of biotite and one each of muscovite and phlogopite. The ferrous and ferric iron contents of the specimens were determined by chemical analysis and the pleochroism of the specimens also estimated quantitatively

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

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

The general scheme of the atomic structure of the micas was *first elucidated by Pauling*[4] *and the full investigation in the* case of muscovite has been made by Jackson and West[5] It has been shown that all the micas are built more or less according to the same plan The peculiar flaky structure and easy cleavage have been explained as being due to the formation of sheets of linked silicon-oxygen tetrahedra A sheet is formed by linking the oxygen atoms at the corners of the tetrahedra so that they are all in the same plane and the result is a hexagonal network Two such sheets placed with the vertices of the tetrahedra pointing inwards form a double sheet, the oxygen atoms at the vertices being cross-linked by aluminium atoms in muscovite, and magnesium and iron atoms in phlogopite and biotite Hydroxyl groups are incorporated, linked to a Al, Mg or Fe alone We have thus a firmly bound double-sheet and the mica structure is a succession of such double-sheets interspaced alternately by sheets of potassium atoms The iron atoms occupy positions of six co-ordination and are surrounded by an octahedral grouping of oxygen atoms and hydroxyl groups X-ray evidence has shown that such a grouping is present in the hydrated sulphates and double-sulphates of iron, cobalt, nickel, the water molecules in these salts constituting the octahedral environment The crystalline electric fields due to such an arrangement are presumably of a highly asymmetric character as has been pointed out by Krishnan recently

The chemical composition of the micas is variable within wide limits Since the magnetic properties are determined by the iron content, as will be seen later, it is essential to know accurately the amount of iron present In fact many properties of mica show a direct dependence on chemical composition Kunitz[6] has made a detailed study combining optical and density determinations with chemical analysis He established three series of isomorphous replacements and showed that the change in optical properties within one series depended mainly on the iron content Similar classifications have been made by Hallimond, Winchell and Jakobs, and recently Niggli[7] while discussing a recent paper by J Holzner on the crystal structure of biotite, has summarised the evidence from reliable chemical analysis and has pointed out the variability of the three types, i e, the muscovite type, the lithia mica type and the phlogopite-biotite type A consideration of the physical properties in relation to chemical constitution shows that we cannot speak of a continuous transition from one group to another This is probably due to the fact that the properties depend on the structure also besides chemical composition, and differences among the three types exist although the general plan of their architecture is similar. G Nagelschmidt[8] has recently found from an examination of the X-ray powder diagrams of ei different micas of known composition, density and optical propert that they belong to at least two distinct types, the musco type and the phlogopite-biotite type. The lithia mica type cc not, however, be distinguished

The principles governing isomorphous substitution in the m were established by the work of Mauguin[9] who measured the dim sions of the unit cell in varieties of known density and composi Ideal formulæ have been assigned based on such measurements follows .

Muscovite	K Al$_2$ (AlSi$_3$O$_{10}$) (OH)$_2$
Phlogopite	K Mg$_3$ (AlSi$_3$O$_{10}$) (OH)$_2$
Biotite	K (Mg, Fe)$_3$ (AlSi$_3$O$_{10}$) (OH)$_2$

3. *Determination of Magnetic Anisotropy*

The magnetic anisotropy has been measured by the torsi method The micas crystallise in the monoclinic system and t are three principal susceptibilities of which two lie in the symn plane and the third along the symmetry axis We have to deter the quantities $(\chi_1 - \chi_2)$, $(\chi_1 - \chi_3)$ and the relative orientation of axes of the magnetic ellipsoid with respect to the crystallogr axes χ_1 and χ_2 are the principal susceptibilities in the *b* (plane, χ_2 being nearer the '*a*'- axis and χ_3 is the prin susceptibility in the direction of the '*b*' axis The mica speci was suspended in the uniform magnetic field as follows —(1) the cleavage plane horizontal, (2) with the '*b*'-axis vertical (3) with the '*b*'-axis horizontal and the cleavage plane ver We thus directly determine the quantities $(\chi_3 - \chi_a)$, $(\chi_1 - \chi_2)$ $(\chi_3 - \chi_N)$ where χ_a is the susceptibility along the '*a*' axis and that perpendicular to the cleavage plane. From (2) we can dir get the angle which the χ_2 axis makes with '*a*'-axis This can also be calculated from the known values of $\chi_3 - \chi_N$ $\chi_3 - \chi_a$ for

$$\chi_3 - \chi_N = \chi_3 - (\chi_2 \sin^2\theta + \chi_1 \cos^2\theta)$$
$$\chi_3 - \chi_a = \chi_3 - (\chi_2 \cos^2\theta + \chi_1 \sin^2\theta)$$

Solving the simultaneous equation we get both θ and $(\chi_3-\chi_1)$ In the case of the micas matters are very much simplified, since the χ_2-direction was found to coincide with the direction of the '*a*'-axis

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

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

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

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

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

In the case of mica which was available in the form of thin plates only we cannot neglect the effect due to the anisotropy of shape of the specimen For, the paramagnetic susceptibility is fairly high, especially in the case of the biotites, and in some cases the magnetic anisotropy also is comparatively small The possible errors on this account were eliminated by adopting the device of Krishnan of immersing the crystal in a liquid bath of the same mean susceptibility, for phlogopite and muscovite An aqueous solution of manganese chloride was employed For determining the anisotropy in the cleavage plane, which was found to be very feeble, discs of the material 5 5 mm. in diameter were prepared In this case no correction for anisotropy of shape is necessary

In the case of the biotites the paramagnetic susceptibility was too high for a liquid-bath to be employed conveniently Small plates 1 cm by 4 mm were cut out, cleaned with dilute acid and distilled water and placed one above the other to form a block 10 × 4 × 4 mm using traces of diamagnetic shellac for attaching them Particular care was taken to see that the crystallographic directions of the plates coincided when cutting them out The long edges were carefully rounded off so that a cylinder, 10 mm height and 4 mm diameter, was obtained A silk thread was further wound round the cylinder so that the pieces might not fall off It was finally cleaned with dilute sulphuric acid and distilled water For determining the magnetic anisotropy in the cleavage plane, discs 5 5 mm in diameter were used Only the value of $\chi_{\parallel r} - \chi_{\perp r}$ is given for biotite and phlogopite since the anisotropy in the cleavage plane was negligibly small.

