

S T U D I E S O N T H E D I A M A G N E T I C
A N I S O T R O P Y O F C R Y S T A L S

Thesis by

Horst Walter Hoyer

In Partial Fulfillment of the Requirements
For the Degree of
Master of Science in Chemistry

California Institute of Technology
Pasadena, California

1948

ACKNOWLEDGEMENT

The writer wishes to thank Professore Linus Pauling and Dr. E.W. Hughes, the former for suggesting the problem and supplying the necessary crystals, the latter for valuable advice in constructing the apparatus and carrying out the investigation.

SUMMARY

Apparatus for the measurement of magnetic anisotropy has been constructed. It is based upon a method first developed by Krishnan in which the torsional force due to the twist on a fine quartz fiber is used to measure the couple acting on the crystal resulting from its anisotropy. By this means the diamagnetic anisotropy of iodoform, arsenic triiodide and potassium chloroplatinite were measured. The results obtained with the last named compound indicated the presence of ferromagnetic impurities. A table of the diamagnetic anisotropy of organic compounds measured to January 1948 has been compiled.

INTRODUCTION

Although Ampere in 1825 suggested that molecular currents might explain induced and permanent magnetization, it was not until 1845 that Faraday made the fundamental discovery that all substances are affected by a magnetic field. The force F in dynes between two magnetic poles of pole strengths m_1 and m_2 in any medium is given by

$$F = \frac{1}{\mu} \frac{m_1 m_2}{r^2}$$

where r is the distance in cm. between the poles and μ is called the magnetic permeability of the medium and is unity in a vacuum. Those substances for which μ is greater than unity are called paramagnetic. If μ is less than unity the substance is diamagnetic.

Calling the magnetic field strength H , where H is measured in gauss, the magnetic induction B of a given homogeneous medium for a given field direction is the product μH . I, the intensity of magnetization induced in that medium by the field is given by

$$B = H + 4\pi I$$

Therefore

$$\mu = \frac{4\pi I}{H} + 1$$

Now the mass and volume susceptibilities, χ and κ , may be

defined as

$$\chi = \frac{\kappa}{\rho} = \frac{I}{H}$$

where ρ = density of the substance. The units for χ are c.g.s.e.m.u. Therefore

$$\mu = 1 + 4\pi\rho\chi$$

Since for diamagnetic substances μ is less than one, χ must be negative.

Many substances possess different magnetic properties in different directions. In general a crystal possesses three orthogonal axes defining the directions of three principal magnetic susceptibilities which are not necessarily equal.

Krishnan, Guha and Banerjee⁽¹⁾ made the first extensive studies of these principal diamagnetic susceptibilities of crystals. They showed that aromatic organic molecules possess a pronounced anisotropy and that the susceptibility perpendicular to the plane of the molecule was much more diamagnetic than the two susceptibilities in that plane. They also suggested the possibility of determining the orientation of molecules in the crystal from a knowledge of the principal susceptibilities of the molecule and the crystal. Later work by Lonsdale⁽²⁾ showed that planar organic conjugated compounds in general possess a greater susceptibility when the applied field is perpendicular to the plane

of the molecule.

THEORY

The first reasonably successful theory of magnetism was that of Weber (1847) who assumed that the magnetic elements are molecules containing orbital electric charges. For a magnetic body these charges are in steady motion in their orbits while for diamagnetic bodies the charges are at rest and are set into motion by electromagnetic induction upon the application of the magnetic field. Electromagnetic induction also acts upon magnetic bodies to change the velocities of the charges in permanent motion but the diamagnetic effect is negligible in comparison with the original moment. However it remained for Langevin in 1905 to develop a theory of diamagnetism based upon the electron structure of matter.

The application of a magnetic field to an electron system in an equilibrium state under the influence of a center of force is equivalent to the superposition of an angular velocity of precession, the Larmor precession, given numerically by

$$\omega = - \frac{e}{2mc} H$$

where H is the field strength in gauss

e the electronic charge

m the electronic mass and

c the velocity of light, all in c.g.s. units.

Now the motion of an electron in an orbit of radius r with angular velocity ω produces at a distance the same mean

4.

magnetic field as a magnet of moment M as given by

$$M = \frac{e}{2c} r^2 \omega$$

Therefore the modification of the magnetic moment corresponding to a noncircular orbit by a field will be given by

$$dM = - \frac{e^2 \overline{r_1^2}}{4mc^2} H$$

$\overline{r_1^2}$ is the mean square radius of the electron orbit projected on a plane at right angles to the direction of the field.

