STANFORD RESEARCH INSTITUTE
MENLO PARK, CALIFORNIA
SRI

0

UNPUBLISHED PRELIMINARY DATA

October 14, 1964

FACILITY FORM 602
N65-10838 (ACCESSION NUMBER)
(THRU)
10 (PAGES)
1 (CODE)
CR 59506 (NASA CR OR TMX OR AD NUMBER)
06 (CATEGORY)

Progress Report No. 4

Covering Period May, June, and July 1964

MAGNETIC PROPERTIES OF SOME MACROMOLECULES OF BIOLOGICAL INTEREST

Prepared for

National Aeronautics and Space Administration
Office of Research Grants and Contracts
Code SC
Washington 25, D.C.

Contract NASr 49(16), SRI Project 4644

Introduction

This report outlines progress during the fourth three-month period of a basic research study. The aims of the research are to measure the magnetic susceptibility of some selected macromolecules, using a new superconducting detection system, and to correlate the results of these measurements with the structure and with the physical and chemical properties of the compounds. Of particular interest is the possibility of detecting effects due to the quantized collective motion of electrons in large organic molecules. When these molecules are subjected to high magnetic fields, their diamagnetic susceptibility may change in a way which will be related to the multiple connectivity of the molecules. These changes may give information about molecular structure and it then may be possible also to identify certain biological molecules by magnetic susceptibility measurements.

The ultimate motivation for these measurements springs from the idea expressed by Fritz London that the property of long-range ordering of the momentum, which characterizes the electrons in a superconductor

OTS PRICE

XEROX $ 1.00
MICROFILM $ .50

and results in the appearance of macroscopic quantum phenomena, may be of more general significance and, in particular, may be important in understanding the macromolecules of biochemistry.[1] This ordering, if present, should affect the magnetic susceptibility of the molecules and may be detectable with the techniques being developed in this research.

A primary incentive for these measurements is the recent appearance of extremely sensitive new techniques for measuring magnetic flux. These techniques were originated at Stanford University in conjunction with experiments on quantized magnetic flux in superconductors.[2] Together with superconducting shields and superconducting persistent current magnets, these techniques make possible entirely new kinds of magnetic measurements.

An aim of this research is to adapt the new techniques, which have sensitivity and magnetic field range potentialities much greater than existing methods, to the measurement of magnetic susceptibility.

An apparatus for measuring magnetic susceptibility using a modulated inductance detector (a superconducting circuit[2] capable of detecting very small changes in magnetic flux) has been designed, constructed, and tested. Details of the circuit and of the apparatus were given in Progress Reports No. 2 and No. 3.

During the present report period, the apparatus was calibrated using a superconducting sample and measurements were made on two samples of coronene.

Calibration of Susceptibility Apparatus

A detailed description of the operation of the susceptibility apparatus was given in Progress Report No. 2. To clarify the calibration procedure, a schematic diagram of the susceptibility cryostat is shown in Fig. 1 and description of its operation is repeated here.

Coils L_1, L_2, and L_3 in Fig. 1 are interconnected to form a closed superconducting circuit. If the magnetic flux linking one of the coils, say L_1, is changed, an EMF is generated, causing a current to flow around the circuit. Since the resistance is zero, the current will persist and will induce, in coils L_1, L_2, and L_3, magnetic flux changes whose sum is just equal and opposite to the flux change made externally on L_1, thus leaving the total flux linked by the circuit (i.e., all three coils) unchanged. The persistent current is proportional to the external flux change made through L_1 and is a permanent record of that change. A

---

[1] London, F., Superfluids, Vol. 1, p. 9. John Wiley and Sons, New York, 1950

[2] Deaver, B. S., Jr., and W. M. Fairbank, Proc. of the Eighth International Conference on Low-Temperature Physics. R. O. Davies ed., Butterworth, Washington, D.C., 1963, p.116