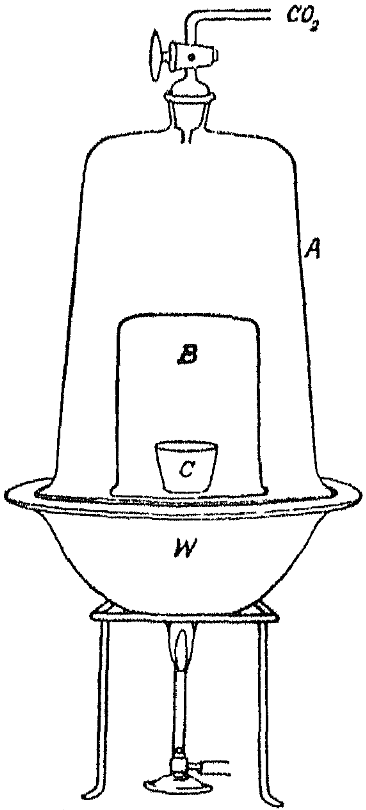
The absolute susceptibilities were determined by the torsion lance made by author.

5. Determination of Ferrous and Ferric Iron in the Specimens

The percentage of total iron and ferrous iron in the micas were termined by the following methods[10].

Total Iron.—The sample was ground to a fine powder in an ate mortar, and about 0·5 g of the powder weighed in platinum ucible and then fused with fusion mixture (two parts of Na_2CO_3 and e part of K_2CO_3). The fused mass after cooling was dissolved in lute HCl in a silica dish, evaporated to dryness over a water-bath, dissolved in dilute HCl, and the silica filtered off, washed on the ter, and weighed after ignition. The filtrate was heated up to iling point and a little concentrated nitric acid added followed by g of ammonium chloride. Ammonia was then slowly added to the iling solution until all the aluminium and iron were precipitated as droxide and the solution became slightly alkaline. The precipitate s then filtered off, washed on the filter with a warm solution of nmonium nitrate and ignited in a platinum crucible and weighed. e ignited mass was then fused with sodium bisulphate and after oling dissolved in dilute sulphuric acid. The solution was then run rough a Jones' reductor (an improved form of which has been vised by the author and reported elsewhere) in an atmosphere of rbon dioxide and finally titrated against standard permanganate.

Ferrous Iron.—The accurate determination of ferrous iron in licate rocks is a matter of considerable difficulty. The modified ratt method recommended by Hillebrand was adopted. A weighed antity of mica was carefully ground in an agate mortar under pure cohol for about an hour. A thorough grinding is necessary since arse particles take a very long time to get dissolved in HF. The ound mass was carefully washed down into a platinum crucible with r-free water and 10 c.c. of cold dilute sulphuric acid added. The ucible was supported over a water-bath and surrounded by an atmosphere of CO_2 by the arrangement shown in Fig 32. 6 c c of 40% hydrofluoric acid (Kahlbaum's analytical reagent) were quickly introduced into the crucible which was then covered with the lid and the water-bath heated, carbon dioxide being passed all the time The reaction was allowed to go on for 3 hours. Meanwhile a solution



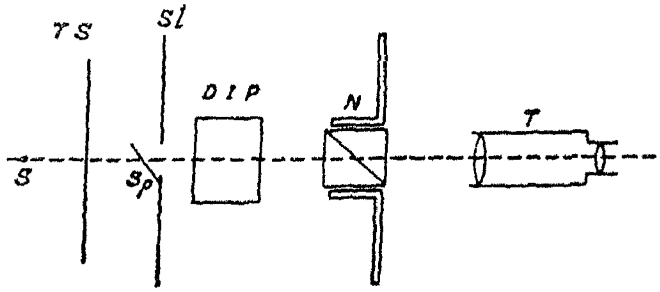
A—Bell-jar
B—Beaker
C—Platinum Crucible
W—Water-bath
Fig. 32

containing 50 g of boric acid and 20 c c of sulphuric acid in 300 c c of air-free water was prepared and the crucible and contents, after the reaction was over, were quickly transferred into the cold boric acid solution and titrated immediately against standard permanganate until a pink colour lasting for a minute or two was obtained.

blank experiment was performed under similar conditions ous ammonium sulphate About 0 5 g was weighed and in 300 c c. of dilute sulphuric acid and immediately titrated ermanganate Another 0 5 g was weighed in a platinum and the ferrous iron determined by the modified Pratt as described above, using 6 c c. of HF The necessary n was found to be + 0 28 c c of permanganate

Measurement of the Pleochroism of the Micas

comparative measure of the pleochroism of the micas was by the following experimental arrangement based on the of Cornu's method *for determining the percentage of polaris-* (Fig 33)