For spherically symmetrical atoms the mean square of the actual orbital radius, $\overline{r^2}$, is related to $\overline{r_1^2}$ by

$$\overline{r_1^2} = \frac{2}{3} \overline{r^2}$$

Summing over the n electrons of the atom and noting that the atomic susceptibility χ_A is related to dM by

$$\chi_A = dM \frac{N}{H}$$

N = Avogadro's number

$$\begin{aligned} \chi_A &= - \frac{Ne^2}{6mc^2} \sum_n \overline{r^2} \\ &= -2.84 \times 10^{-10} \sum_n \overline{r^2} \end{aligned}$$

Quantum mechanical methods for evaluation of the diamagnetic susceptibility have been developed by Pauling,⁽³⁾ Van Vleck,⁽⁴⁾ Slater⁽⁵⁾ and Gray and Cruickshank⁽⁶⁾ among others. The methods generally differ in the determination of the quantity r . In

the Pauling and Van Vleck method the expression for susceptibility becomes

$$\chi = -2.01 \times 10^{-6} \sum_K \frac{n_K^4}{(Z - S_{m_K})^2} \left[1 - \frac{3\ell_K(\ell_K - 1) - 1}{5n_K^2} \right]$$

where Z = atomic number, S_m = screening constant while n and ℓ are the principal and secondary quantum numbers respectively summed over K electrons.

Values thus calculated are generally too high. This deviation becomes more pronounced as the ion or molecule becomes more massive. For example, the experimentally determined susceptibility of iodoform is -117.1×10^{-6} . Pauling obtains $\chi_m = -212.1 \times 10^{-6}$. Slater obtains values slightly nearer the observed values by adopting modified screening constants. For iodoform his method yields $\chi_m = -161.3 \times 10^{-6}$.

The method of Gray and Cruickshank⁽⁶⁾ gives the closest approach to the experimental value. They apply the Pauling formula but in addition consider the effect due to the unequal sharing of charge between atoms. This unequal distribution of charge is assumed to be given by the residual electric charges as derived from dipole moments of the actual molecule. In this manner it is possible to express the fractional time each atom of a molecule possesses a given charge. This fraction of the atomic diamagnetism of the particular atom then represents its contribution to the diamagnetism of the molecule. A simple example is HCl.

The dipole moment μ is related to the residual charge, Δe_m and to the separation d between atoms by

6.

$$\begin{aligned}\Delta e_m &= \frac{\mu}{d} \\ &= \frac{1.03 \times 10^{-18}}{1.27 \times 10^{-8}} \\ &= 0.81 \times 10^{-10} \text{ e.s.u.}\end{aligned}$$

Expressed in terms of the charge of one electron this becomes

$$\Delta e = \frac{0.81 \times 10^{-10}}{4.80 \times 10^{-10}} = 0.169$$

This is interpreted to mean that the charges on H and Cl are +1 and -1 for 0.17 of the time and 0 for 0.83 of the time. The values for the diamagnetism due to H^+ , H° , Cl^- and Cl° are calculated by the Pauling formula and the appropriate fractions taken. For iodoform their method gives $\chi_m = -136.8 \times 10$.

A quantitative theory of the anisotropy of aromatic ring systems was first developed by Pauling⁽⁸⁾ on the assumption that the $2p_z$ electrons were free to move under the influence of the impressed field from carbon atom to adjacent carbon atom. The contribution of these six (for benzene) electrons to the magnetic susceptibility for fields normal to the benzene ring is given by the Pauli expression:

$$\chi = -\frac{Ne^2}{4\pi mc^2} (\overline{e^2})_{ave}$$

where $(\overline{e^2})_{ave}$ is the mean square distance of the electron from the z axis. Due to the nodal plane of the wave functions

perpendicular to the z axis the same electrons make only a very small contribution to the susceptibility with the field in the nuclear plane. If, for $(\rho^2)_{av}$ we use the value R^2 , in which R is the distance from the center of the benzene molecule to the carbon nuclei, 1.39\AA , the calculated anisotropy is $\Delta K = -49.2 \times 10^{-6}$. The value calculated from the Cotton Mouton constant for benzene and the depolarisation factor for transverse scattering of unpolarized incident light is -54.0×10^{-6} . The method has been extended to condensed aromatic ring systems with reasonably good agreement with directly determined experimental values.

MEASUREMENT

There are three general types of magnetic measurements possible with crystals, average susceptibility, principal susceptibility and magnetic anisotropy, ie. the variation of intensity of magnetization with direction in crystalline matter. Both the Gouy and Faraday methods measure average susceptibility but the latter method is also adaptable to the measurement of principal susceptibilities. The method developed by Krishnan⁽⁹⁾ and used in the present work is used for the determination of magnetic anisotropy.

In the Gouy method a cylindrical sample of matter is suspended from one arm of a balance so that it hangs between the poles of a magnet. One end of the sample is in a region of large field intensity and the other in a region of negligible intensity. The sample will experience a force along

its length which is balanced by weights on the other arm of the balance. The relation between the volume susceptibility, κ_1 , of the sample, and of the surrounding air, κ_2 , to the apparent change in weight Δw of the sample on application of the field is

$$\frac{1}{2}(\kappa_1 - \kappa_2) H^2 A = g \Delta w$$

where g is the gravitational constant

H is the maximum field strength

A is the cross-sectional area of the sample.