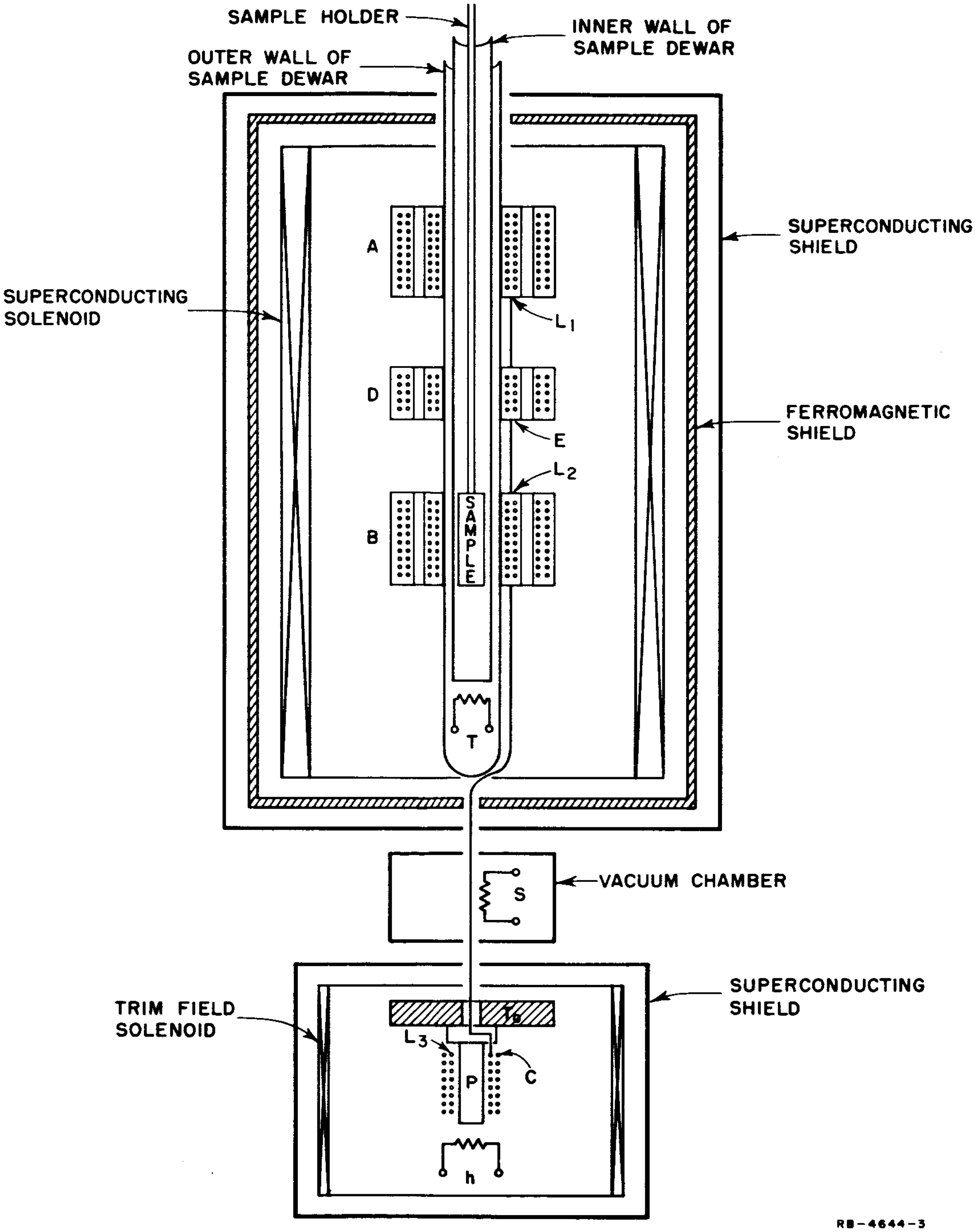


FIG. 1 SCHEMATIC DIAGRAM OF SUSCEPTIBILITY CRYOSTAT

measurement of this persistent current is then a measure of the flux change. If the flux change is caused by removal from L_1 of a sample magnetized by an external field, H, then the current will be proportional to the magnetization (or susceptibility) of the sample.

The persistent current is measured by using a modulated inductance detector (shown in the lower part of Fig. 1). Coil L_3 and a secondary coil, C, are wound around a superconducting post, P. The superconducting post is thoroughly grounded at one end to a temperature, T_0, below its superconducting transition temperature. The other end can be heated periodically so that the post rises above its superconducting transition temperature and then cools back to the superconducting state. When the post is normal (i.e., not superconducting), the current flowing in L_3 causes a magnetic flux to link both L_3 and C. When the post goes superconducting, the magnetic flux inside the post is expelled because of the Meissner effect, thus changing the amount of flux linking L_3 and C. As the post is heated and cooled periodically, the periodic variation of the flux in C causes an alternating voltage across the coil, C. This voltage can be measured and is proportional to the persistent current flowing in the circuit L_1-L_2-L_3.

Although in principle a single search coil is sufficient for measurement of the magnetization or susceptibility of the sample, a better design uses two coils, L_1 and L_2. These coils are identical in size and number of turns. However, the windings of L_1 are made in the opposite direction to those of L_2.