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

FIG 33

The specimens were used in the form of thin plates freshly d, and of the same thickness 0 05 mm, selected from a very umber of cleaved plates The mica plates were mounted i the slit at an angle of 45° with the '*b*' axis horizontal The -image prism was placed with the vibration directions vertical orizontal, and the distance from the slit was adjusted until the nages, as seen through the telemicroscope, just touched one er The horizontal vibrations are absorbed much more than the al and the images are of unequal intensity By suitably rotating icol, the intensities can be equalised If 2θ is the angle between two positions of the Nicol on either side of the vertical, for which the intensities are equalised, then $\frac{I_v}{I_h}$ $\tan\theta$ A correction has to be introduced in the value of θ to eliminate errors due to reflection etc, at the faces of the plates. For this a blank experiment was performed with a glass microscope coverslip of nearly the same refractive index of the mica plates and the necessary correction applied to the value as θ The results are approximate only but afford a good comparative measure of the pleochroism of the micas

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

7. *Results*

The results are presented in the tables shown below

TABLE I

Specific Magnetic Anisotropy of Phlogopite and Biotite

C G S E M Units Temperature 25°C

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

$\chi_{\parallel l}$ = Susceptibility $\parallel l$ to the cleavage plane, $\chi_{\perp r}$ that $\perp r$ to the cleavage plane

Specific Magnetic Anisotropy of Muscovite.

Mode of Suspension	Orientation	Anisotropy $\Delta\chi \times 10^6$	Remarks
avage plane horizontal	'*b*'-Axis perpendicular to the field	$\chi_2-\chi_3=0\ 11$	
Axis vertical	Cleavage plane parallel to the field	$\chi_2-\chi_1=0\ 70$	The χ-direction coincides with the '*a*'-axis
Axis horizontal id cleavage lane vertical	Do	$\chi_3-\chi_1=0\ 61$	

TABLE II

Mean Susceptibility of the Micas at 25°C

Specimen	$\chi \times 10^6$
Muscovite	8 01
Phlogopite .. .	7 85
Biotite (Canada)	30 8
,, (Ural Mts) . . .	40 6
,, (Bihar) . . .	43 8

TABLE III

Pleochroism of the Micas

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

TABLE IV

C G S E M Units Temperature 25°C

Description of Specimen (Colour of the Biotites refers to very thin plates)	Mean Susceptibility $\chi \times 10^6$	Magnetic Anisotropy $(\chi_{\parallel} - \chi_{\perp}) \times 10^6$	$\chi_{\parallel} \times 10^6$	$\chi_{\perp} \times 10^6$	Total Iron %	Ferrous Iron %	Ferric Iron %	Magnetic Anisotropy referred to a gm ion of $Fe^{++} \times 10^6$
Muscovite, Clear, tinge of green	8.01	0.65	8.23	7.58	3.93	1.79	2.14	..
Phlogopite, Brownish yellow, Submetallic lustre .	7.85	1.38	8.31	6.93	4.[illegible]	3.18	1.06	2420
Biotite (Canada) Dark greenish brown .	30.8	6.95	32.9	25.6	15.2	13.1	2.12	2670
Biotite (Ural Mts.) Dark brown	40.6	10.3	44.0	33.7	21.8	19.6	2.22	2930
Biotite (Bihar) Dark reddish brown	43.8	12.4	47.8	35.4	23.1	22.2	0.9	3120

8. Discussion of Results

Both the susceptibility and the magnetic anisotropy are seen to depend upon the amount of iron present. The biotites exhibit a fairly large magnetic anisotropy and the paramagnetic susceptibility is also correspondingly high. The values for muscovite and phlogopite are comparatively small. In the case of the biotites the mean susceptibility is seen to increase with the percentage of iron almost linearly (Fig. 34).

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

It will be of interest to calculate in a rough way the approximate Bohr magneton values for the biotites. The susceptibility of the biotites is amenable to theoretical considerations for the following reasons. (1) The percentage of iron is very high and we may neglect the diamagnetic term in the susceptibility, (2) Most of the iron is present in the ferrous state, (3) The disturbing effects due to possible minute traces of inclusions can be safely ignored. (In fact, the biotite samples were particularly free from defects). Considering only the total iron present, the effective Bohr magneton value is obtained according to the formula $P_{B_{eff}} = 2{\cdot}84\sqrt{\chi_M T}$.

$P_{B_{eff}}$

Biotite (Canada) $= 5{\cdot}2$
Biotite (Ural Mts.) $= 5{\cdot}0$
Biotite (Bihar) $= 5{\cdot}0$

The values are seen to be much lower than the theoretical values to be expected in the case of the free paramagnetic ion, just as in the case of other solid salts of iron. They are found to approach the