In the Faraday method an inhomogeneous field is produced by inclining the poles of a magnet towards one another. The sample is suspended in the inhomogeneous field and its displacement is measured from the position it occupies in the absence of the field. The force acting on the sample with the field on is

$$f = m \chi H \frac{dH}{dy}$$

where m is the mass of the sample

χ its mass susceptibility

$\frac{dH}{dy}$ the rate of change of field strength along the y axis.

By orientating the crystal so that the force is exerted only along one magnetic axis it is possible to determine a principal magnetic susceptibility of the crystal. However a much more convenient method has been developed by Krishnan.⁽⁷⁾

Any diamagnetic crystal suspended by a thin fiber in a magnetic field is subjected to several forces. First there is a lateral force tending to move it to the weakest portion of the field. This effect, and a second due to the shape asymmetry of the crystal may be conveniently eliminated by using a homogeneous field. A third effect acting is a couple due to the difference in principal susceptibilities of the crystal. If the crystal is suspended by means of a thin quartz fiber with χ_3 vertical and normal to the magnetic field then the crystal may be twisted from its equilibrium position until the torsional force acting on it just exceeds the restoring couple due to the field. At this angle the crystal rapidly turns through several revolutions. Measurement of this angle for two different suspensions of the crystal permits calculation of χ_1, χ_2 and χ_3 . An independent determination of the mean susceptibility makes possible the calculation of the absolute susceptibilities from the relation

$$\chi_{ave} = \frac{1}{3} [\chi_1 + \chi_2 + \chi_3]$$

To simplify the derivation of the equation relating field strength H with susceptibility consider a crystal suspended with χ_3 vertical and perpendicular to H with χ_1 the axis of greatest susceptibility in the plane \perp to χ_3 . Then χ_H the susceptibility along the field is

$$\chi_H = \chi_1 \cos^2 \varphi + \chi_2 \sin^2 \varphi$$

where φ is the angle between χ_1 and H . The couple acting on

the crystal is

$$\begin{aligned}\frac{dE}{d\varphi} &= \frac{d}{d\varphi} \left(-\frac{1}{2} \chi_1 H^2 V \right) \\ &= \frac{1}{2} H^2 V (\chi_1 - \chi_2) \sin 2\varphi\end{aligned}$$

where E is the energy and V the volume of the crystal. The angle at which χ_1 lies along H is taken as $\varphi = 0$,

Let c be the torsional constant of the fiber from which the crystal is suspended and use χ molar instead of χ per unit volume. Then

$$C \varphi = \frac{1}{2} \frac{m}{M} H^2 \sin 2\varphi (\chi_1 - \chi_2)$$

φ = angle through which fiber is twisted

m = mass of crystal

M = molecular weight of the crystal

At an angle $\varphi = 45^\circ$ the couple is a maximum. Let the corresponding φ be φ_c then

$$C \left(\varphi_c - \frac{\pi}{4} \right) = \frac{m}{2M} H^2 (\chi_1 - \chi_2)$$

If c and H are known the anisotropy of the crystal in the plane perpendicular to the suspension axis may be calculated from the angle through which the fiber must be twisted to rotate the crystal $\frac{\pi}{4}$ radians from its normal rest position in the field.

APPARATUS

Measurement of magnetic anisotropy were made by a method

developed by Krishnan.⁽⁹⁾ The apparatus (see Figure 2) which was designed and constructed for this work is similar to that described by Rogers.⁽¹⁰⁾ A quartz fiber approximately $3\mu - 5\mu$ in diameter and 70 cm. long is prepared by the method of Strong.⁽¹¹⁾ This fiber is attached to the lower end of a female joint (c) which in turn fitted around the lower end of a sleeve bearing (B). The outer rim (A) of the torsion head was calibrated in degrees and equipped with a vernier scale which was, however, soon found unnecessary. For convenience in turning the torsion head an "O" belt connected it to a shaft (F) which was turned at a convenient height by the disk and handle (G). The crystal to be measured was suspended at the lower end of the quartz fiber and hung between the pole pieces of the electromagnet (E). These pole pieces were cylindrical with a diameter of 7.5 cm. and a separation of 2 cm. An iron housing (D) protected the fiber from accidental breakage and disturbance during measurements.

The magnet consisted of four windings, each with approximately 290 turns of #12 enameled cotton covered copper wire. Each winding was flanked by two pancake cooling coils of $3/8$ inch copper tubing through which refrigerated water was passed during the determination .

The field of the magnet may be calibrated by means of a search coil consisting of a known number of turns of copper wire on a non-magnetic core and a ballistic galvanometer in

series with the search coil. Figure 1 is the resulting data plotted as field strength versus current through the magnet.

The torsional constant of the fiber may be calculated by observing the period of oscillation of a substance of known mass and shape or by determining the angle of rotation of a crystal of known anisotropy. Since considerable difficulty was observed in obtaining reproducible results by the former method the latter was adopted. Crystals of 1,3,5 triphenylbenzene, the anisotropy of which has been determined by Krishnan¹¹ and checked by Lonsdale, were adopted as a standard. Since the area of the search coil used in calibrating the field was not known very precisely, it was thought best to determine the ratio

$$\frac{m}{M} \frac{(\chi_1 - \chi_2)}{\alpha_c - \pi/4} = \frac{2c}{H^2}$$

which is a constant at constant current. This value was determined at field strengths of approximately 4000, 6000 and 8000 gauss. In most cases it was possible to make all subsequent measurements at 4000 and 6000 gauss.