The sample whose magnetization or susceptibility is to be measured is placed inside coil L_2 in the presence of a uniform magnetic field, H, applied to both L_1 and L_2. Any persistent current already present in the circuit L_1-L_2-L_3 is eliminated by momentarily heating a small region of the circuit with the switch heater, S, causing a normal resistance in that part of the circuit and thus causing all current to decay to zero. Then the heater is turned off and the circuit is allowed to return to the superconducting state.

Now the sample is moved from coil L_2 into coil L_1; since coil L_1 has its windings in the opposite direction, the change in flux in the circuit (because of the movement of the sample) is twice that which would have occurred had the sample simply been removed from coil L_2.

The output voltage at coil C from the modulator is proportional to this flux change, $\Delta\varphi_{sample}$, and can be used as a measure of the susceptibility of the sample.

An improved technique is to use a coil B concentric with coil L_2 to introduce an opposing flux change $\Delta\varphi_B$ into coil L_2. When the flux change due to the current in B is exactly equal to the change caused by movement of the sample from L_2 to L_1 there will be zero output from coil C. The current I_{null} flowing in coil B is then a direct measure of the magnetization of the sample, and the detection circuit is being used simply as a null detector of high sensitivity, eliminating dependence on the gain characteristics of the detection system.

The device can be calibrated either against a sample of known shape and susceptibility or by calculation from the geometry of coils B and L_2 and the size and position of the sample. Presently the device is constructed to accommodate cylindrical samples about 1-cm long and up to 0.15 cm in diameter.

When the sample is moved from L_2 into L_1 with a field H applied along the axis of the coils, there is a flux change ($\Delta\varphi_{\text{sample}}$) in the circuit L_1-L_2-L_3 (due to the change in sample position) which is given by

$$\Delta\varphi_{\text{sample}} = (\varphi_{L_1} + \varphi_{L_2})_{\text{initial}} - (\varphi_{L_1} + \varphi_{L_2})_{\text{final}} \tag{1}$$

where $\varphi = \int \bar{B}\cdot d\bar{A}$ is evaluated for each coil, and where A is the area element, $\bar{B} = \bar{H} + 4\pi\bar{I}$, and I is the magnetization per unit volume of the sample. This flux change measures only the magnetization parallel to the axis of the coils.

For the weakly magnetic material being studied in our experiments, the samples can be assumed to be uniformly magnetized cylinders. Then, if L_1 and L_2 are identical coils with the same applied field, the flux change is closely approximated by

$$\Delta\varphi_{\text{sample}} = 2\alpha(4\pi IA), \tag{2}$$

where A is the cross sectional area of the sample, and α is the fraction of the flux ($4\pi IA$) from the sample coupled by the coils.

The magnetic susceptibility κ is defined by

$$I = \kappa H \tag{3}$$

and the specific susceptibility χ is given by

$$\chi = \kappa/\rho \tag{4}$$

where ρ is the density.

Thus, from Eq. (2)

$$\chi = \frac{\Delta\varphi_{\text{sample}}}{8\pi\alpha\rho AH} \qquad (5)$$

A current in coil B produces a flux change in the circuit

$$(\Delta\varphi)_B = k\ i_B \qquad (6)$$

where k is a constant depending on the geometry of coils B and L_2. If the current in coil B is set at that value i_{null} for which the signal from the modulator is zero, then

$$(\Delta\varphi)_B = k\ i_{\text{null}} = (\Delta\varphi)_{\text{sample}} \qquad (7)$$

Then from Eqs. (5) and (7)