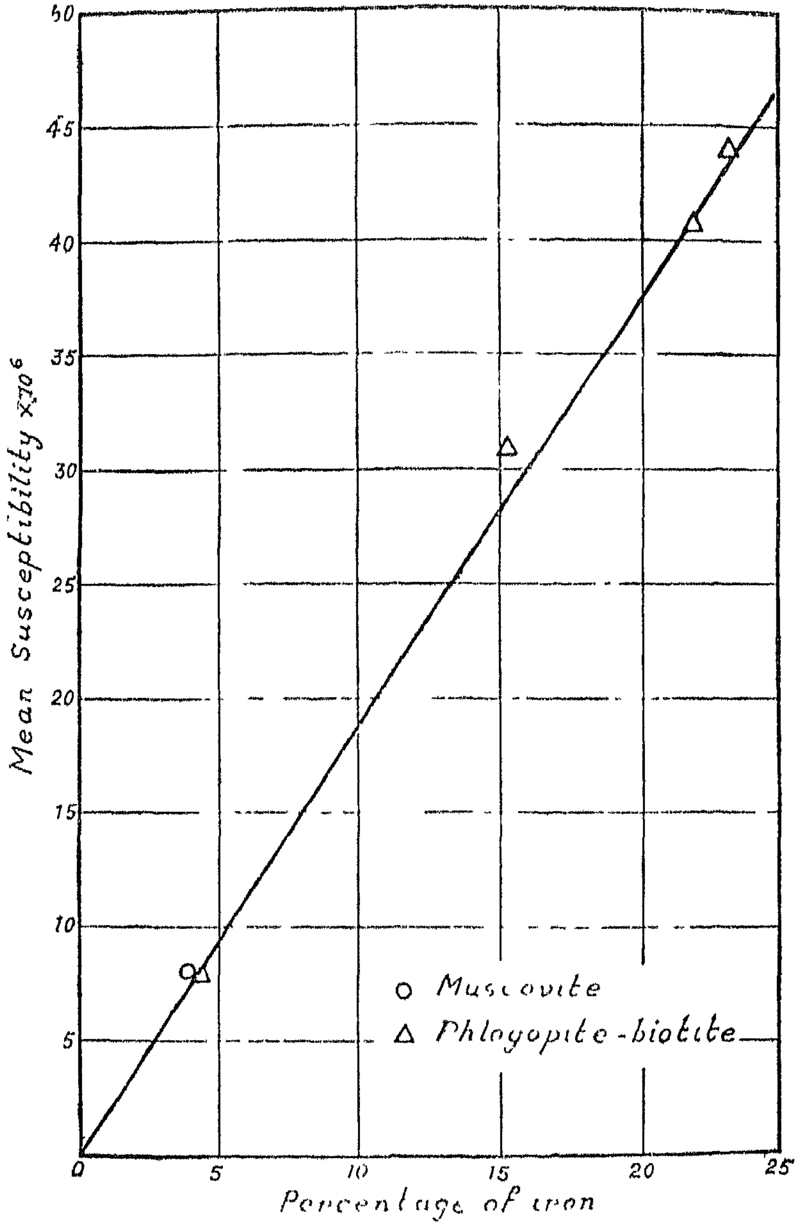


Fig. 31

spin-only value of Fe^{++}, which is equal to 4.92 Bohr magnetons. The significance of this fact in the light of Van Vleck's theory of the quenching of the orbital moments by the crystalline electric fields in paramagnetic solids will be discussed later.

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

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

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

9. *Magnetic Anisotropy and Chemical Constitution*

The specific magnetic anisotropy is plotted as a function of the ferrous iron and ferric iron respectively in Fig 35 Since phlogopite biotite belong to the same group, we can study the characteristics is group from the results obtained In the first place, there seems e no obvious connection between the ferric iron-content and the otropy On the other hand, the magnetic anisotropy increases othy with the percentage of ferrous iron But the relationship is linear and for large percentages of iron, the curve becomes

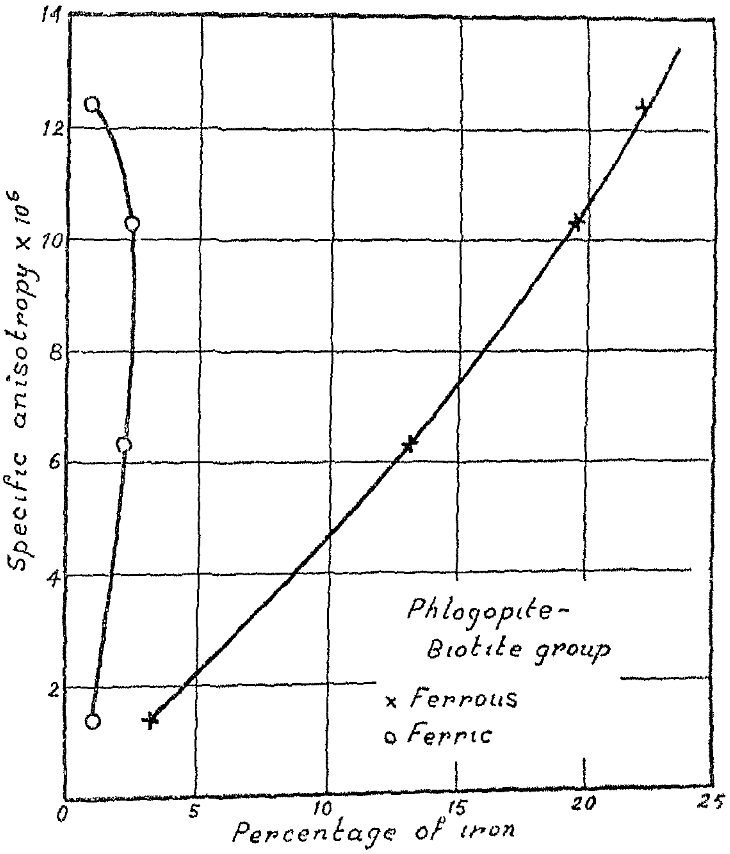


FIG 35

eper In table IV, the gram ionic anisotropy for Fe^{++} is given us shows a remarkable increase with the percentage of ferrous iron the biotites (Fig 36) It is likely that this increase is due to eraction between neighbouring iron atoms in the sheet The ture of this interaction will be discussed later.

The results obtained are significant in the light of recent theoretical developments due to Van Vleck and Penney and Schlapp, which have been summarised in the introductory chapter.