METHOD

The crystal to be examined was first weighed on a microbalance and then mounted with the desired direction vertical on a two-circle goniometer. A short piece of glass fiber was attached to the crystal with a trace of shellac and then, while the shellac was still fluid, was orientated by means of a micromanipulator until the length of the fiber coinci-

ded with the axis of the goniometer. The micromanipulator maintained the fiber in this position until the shellac had dried.

The glass fiber and crystal were then removed from the goniometer and attached to the quartz fiber. Measurements were then taken at approximately 4000 and 6000 gauss. In general four measurements were made at each field strength and averaged.

When the magnet is first activated the crystal turns so that the maximum susceptibility of the desired zone lies along the field. By adjusting the torsion head it is possible to attain a position at which the crystal remains in the same position in the presence or absence of the field. This is the zero point for the determination. As the torsion head is now turned from this zero point the crystal slowly turns at a much smaller angle. When the crystal has turned through 45° any further turning of the torsion head will cause the crystal to spin rapidly around.

The orientation of the crystal in the zero point position may be conveniently determined with the aid of a telescope equipped with a right angle prism so that observations be taken with the line of sight along the suspension axis. A piece of straight iron or nickel wire is suspended between the poles of the magnet and the cross-hairs of the telescope adjusted to it. The telescope was equipped with a calibrated dial so that the angle between the zero posi-

tion of the cross-hairs and a prominent edge of the crystal could be readily measured.

RESULTS

The equation relating anisotropy to field strength and angle of twist may be written

$$\frac{m(\chi_1 - \chi_2)}{M(\alpha_c - \pi/4)} = \frac{2C}{H^2}$$

a constant at constant current

This value was determined for four crystals of triphenylbenzene weighing 1.189, 1.484, 3.185 and 0.744 mg at current strengths corresponding to 4,000, 6,000 and 8,000 gauss.

The values obtained were:

4,000 gauss	$1.35 \pm 5 \times 10^{-12}$
6,000 gauss	$0.559 \pm 11 \times 10^{-12}$
8,000 gauss	$0.29 \pm 3 \times 10^{-12}$

The values for 4,000 and 6,000 gauss were used in almost all subsequent work .

The calibration was checked against crystals of known anisotropy, potassium chlorate and catechol. For potassium chlorate the average obtained was 1.76×10^{-6} . Krishnan⁽¹⁾ reports 1.73×10^{-6} . Catechol gave values of 2.78 and 2.80×10^{-6} with the "c" axis vertical. Krishnan had reported 2.7×10^{-6} . With the "b" axis vertical the reported value is 30.5×10^{-6} . Measurements on two different crystals with this axis vertical gave an average of $26.2 \pm 0.3 \times 10^{-6}$.

Crystals of iodoform, arsenic triiodide and potassium chloroplatinite were provided by Professor Linus Pauling.

The crystals of iodoform are hexagonal, Groth⁽¹²⁾ reports $a:c = 1:1.1084$. Higgins and Noble⁽¹³⁾ report $a. = 6.818\text{\AA}$, $c. = 7.524\text{\AA}$, $Z = 2$ molecules per unit cell. The mean of measurements on three crystals of 33.93, 5.88 and 14.77 mg. was

$$\chi_{\parallel} - \chi_{\perp} = 28.6 \pm 0.4 \times 10^{-6}$$

where the 0.4 is the average deviation of the individual values from the mean. The mean experimental value has been reported by French and Trew⁽¹⁴⁾ as

$$\chi_{ave} = -117.1 \times 10^{-6}$$

Therefore since

$$\chi_{ave} = \frac{1}{3} [\chi_{\parallel} + 2\chi_{\perp}]$$

$$\chi_{\perp} = -128.8 \times 10^{-6}$$

$$\chi_{\parallel} = -100.2 \times 10^{-6}$$

The notation adopted is that of Krishnan⁽¹¹⁾ in which, for magnetically uniaxial crystals the gram molecular susceptibilities along and perpendicular to the axis are represented by χ_{\parallel} and χ_{\perp} respectively. A complete description of the notation is given in the last section.