$$\chi = \frac{k\ i_{\text{null}}}{8\pi\alpha\rho AH} \qquad (8)$$

and since $\ell A = V$, ℓ being the length of the sample, and ρV = mass,

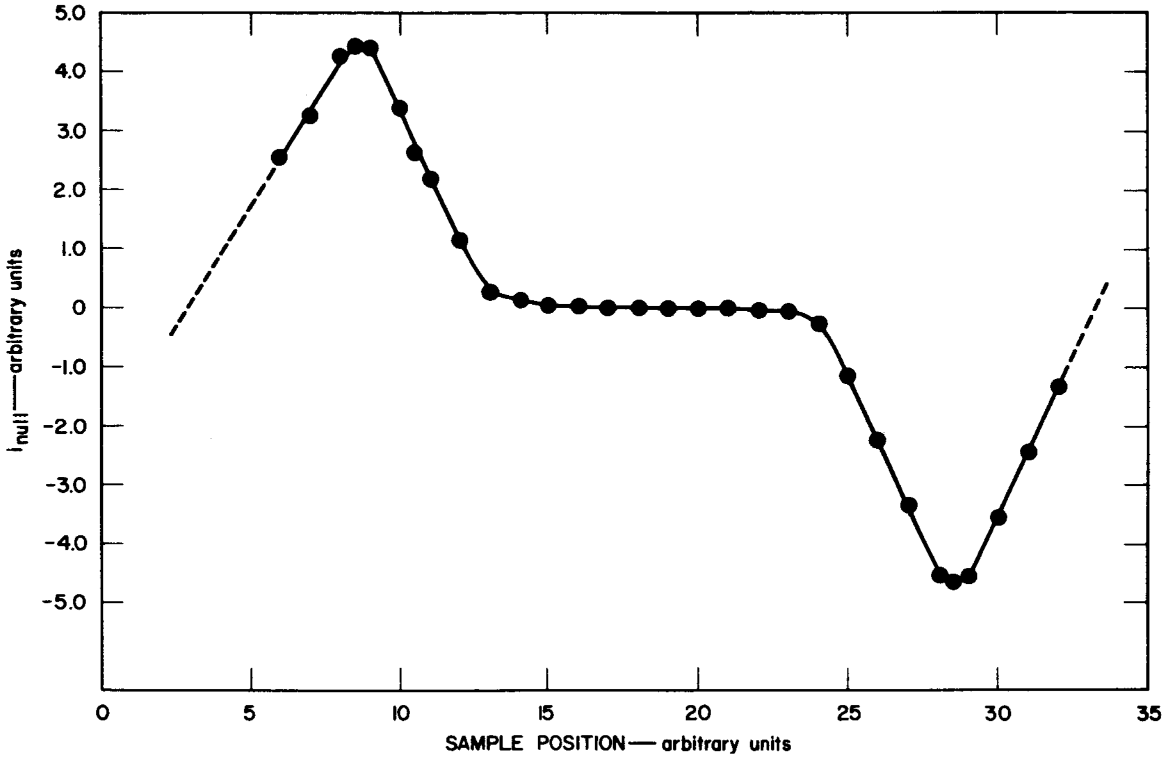
$$\chi = \beta(\ell/\alpha)\ 1/\text{mass}\ i_{\text{null}}/H \qquad (9)$$

The constant β (= $k/8\pi$) can be determined by calculation from the coil geometry or as mentioned above by measuring a sample of known susceptibility.

A calibration of the latter type and a determination of the response as a function of sample position were made using a small lead (99.99%) rod. This rod, 0.020-cm diameter and 1.10-cm long, was cooled below its superconducting transition temperature (~ 7°K) in zero magnetic field (less than 10^{-2} gauss) and assumed to be perfectly diamagnetic so that

$$\kappa = -1/4\pi \ .$$

The response of the system to the flux change caused by moving the lead rod in an applied field of about 100 gauss from a position slightly below center of the lower coil L_2 to a point just above center of the coil L_1 is shown in Fig. 2.



RB-4644-9

FIG. 2 RESPONSE AS A FUNCTION OF SAMPLE POSITION

The calibration procedure was as follows:

1. The lead rod was placed in the lower coil at a position of maximum response (~ 7.8 in Fig. 2).
2. The persistent current in the circuit was decayed to zero with switch S.
3. The rod was removed to the position of maximum response in the upper coil (~ 28.5 in Fig. 2).
4. The current i_{null} in coil B required to give zero output from the modulator was measured.

Some data obtained with this procedure are shown in Fig. 3. The average slope of the line in Fig. 3 was used to determine the constant β in Eq.(7).

Measurement on Coronene

As discussed in Report No. 3, measurements on a first sample of coronene ($C_{24}H_{12}$) showed a large paramagnetism which was attributed to contamination of the sample during the mounting procedure. Measurements have been made on two more samples of the same material with the results given in Table I.

Table I

SUSCEPTIBILITY OF CORONENE AT 20°K

H kilogauss	$-\chi \cdot 10^{-6}$
15.3	0.830
18.9	0.724
21.5	0.775
25.2	0.822
28.0	0.927

Because of the ring structure of coronene, the susceptibility is very anisotropic; however, these measurements were made on polycrystalline samples and thus represent the susceptibility averaged over all directions. The mean value of the data in Table I is -0.816×10^{-6}. (Akamatsu and Matsunaga[3] report a value of -0.810×10^{-6} for the mean susceptibility at 20°C and 23 kilogauss.)