The object of the theory is to account for the following features in the magnetic behaviour of paramagnetic solids, namely (1) the departure from the Curie law and the appearance of cryomagnetic anomalies at low temperatures, (2) the relative contributions of the spin and orbital moments to the susceptibility and (3) the magnetic anisotropy of the crystals. It is based on the earlier work of Bethe and Kramers on the Stark splitting of the energy level of atoms and ions under the influence of crystalline electric fields, and the salient features of the theory have been already dealt with, earlier. The main results for the salts of the iron group are as follows: Since the magnetically effective $3d$ electrons are in the outermost shell, due

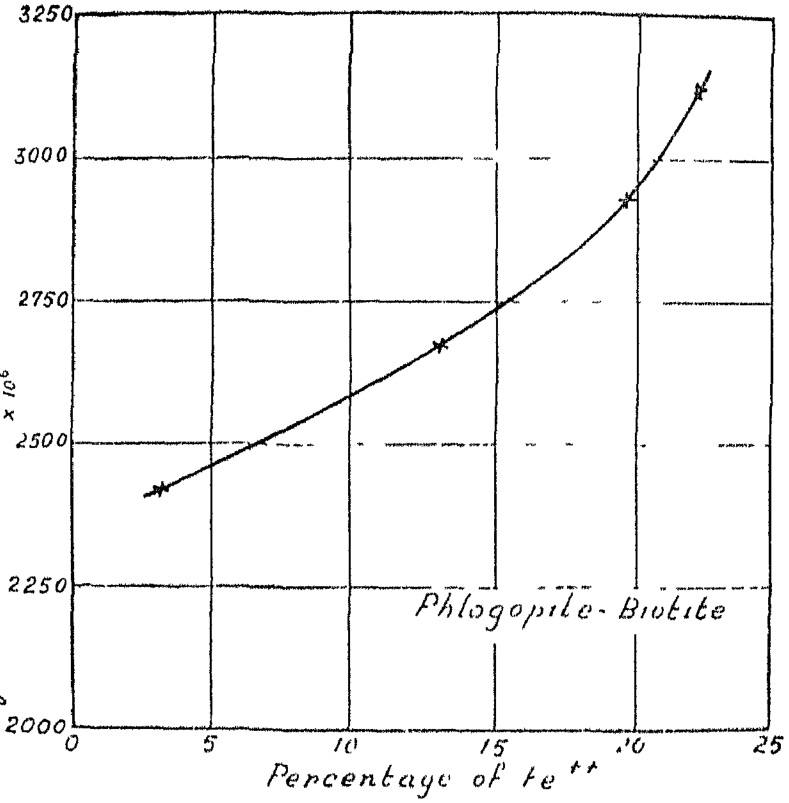


FIG. 16

to the influence of the crystalline electric fields of the neighbouring atoms, the orbital moment makes practically no contribution to the susceptibility. The orbital moment is then said to be quenched. The spins, however, are not directly affected by the crystalline fields and hence contribute fully to the susceptibility. An asymmetric crystalline field produces asymmetric partial freezing of the orbital moments and due to the coupling between orbit and spin, since the remnants of the orbital moment are anisotropic, the freedom of the spins to orientate themselves along different directions will be different. Hence the crystal exhibits magnetic anisotropy. Due to the partial quenching of the orbital moments the susceptibility lies between the limits given by $P_{B'}=\sqrt{4S(S+1)}$ and $P_{B'}=\sqrt{4S(S+1)+L(L+1)}$. In fact we have pointed out earlier that in the biotites this is the case, the Bohr magneton values approaching the *spin-only* value. One important consequence of Van Vleck's theory is that manganous and ferric salts should not exhibit any marked anisotropy, since Mn^{++} and Fe^{+++} *ions are in the S-state and therefore, have no orbital moment* to be quenched. The *present investigation also shows how the magnetic anisotropy of biotite is not dependent on the amount of ferric iron in the specimens.*

In many hydrated paramagnetic crystals which exhibit large magnetic anisotropy, there is evidence from X-ray analysis that we have an octahedral arrangement of water molecules round the paramagnetic ion. Recent experimental work shows that the crystalline electric fields due to such an arrangement deviates widely from cubic symmetry and most probably possesses only hexagonal symmetry. Usually in such paramagnetic crystals there are a number of these complexes (formed by the paramagnetic ion and its environment of six water molecules) in the unit cell, differently oriented with respect to each other, such that crystalline magnetic properties may have only the lower rhombic symmetry. But in the micas the case is much simpler. Here the octahedral group around the Fe^{++} ion consists of four oxygen atoms and two hydroxyl groups and all the groups are arranged parallel to each other, in layers, in the crystal lattice. Hence the anisotropy of the crystal actually corresponds to that of the individual paramagnetic complexes. The hexagonal symmetry of phlogopite and biotite, as regards the magnetic properties, lends support to the view that the crystalline electric fields due to the octahedral grouping possess the same symmetry. In the case of muscovite, however, the departure from hexagonal symmetry may be attributed to the staggering of the sheets relative to each other which is responsible for the monoclinic angle of 95°, and which probably introduces slight departures from the octahedral symmetry of the environment round the Fe^{++} ion. Since the *3d* electrons occupy the outer shell, they are very susceptible to slight changes in the positions of the surrounding atoms, which can cause considerable variation in the character of the crystalline fields influencing these outer electrons. The magnetic anisotropy of the paramagnetic complex $Fe(OH)_6$ referred to a gram ion, is most probably the value obtained for phlogopite since, here, the magnetic dilution is large enough for the interaction due to neighbouring paramagnetic atoms to be ignored.