Arsenic triiodide is trigonal with $a:c = 1:2.998$ according to Groth. The average magnetic susceptibility is reported by Ghulam Farid⁽¹⁴⁾ as

$$\chi_{ave} = -109.4 \times 10^{-6}$$

The mean of several measurements on two crystals of 18.27 and 10.65 mg. was

$$\chi_{\parallel} - \chi_{\perp} = 7.67 \pm 0.13 \times 10^{-6}$$

Therefore

$$\chi_{\parallel} = -104.2 \times 10^{-6}$$

$$\chi_{\perp} = -111.9 \times 10^{-6}$$

Potassium chloroplatinite, K_2PtCl_4 , is tetragonal with $a:c = 1:0.4161$ according to Groth.⁽¹²⁾ The structure has been determined by Dickinson.⁽¹⁵⁾ $Z = 1$ molecule per unit cell. Magnetic measurements gave irregular results with poor reproducibility among the different crystals. While two crystals did give identical orientation in the magnetic field, another orientated at 21° to this position and gave much lower anisotropy values. Furthermore in all three cases the anisotropy decreased with increasing field strength. The values obtained are:

at 4,000 gauss

$$\begin{aligned} \chi_{\parallel} - \chi_{\perp} &= \begin{array}{r} -47.2 \\ -66.2 \\ \hline -33.8 \end{array} \\ &= -49.1 \times 10^{-6} \end{aligned}$$

at 6,000 gauss

$$\begin{aligned} \chi_{\parallel} - \chi_{\perp} &= \begin{array}{r} -37.9 \\ -35.0 \\ \hline -19.3 \end{array} \\ &= -30.7 \times 10^{-6} \end{aligned}$$

Feytis⁽¹⁶⁾ reports the mean susceptibility of K_2PtCl_4 as

$$\chi_{ave} = -147.74 \times 10^{-6}$$

Therefore at 4,000 gauss:

$$\chi_{||} = -180.5 \times 10^{-6}$$

$$\chi_{\perp} = -131.4 \times 10^{-6}$$

while at 6,000 gauss:

$$\chi_{||} = -168.2 \times 10^{-6}$$

$$\chi_{\perp} = -137.5 \times 10^{-6}$$

DISCUSSION OF RESULTS

The results obtained with potassium chloroplatinite are most unexpected and should perhaps be taken with a grain of salt. The anisotropies are exceptionally high and the variation of susceptibility with field strength has never been previously observed. Iron is a common constituent of native platinum. Only a trace of a paramagnetic substance is necessary to invalidate diamagnetic measurements. However this possibility does not explain the variation of the anisotropy with field strength since, on the classical Langevin theory, paramagnetism as well as diamagnetism is independent of field strength. Furthermore there is no prior published work on the anisotropy of platinum compounds and other diamagnetic compounds of the transition metals

except that of potassium nickelocyanide, $K_2Ni(CN)_4$ by Rogers⁽¹⁰⁾ who only reports $\chi_1 = -127.8$ $\chi_2 = -148.0$ $\chi_3 = -144.2 \times 10$.

The most likely explanation is that traces of a ferromagnetic impurity were introduced at some step in the preparative process. Ferromagnetic substances do show a marked dependence upon field strength. Only small agglomerates of such impurities would be necessary to explain the observed behavior.

It seems desirable that specially purified potassium chloroplatinite be prepared and the above measurements repeated. Although the crystals available were tested for diamagnetism the results were inconclusive.

Iodoform and arsenic triiodide are noteworthy in the wide deviation of their experimental average susceptibilities from the semi-theoretical values of Pascal. Pascal's value for iodoform, uncorrected for bond deviations, is -142.7×10^{-6} as compared with an experimental value of -117.1 . The theoretical value for arsenic triiodide is -178.0×10^{-6} , the experimental is -109.3 . Furthermore this deviation increases as the atomic number of the atoms attached to the core atom increases. The deviations for the trihalomethanes are:

$CHCl_3$ -10

$CHBr_3$ -17

CHI_3 -25

The discrepancy cannot be explained on the assumption that the field induced by one halide atom due to its diamagnetism decreases the effect of the external field at the remaining

two halide atoms. Calculation shows this internal field to be of the order of 10^{-1} gauss at the distances involved in iodoform.

Electronic interaction of the halogen atoms sufficient to distort the electron orbitals may account for this deviation. Even on a classical basis, however, it is difficult to see how a quantitative or semiquantitative treatment of such an interaction may be carried out.

A TABLE OF DIAMAGNETIC ANISOTROPIES OF ORGANIC COMPOUNDS

The notation adopted is that of Krishnan.^(1,9) In the case of magnetically uniaxial crystals, the gram molecular susceptibilities along and perpendicular to the axis are represented by χ_{\parallel} and χ_{\perp} respectively. In crystals belonging to the orthorhombic system, the three crystallographic axes coincide with the magnetic axes and the susceptibilities along them are denoted by χ_a , χ_b , and χ_c . For monoclinic crystals the (010) plane must contain two of the magnetic axes; these are denoted by χ_1 and χ_2 where χ_1 is greater than χ_2 . The third axis, χ_3 lies along the "b" axis. The χ_1 axis makes an angle ψ with the "c" axis and $\beta - \psi$ to the "a" axis, β being the obtuse angle between the "c" and "a" axes. K_1 and K_2 are the molecular susceptibilities in the plane of the molecule, K_3 is normal to that plane.