---

[3] Akamatsu and Matsunaga, Chem. Soc. Japan, Bull. 29, 800 (1956)

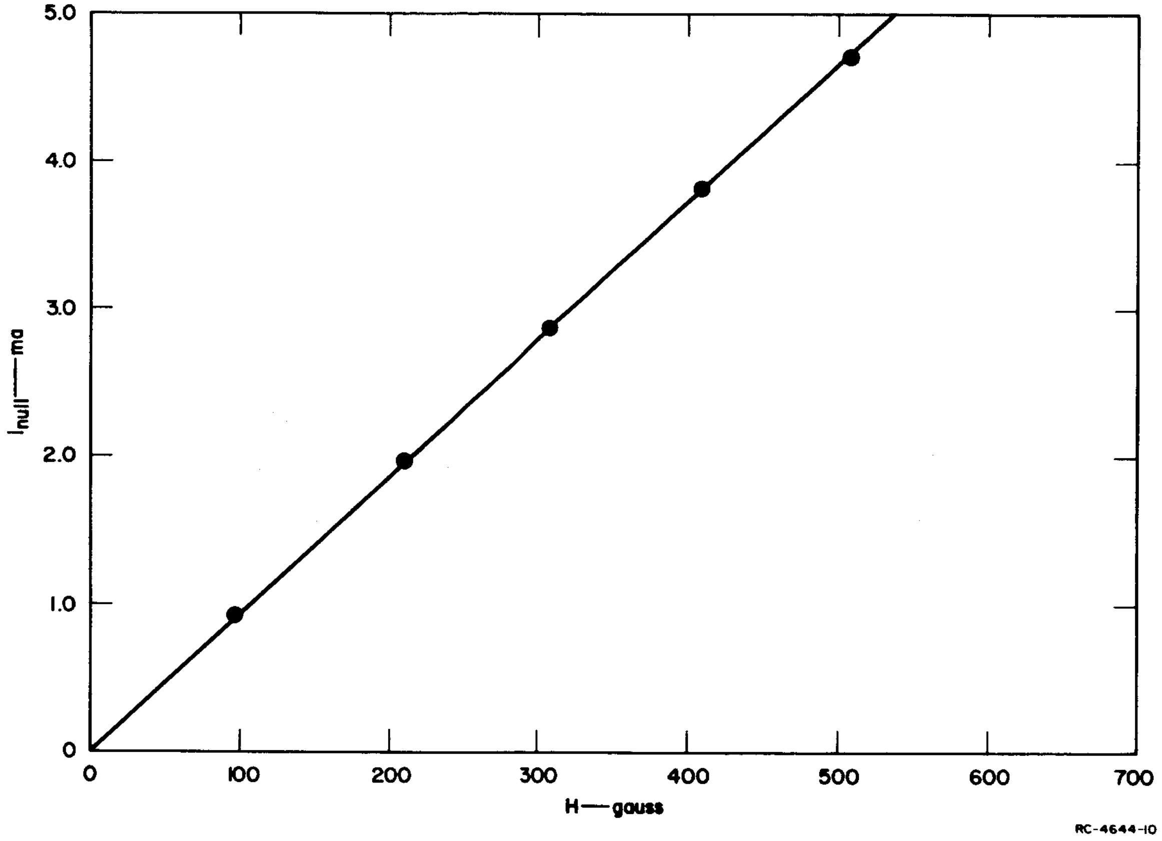


FIG. 3 SENSITIVITY CALIBRATION WITH LEAD CYLINDER

One of the objectives of this research is to look for variations of the diamagnetic susceptibility with magnetic field; however, the variations shown by the data in Table I probably are not due to the magnetic field, but are believed to result from a systematic error which was not identified in time to remedy it during these measurements. We believe the error arises from variations of the temperature of the inner wall of the sample dewar, which was made of beryllium-copper alloy. This alloy is slightly paramagnetic; the heating of the wall caused by moving the sample in the measurement process caused a change in the susceptibility of this wall and thus a flux change in the pickup coils L_1 and L_2.

Future Work

The sample dewar will be redesigned to eliminate the temperature variation. We expect to use high purity quartz tubes for both the inner and outer walls; a liner of high purity copper (slotted along the length to prevent eddy current damping of the ac signals) will be placed inside the dewar and connected at its upper end to a copper block maintained at a controlled temperature to keep the sample at a uniform temperature independent of position in the dewar. If these modifications are completed in time we will repeat the measurements on coronene.

During the next reporting period a final report will be prepared.

Bascom S. Deaver, Jr.
Bascom S. Deaver, Jr.
Physicist
Nuclear Physics Department

Approved:

EM Kinderman
E. M. Kinderman, Manager
Nuclear Physics Department