The rapid increase in the magnetic anisotropy of the biotites with the percentage of iron is a new feature and gives an insight into the effect of the concentration of the paramagnetic ion on the magnetic anisotropy. The explanation in this case seems to be that it is due to interactions between neighbouring iron atoms. The peculiar structure of mica is very favourable for such interaction to take place, since, the iron atoms lie all in the same plane and their population is sufficiently high in the biotites for most of them to occupy neighbouring positions of six co-ordination. Interactions of this character are not taken into account by Van Vleck's original theory which is strictly applicable only in the case of salts of considerable magnetic dilution, e g, the hydrated sulphates and double sulphates of the transition elements. The 'exchange effects', which are formally equivalent to a strong coupling between the spins of interacting electrons might also exist, but these cannot give rise to any anisotropy as has been pointed out by Van Vleck.

It is very likely that the interactions are purely magnetic interactions between the spins of neighbouring paramagnetic ions. There appears to be no theoretical treatment of the effect of such interactions on the magnetic anisotropy, although Van Vleck[11] has recently investigated the effect of dipole-dipole coupling on the susceptibility of paramagnetic salts The dipole interaction is represented in the Lorentz method by a local field $H'=H+\frac{4\pi I}{3}$ this being the field acting on the individual ion This average field is derived by assuming that the introduction of the spherical Lorentz cavity is without influence on the magnetization of the material outside the cavity In the unmagnetized state, the Lorentz field becomes zero Hence according to this there will be no interaction of the magnetic dipoles when there is no external field, unless the temperature is below the Curie point, when the crystal gets permanently magnetized Onsager[12] has taken into account the influence of the cavity and its contents on the surrounding medium, and has obtained a modified expression for the local field His method predicts no Curie point and further indicates that there can be coupling between the magnetic dipoles even when the external field is zero As pointed out by Van Vleck, the local fields are of the Onsager type rather than the simple Lorentz type Van Vleck's treatment of the influence of dipole-dipole interaction consists in calculating the partition function for an assemblage of dipoles as a power series in the ratio of t/T where t is the temperature characterising the energy of coupling of two dipoles and T is the absolute temperature The effect on the paramagnetic susceptibility of the substance has been considered, with a view to discover whether magnetic interactions of this character can lead to ferromagnetic behaviour The results were inconclusive regarding this point The effect of dipole-dipole interactions in salts of considerable magnetic dilution may become perceptible only at low temperatures whereas in the case of salts having a high concentration of the paramagnetic ion, even at ordinary temperatures the influence on the paramagnetic susceptibility and anisotropy may be expected to be considerable, and although no conclusive theoretical evidence is available as yet, we may even expect ferromagnetic behaviour to occur due to such interactions, as distinct from ferromagnetism arising from exchange interactions. It is not unlikely that the ferromagnetism observed by Weiss[13] in pyrrhotite in the basal plane only may be due to interactions of this character and, not due to exchange interactions leading to domain formation, since, if there is domain formation in this crystal as in ordinary ferromagnetics, we should expect *a ferromagnetic behaviour irrespective of direction in the crystal*. On the other hand, dipole-dipole interactions may possibly produce *directional* ferromagnetism. There appears to be no theoretical treatment of the ferromagnetism occurring side by side with paramagnetism in a crystal like pyrrhotite.

In the absence of any rigorous theoretical treatment of the influence of magnetic interactions on the paramagnetic anisotropy, it is not possible to verify the experimental results quantitatively in the case of biotite. It is not, however, difficult to see why the magnetic anisotropy should be enhanced by interactions. In the case in which the applied field is parallel to the cleavage plane, the mutual action of the dipoles will be to increase the magnitude of the local field acting on the paramagnetic ions which are arranged in monatomic layers, and hence the susceptibility is enhanced. In the other case in which the field is perpendicular to the cleavage plane, the mutual action of the neighbouring dipoles will actually tend to decrease the magnitude of the local field. The magnetic anisotropy as a consequence will be enhanced. In short, the increase of anisotropy due to magnetic interactions may be ascribed to anisotropy of the local field acting on the paramagnetic ion.

For dipole–dipole interaction to take place, the paramagnetic ions should lie adjacent to each other. When the percentage of iron in biotite is small this condition is obviously not realised and in the layer of (Fe, Mg) atoms, the Fe atoms are mostly surrounded by Mg atoms. But when the percentage of iron is high and that of magnesium correspondingly less, most of the Fe atoms are neighbours in the positions of six-coordination and the conditions are favourable for magnetic interactions to take place. In other words, when the neighbouring ions are diamagnetic, the local field acting on the paramagnetic ion is practically the same as the applied field inside the material But when the nearest neighbours are paramagnetic and asymmetrically arranged around it, the local field will differ considerably from the average field inside the material and will also be asymmetric, its character and magnitude depending upon the direction of the applied field

10. Pleochroism of the Biotites

There is, as yet, no satisfactory explanation of the pleochroism of the biotites The intimate relationship between colour of inorganic salts and paramagnetism is well-known, for salts of the transition elements which are coloured are also paramagnetic Saha[14] has put forward a theory of the origin of colour in inorganic salts according to which absorption in the visible region of light is due to transitions involving the reversal of the spin-vector of the one of the *3d* electrons of the paramagnetic ion Such transitions although forbidden for the free paramagnetic ion are assumed to be possible in solids and in solutions