MONOCLINIC SYSTEM

Compound	Crystal Susceptibility $\times 10^6$				Molecular Susceptibility $\times 10^6$			Reference
	$-\chi_1$	$-\chi_2$	$-\chi_3$	φ	$-K_1$	$-K_2$	$-K_3$	
p-acetotoluide	78.7	1103	841	76.0°				17
anthracene	45.9	2332	919	8.0°	45.9	52.7	2725	1
azobenzene (trans)	932	1425	881	65.6°	764	540	1934	18
benzenehexa- chloride	1589	1608	1614	-60.8°				17
benzidine	881	1283	1188	80.0°				17
p-benzoquinone	27.1	67.1	25.9	31.2°	24.2	27.9	68.0	9
1,2benzpyrene	1048	2608	1866	()				17
biphenyl	634	1465	98.9	20.1	66.9	66.9	1747	1
bromanil	1358	1553	1354	13.7°				17
catechol	485	79.0	763	2.2°				9
chloranil	939	1162	962	13.4°				17
chrysene	88.0	258.	136.1	12.7°	88.0	83.3	3108	9&19
cinnamic acid (trans)	584	85.2	1214	-74.4°				18
coronene	90.	270.	300.	20.°	90.	90.	480.	10
cyanuric acid dihydrate	$\chi_1 - \chi_2 = 24.2$		$\chi_3 - \chi_2 = 23.9$					20
cyanuric tri- chloride	72.2	101.2	70.9	()	70.9	71.2	101.3°	19&21
cyclodiketone $C_{24}H_{44}O_2$	$\chi_1 - \chi_2 = 55.2$		$\chi_3 - \chi_2 = 28.0$					18
1,2,5,6dibenz- anthracene	109.	150.	310.	13.5°	110.	110.	358.	22
dibenzil	905	1465	98.9	83.9°	917	917	1995	1
p-dibromo- benzene	863	1185	954	87.0°				9

Compound								Reference
	$-\chi_1$	$-\chi_2$	$-\chi_3$	φ	$-K_1$	$-K_2$	$-K_3$	
p-dichloro-benzene	70.0	106.2	79.9	86.9°				9
4,4'-dichloro-diphenyl	129.9	165.0	104.5	-28.5°				9
dimesityl	161.2	188.7	165.0	-55.8°				9
dihydro-anthracene	95.3	168.3	102.3	-37°				17
p-dinitro-benzene	37.8	91.4	78.8	-36.6°				9
diphenic acid	120.2	138.0	138.2	-3.4°				9
diphenyl acetylene	98.5	149.4	99.9	-62.5°	81.5	67.8	198.5	2
diphenylamine	77.5	124.4	125.3	()				17
p-diphenyl-benzene	96.8	21.4	145.4	-14.3°	96.8	88.1	271.3	9 & 19
diphenyldi-acetylene	93.8	188.	109.6	-88.5°	109.4	75.3	206.7	24
diphenylethylene (sym)	99.9	146.8	98.8	-66.0°	85.8	50.1	209.6	2
durene	77.3	117.0	109.3	-20.2°	77.3	85.6	140.7	9
fluoranthrene	88.6	198.	128.6	9.6°				9
fluorene	72.6	156.6	109.6	10.9°	72.6	72.6	193.6	9
hexachloro-benzene	129.4	136.2	171.1	52.6°	128.	128.	182.	9
hexamethyl-benzene	101.1	102.7	163.8	()	101.1	102.7	163.8	9
maleic acid	43.3	62.3	42.9	()				18
melamine	58.1	77.6	59.8	25.0°	58.1	58.1	79.2	29
naphthacene	93.	263.	125.	()				17
naphthalene	39.4	161.4	68.7	12.0°	39.4	43.0	187.2	1

Compound								Refer ence
	$-\chi_1$	$-\chi_2$	$-\chi_3$	φ	$-\kappa_1$	$-\kappa_2$	$-\kappa_3$	
naphthalene tetrachloride	1356	1980	1395	-47°				17
naphthazarin	573	1703	771	()	573	573	1401	10
naphthol	605	1124	1224	287°				9
p-naphthol	623	1483	804	94°	466	502	1944	1
naphthoquinone	389	1268	558	-625°				9
oxalic acid dihydrate	531	550	601	()	531	527	624	2
perylene	955	2268	1564	-352°				17
phenanthrene	74.	200.	114.	-31°	74.	74.	240.	9
phthalocyanine	166.	538.	563.	()	165.	120.	982.	2
pyrene	806	178.	206.	250°	806	806	303.	9
quinhydrone	882	1426	1043	151°				17
sorbic acid	558	569	626	()	569	492	436	27
stearic acid	2100	2357	2082	()				18
stearolic acid	1996	2174	2026	()				18
stilbene	974	154.	966	-659°	858	501	2096	9&2
succinic acid	531	581	521	()	531	486	607	18
s-tetrabromo- benzene	1347	1749	1375	-670°				17
1,2,4,6tetra- chlorobenzene	1009	1426	1007	-689°				9
thianthrene	1179	1603	1096	-400°				17
tolane	985	1494	999	-625°	815	678	1985	18
urea nitrate	506	576	495	()				20
urea oxalate	$\chi_1 - \chi_2 = 1254$		$\chi_3 - \chi_2 = 158$					20

ORTHORHOMBIC AND UNIAXIAL SYSTEMS

Compound	Crystal Susceptibility $\times 10^6$					Molecular Sus- ceptibility $\times 10^6$			Refer- ence
	$-\chi_a$	$-\chi_b$	$-\chi_c$	$-\chi_{ }$	$-\chi_{\perp}$	$-K_1$	$-K_2$	$-K_3$	
acetrnaphthene	117.6	72.1	145.6						1
alizarine	113.	84.	194.						17
anthroquinone	103.2	62.0	185.5						17
azobenzene (cis)	157.0	109.7	74.2						18
benzil				80.0	125.6				1
benzophenone	88.0	88.6	149.3						1
p-biphenol	105.7	140.6	89.8						17
cyanuric triazide				102.0	80.0				28
dianthracene	265.7	243.6	175.1						17
1,2,5,6dibenz- anthracene	169.	110.	229.			110.	110.	358.	22
dimethyldibenz- phenanthrene	329.	145.	155.						17
m-dinitrobenzene	43.6	57.3	105.8						17
o-diphenyl- benzene	112.6	132.3	210.3						23
duodecahydro- triphenylene				154.5	209.6				17
i-erythritol				68.7	75.5				18
fluorene alcohol				74.2	125.				18
fluorenone	72.1	129.0	97.3						9
hexaethylbenzene				$\chi_{\perp} - \chi_{ } = 66.$					25
hydrazobenzene	88.0	88.6	149.3						1
hydroquinone				63.	64.				9
iodoform				100.2	128.8				
maleic anhydride	42.1	32.9	32.5						18

Compound									Reference
	$-\chi_a$	$-\chi_b$	$-\chi_c$	$-\chi_{11}$	$-\chi_{12}$	$-K_1$	$-K_2$	$-K_3$	
d mannitol	1133	1000	1056						18
naphthyl- amine	929	895	1096						9
m-nitroaniline	646	666	771						9
pentaerythritol				836	883				18
pentaerythritol tetraacetate				1597	1820				18
pentaerythritol tetranitrate				1249	1164				18
pentaerythritol tetraphenyl- ether				2909	2791				18
phloroglucinol	1201	831	841						17
resorcinol	664	742	610			492	492	1032	26
retene	244	147	105						17
salol	1211	908	1526						1
succinic an- hydride	507	443	476						18
o-toluidine	1173	2002	1206						9
p-toluidine	647	892	661						17
s-trinitro- benzene	676	745	810						17
1,3,5triphenyl benzene	313	155	1401						9
triphenyl- carbinol				1694	1747				9
triphenyl- methane	1733	1489	1660						17
urea				3184	3441				20

TRICLINIC SYSTEM

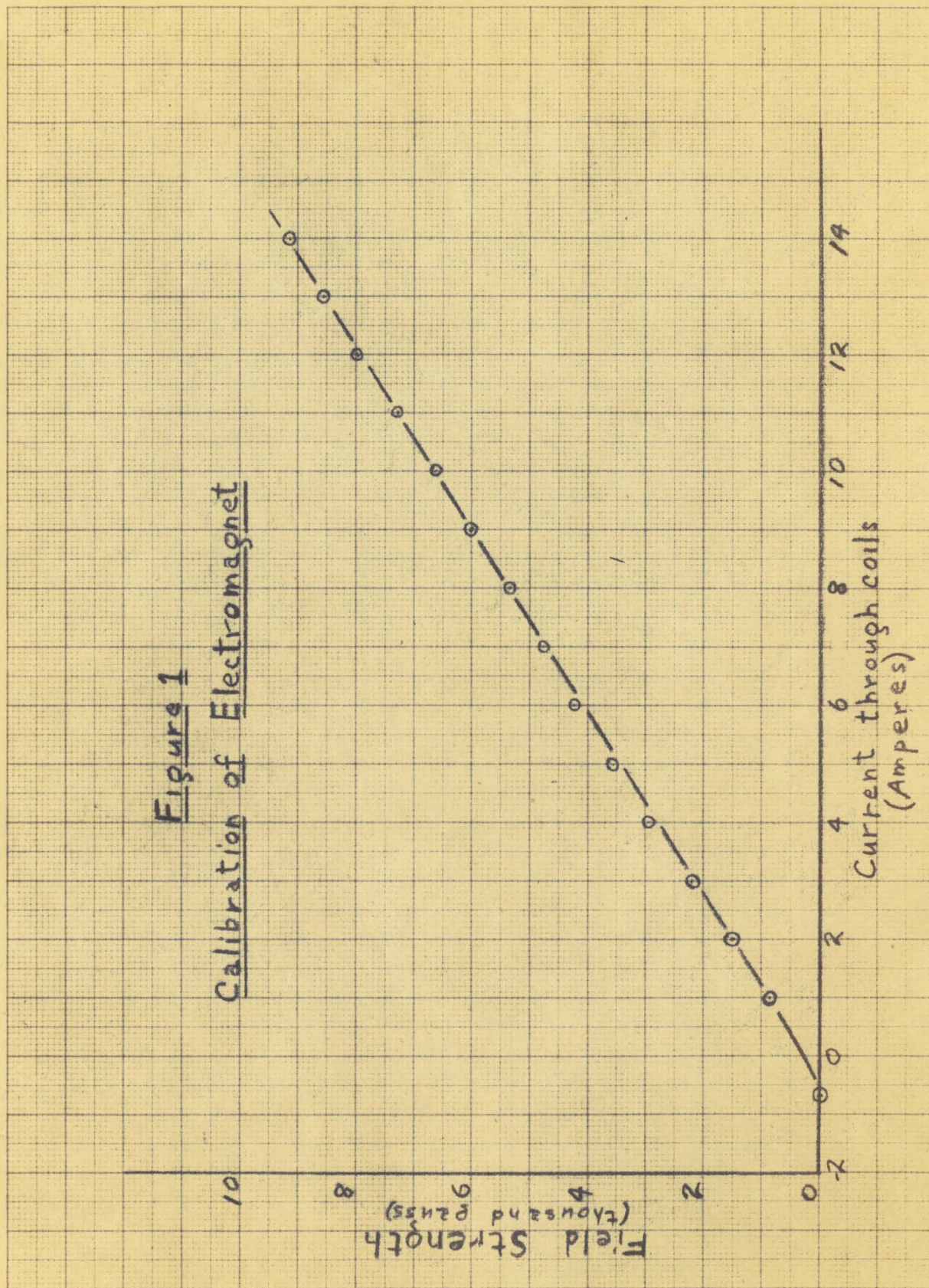
Compound	Crystal Susceptibility			Reference
	$-\chi_1$	$-\chi_2$	$-\chi_3$	
trans-trans-methyl fumarate	57.4	70.9	88.4	30
trans-trans-methyl muconate	67.0	82.6	109.2	30