The connection between colour and paramagnetism at once suggests a corresponding relationship between pleochroism and paramagnetic anisotropy and the examination by the author of the available data on the pleochroism and paramagnetic anisotropy of salts of the iron group of elements has revealed that strong paramagnetic anisotropy is generally associated with marked pleochroism This enquiry proved to be fruitful in another way The author could not find any reference to the pleochroic properties of $FeSO_4\,(NH_4)_2SO_4\,6H_2O$ in the literature on the subject This substance is known to be highly anisotropic magnetically and we should expect a marked pleochroism also A large crystal was examined in the (010) plane and it was found that the colour is pale green for light vibrations in the γ-direction and yellow when the vibrations are in the α-direction

The bearing of the above on the pleochroism of the biotites is obvious, for we have seen that pleochroism is most pronounced in the varieties rich in ferrous iron, and the magnetic anisotropy also increases with the iron content The two phenomena are evidently closely related If the mechanism of absorption of light in biotite by the iron atom is the same as suggested by Saha, the pleochroism implies that the reversal of the spin vector can take place only when the light vibrations are parallel to the cleavage plane and not when they are perpendicular This restriction in the orientation of the spins is evidently due to the influence of the asymmetric crystalline fields which, according to Van Vleck, act indirectly on the spins through the *spin-orbit* coupling and which are responsible for the large magnetic anisotropy

The close correspondence between the ease of magnetisation parallel to the cleavage plane (the paramagnetic susceptibility parallel to the cleavage plane is much greater than that perpendicular to it) and the readiness with which the spins respond to the electric field of the light wave when this is parallel to the cleavage plane, is very striking and is strongly suggestive of the fact that the polarisation of absorption in the biotites is chiefly due to the influence of the asymmetric crystalline fields acting on the paramagnetic ion, enhanced, however, by the magnetic interactions The recent work of Krishnan and Chakrabarty[16] on the polarisation of the absorption lines of single crystals of the hydrated sulphates or Pr and Nd is interesting in this connection They find that " many of the absorption lines are strongly polarised, some of them being confined almost wholly to vibrations along one or another of the principal axes of the optical ellipsoid of the crystal and that these variations in the direction of polarisation occur even among the lines of the same group, in other words, among the Stark components which originate from the same absorption line of the free ion, some are polarised strongly in one direction and some strongly in another " These crystals also show strong magnetic anisotropy From these facts Krishnan concludes that the crystalline electric fields which produce the Stark splitting are also highly anisotropic

The nature and disposition of the magnetic carriers in biotite may now be understood from the following picture We consider first of all the simple case where magnetic interactions do not occur We assume that the magnetic carriers are orientated with the magnetic axes more nearly parallel to the cleavage plane due to the coupling between orbit and spin, randomness of orientation existing in azimuth Under the influence of a magnetic field parallel to the cleavage plane, we get the usual paramagnetism, although considerably diminished in magnitude But when the field is normal to the cleavage plane, the resolved part of the spin moments perpendicular to the cleavage plane is much less on account of the restrictive action of the crystal fields, and we get a much lower susceptibility Thus the high magnetic anisotropy may be explained Our picture also reveals how the reversals of the spin vector can take place in the cleavage plane but not perpendicular to it, since, the spins are directed more nearly parallel to the cleavage plane and can freely orientate themselves in azimuth The pleochroism also is thus explained This physical picture although somewhat native is sufficient to explain both phenomena A rigorous treatment of pleochroism taking into account the Stark splitting of the energy levels in the crystal fields is very desirable

It seems very likely that the mutual interaction of neighbouring paramagnetic ions to which we ascribed the enhanced anisotropy in the varieties rich in iron plays a significant part in intensifying the pleochroism When the percentage of ferrous iron exceeds a certain value, the effect due to the interaction of the iron atoms may presumably become enormous as compared with the usual Van Vleck effect of the asymmetric fields and both the magnetic anisotropy and the pleochroism become exceedingly large

Although the connection between pleochroism and paramagnetic anisotropy *seems to be obvious* in the biotites, some significant features relating to the two phenomena have to be explained For instance, *Murmann and* Rotter[16] have observed pleochroism in $MnSO_4$ (NH_4), SO_4, $6H_20$, although this crystal is almost isotropic magnetically Again in the case of a rose-coloured variety of tourmaline containing a considerable percentage of manganese the author has observed pronounced pleochroism, the absorption band in the blue-green being very strongly polarised while the magnetic anisotropy is very feeble The crystal is paramagnetic, $\chi_{mean} = 0.31 \times 10^{-6}$, $\chi_{\perp r} - \chi_{\parallel r}{}^{*} = 0.008 \times 10^{-6}$ C G S E M units Now the ground state of the Mn^{++} is an *S*-state and, therefore, there is no orbital moment to be quenched The feeble anisotropy actually observed is due to the small splitting of the *S*-levels under the influence of the crystalline electric fields. But the higher levels, transitions to which give rise to the absorption bands, not being *S*-levels will naturally experience a large Stark separation in the crystal fields and as a result of asymmetric splitting a strong pleochroism occurs The important fact has to be recognised that whereas the paramagnetic anisotropy of a crystal is determined mainly by the nature of the ground state of the ion and how it is influenced by crystal fields, pleochroism depends essentially on how the two energy states involved in absorption are each affected by these fields In both cases the nature of the crystal fields determines the character of the phenomenon It will also be seen that whatever be the nature of the paramagnetic ion in the crystal, if there is strong pleochroism of the absorption bands which form a group and which are the Stark components of the same absorption line of the free ion, we can conclude that the crystalline fields acting on the ion should be asymmetric

Although, in general, pleochroism in minerals has been known to be associated with a large iron content, the intensity increasing with percentage of iron, instances have been quoted in which anomalies have been noted For instance, Henry[17] remarks from optical observations made on some iron-rich variety of hypersthenes, that the rule that pleochroism increases with increase in iron-content, does not hold for the series as a whole, as some of those rich in iron are only weakly pleochroic The pleochroism in this case was judged by visual observation only, and it will be obvious that the apparent magnitude of the pleochroism will depend upon the

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*$\chi_{\parallel r}$ = Susceptibility parallel to the hexagonal axis

$\chi_{\perp r}$ = " perpendicular " "

position of the absorption maximum in the visible part of the spectrum If the absorption maximum falls in the yellow region, the pleochroism will appear to be much more pronounced than if it is in the violet region Hence visual observations of pleochroism are likely to be misleading and the relation between iron content and pleochroism in minerals will have to be investigated by quantitative measurements on the polarisation of the absorption bands Theoretically, it seems to be justifiable to assume that provided *all other factors remain the same,* the increase in the number of absorption centres will naturally give rise to greater absorption as well as enhanced pleochroism If the absorption centre is the Fe^{++} ion, the larger the number of ions present in unit volume of the mineral, the more intense will be the absorption and also more pronounced the polarisation of the absorption bands

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SUMMARY

In the present memoir I have given an account of my original investigations on several aspects of the dia- and paramagnetic anisotropy of crystals. Recent theoretical and experimental work on the subject which has got a bearing on my work is briefly described in the introductory chapter. In Chapter I, the experimental methods adopted by me in my investigations and the modifications and improvements in technique that I have introduced are described. The theory of the torsional method of determining magnetic anisotropy developed by Krishnan, is also discussed in detail.

In connection with my investigations on crystalline nitrates and carbonates, accurate values of diamagnetic anisotropy were required and an examination of the previous literature on the subject showed that there is considerable discrepancy in the values obtained by earlier workers. I have made careful measurements, especially with a view to understand the influence of crystal structure on the intrinsic anisotropy of the (CO$_3$) and (NO$_3$) groups. The results are presented in Chapter II. It has been found that the character of the environment influences the anisotropy of the nitrate and carbonate ions in their respective crystals to a considerable extent. I have, further, drawn attention to the remarkable difference in the diamagnetic anisotropy of the carbonate and nitrate groups, and I have also suggested an explanation of this difference. The magnetic anisotropy of ammonium and silver nitrates has been determined by me for the first time and the orientations of the nitrate ions in these crystals have been deduced from the magnetic data. I have also attempted a theoretical computation of the diamagnetic anisotropy of the nitrate group from semi-classical considerations.

In chapter III, I have shown how the correlation of the diamagnetic anisotropy of the individual crystallites in a polycrystalline aggregate with the anisotropy of the aggregate itself, enables us to determine the orientations of these crystallites in the latter. This is a

new application of magne-crystallic action and I have successfully applied it in the case of the nacre of iridescent shells and the calcite layer of egg-shells The orientations of the tiny crystallites of aragonite in the former, and of the calcite crystals in the latter, have been deduced purely from the magnetic measurements I have also studied in detail the diamagnetic anisotropy of wood and its various constituents with a view to determine the directional magnetic properties of cellulose and lignin The fibre structure of wood and cellulose have been extensively investigated by the method of X-ray analysis by various workers and the general disposition of the cellulose molecules in the fibre are now well-known The magne-crystallic data clearly show that the direction of maximum diamagnetic susceptibility of the cellulose molecule is along the length of the chain, and that lignin makes no contribution to the anisotropy This is the first direct determination of the molecular diamagnetic anisotropy of a long-chain aliphatic compound and it has been pointed out that the behaviour of saturated long-chain aliphatic compounds in general should be quite similar

The magnetic method of structure analysis, developed by Krishnan and his collaborators and Lonsdale and Krishnan, has been applied by me to the case of rhombic sulphur and the results are given in Chapter IV The agreement with X-ray analysis is only approximate and I have pointed out that a revision of the structure is highly desirable

The temperature variation of the diamagnetic anisotropy of several organic and inorganic crystals has been studied by me by the technique I have developed in this connection Various phenomena like crystal polymorphism and the effect of impurities on the directional magnetic properties of the crystal as the melting point is approached, have been investigated in some detail For instance, polymorphic transitions in ammonium and potassium nitrates could be distinguished by the more or less abrupt changes in the diamagnetic anisotropies of these crystals at the transition temperatures A gradual decrease of diamagnetic anisotropy has been observed in sodium nitrate which has been found to be intimately connected with the anomalous changes of specific heat and thermal expansion of the crystal which occur between 185° and 275°C. I have also shown how it is possible to get an insight into the mechanism by which the presence of impurities lowers the melting point in organic crystals. The rapid decrease of the diamagnetic anisotropy nearabouts the melting point, due to "premelting" in impure crystals, is striking. The results, in general, demonstrate how magne-crystallic action may have a wide application for studying a variety of phenomena.

In the final chapter, I have described my experiments on the magnetic properties of biotite mica in relation to its pleochroism and chemical composition. It has been found that the paramagnetic anisotropy increases with the percentage of ferrous iron in biotite. At high concentrations of Fe^{++}, it has been found that the magnetic anisotropy increases rapidly, evidently due to interaction effects between neighbouring paramagnetic ions. The pleochroism also becomes very intense with increasing iron content. A simple picture of the mechanism of light absorption in biotite has been offered on the basis of Saha's theory of colour in inorganic salts.

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