REFERENCES

1. Krishnan, Gula and Banerjee Trans. Roy. Soc. 234,265, (1935)
2. Lonsdale J. Chem. Soc. p. 364 March 1938
3. Pauling Proc. Roy. Soc. 114, 181, (1927)
4. Van Vleck Phys. Rev. 31, 587, (1928)
5. Slater Phys. Rev. 36, 57, (1930)
6. Gray & Cruickshank T. Rad. Soc. 31, 1491, (1935)
7. French & Trew T. Rad. Soc. 41,439, (1945)
8. Pauling J. Chem. Phys. 4, 673, (1936)
9. Krishnan and Banerjee Trans. Roy. Soc. 234 265, (1935)
10. Rogers J.A.C.S. 69,1506, (1947)
11. Strong Procedures in Experimental Physics Chapt. V
12. Groth Chemische Krystallographie Vol. III p.4
13. Higgins and Noble Am. Mineral. 16, 519, (1931)
14. Ghulam Farid Science and Culture 6, 370, (1940)
15. Dickinson J. Am. Chem. Soc. 44, 2404 (1922)
16. Feytis Comp. rend. 152, 708, (1911)
17. Banerjee Z. Krist. 100, 316, (1938)
18. Lonsdale Proc. Roy. Soc. London A 171, 541, (1939)
19. Lonsdale Report Prog. in Physics IV 368, (1938)
20. Lonsdale Proc. Roy. Soc. London A 177, 272, (1941)
21. Lonsdale Z. Krist. 95, 471, (1938)
22. Krishnan and Banerjee Z. Krist. 91, 173, (1935)
23. Clews and Lonsdale Proc. Roy. Soc. London A 161, 493, (1937)
24. Lonsdale Nature 154, 148, (1940)
25. Ganguli Z. Krist. 93, 42, (1936)

26. Lonsdale Nature 137, 826, (1936)
27. Lonsdale, Robertson & Woodward Proc. Roy. Soc. London
A 178, 43, (1941)
28. Knaggs Proc. Roy. Soc. London A 150, 576, (1935)
29. Knaggs and Lonsdale Proc. Roy. Soc. London A 177, 140,
(1940)
30. Knaggs and Lonsdale J. Chem. Soc. p. 417, (1942)

Figure 1
Calibration of Electromagnet



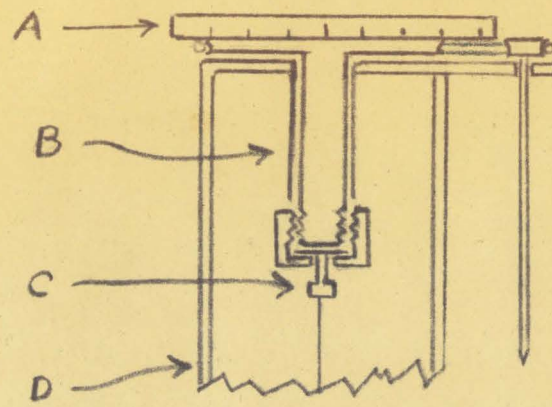


Figure 2
Apparatus

