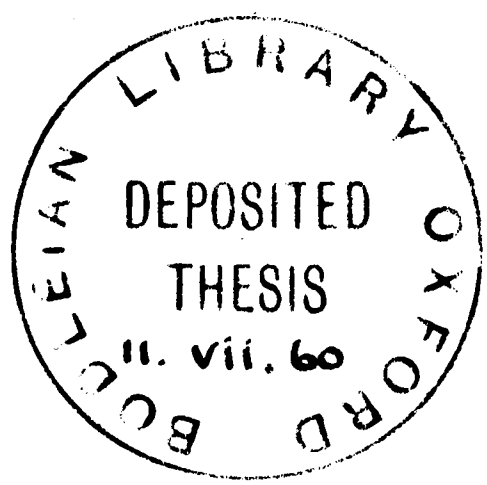
[illegible] NUCLEAR SYSTEMS

This Thesis was submitted for the degree of Doctor of Philosophy at the University of Oxford by M.V. Hobden, Keble College, in Hilary Term 1960.



ABSTRACT

In this thesis are described further developments in the design and construction of apparatus for producing very low temperatures by the technique of adiabatic demagnetization of nuclear spin systems, a technique proposed independently in 1934 by Gorter[1] and by Kurti and Simon[2]. Improved methods of measuring nuclear susceptibilities have led to a more accurate estimate of the value of θ_n, the nuclear interaction temperature, for copper nuclei in copper metal. It is shown that θ_n is four times smaller than the value estimated by Spohr[3] in his earlier experiments and is in fact close to the theoretical value for magnetic dipole interaction. The nuclear spin-conduction electron relaxation time has been measured at various temperatures and this is discussed in relation to nuclear spin relaxation theories.

The cryostat designed for these experiments is described in some detail. A metal helium dewar of large capacity has been designed with close spaced walls in the tail to make best use of the small internal diameter

of the high powered solenoid for producing the strong magnetic fields. The advantages of this particular vessel are explained.

A closed circuit He^3 system is described which enables a thermal shield to be maintained at 0.35°K. This overcomes the disadvantages of the thermal shield cooled by a separate paramagnetic salt, as used by Spohr, allowing the temperature of the paramagnetic heat sink to be measured. This He^3 system was designed to work on the principle of initial condensation at 1°K followed by pumping with a diffusion pump to 0.35°K, using 0.2 cm^3 of liquid (150 cm^3 of gas at N.T.P.). Subsidiary experiments are described to test the performance of this system.

An A.C. method of measuring the nuclear susceptibility has been developed to replace the previous ballistic system. This method employed a balanced A.C. bridge which was unbalanced by the nuclear susceptibility. It was so arranged that the proximity of large masses of metal did not affect the measurements. The improvement in technique has shown that the form of decay of the nuclear susceptibility is exponential and not linear as previously assumed allowing more accurate values of the nuclear spin temperature at

the instant of demagnetization to be found. The lowest spin temperature achieved was 1.3×10^{-6} ^{o}K. It is shown also that the conduction electrons do not become cooled to these temperatures as previously thought[4].

Experiments on copper give a nuclear interaction temperature $\theta_n = 1.75 \times 10^{-7}$ ^{o}K where θ_n is defined in terms of the splitting of the nuclear energy levels due to the internal field. The value of θ_n is calculated using the expression

$$\theta_n = \frac{\mu_n T_f H_i}{k I T_i}$$

where T_i and H_i are the initial temperature and field before demagnetization, T_f is the final spin temperature and μ_n and I are the nuclear magnetic moment and spin.

This value is equal, within the range of experimental and theoretical uncertainty, to that computed on the basis of magnetic dipole, indirect exchange, and pseudo-dipolar interactions. This would seem to indicate that quadrupole splitting is not as important as previously assumed[3]. The relationship of this θ_n to the Curie temperatures of the theories of nuclear ferromagnetism is discussed.

The nuclear spin relaxation time τ has been measured with conduction electron temperatures in the range .012^{o}K

to 0.1^{o}K. These experiments showed the inverse relation of τ and T_e, the conduction electron temperature. Furthermore the values of τT_e (which in this case were measured in zero field) were found to be a factor 3.5 times smaller than those found by Redfield[6] in an external field, using nuclear resonance techniques, above 1^{o}K. Application of an external magnetic field caused the relaxation time to increase. These results are discussed with reference tothe theories of nuclear relaxation in metals by Korringa[7] and more recently by Redfield[8].

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ORDERED NUCLEAR SYSTEMS

Contents

CHAPTER 1

INTRODUCTION TO NUCLEAR COOLING

In 1934 it was proposed by Gorter[1] and by Kurti and Simon[2] that the technique of adiabatic demagnetization for obtaining very low temperatures could be applied to nuclear spin systems. It was pointed out that much lower temperatures could be achieved in this way than by using highly diluted electron paramagnetics and that useful information concerning nuclear spin interactions and ordering would be obtained.[3]

In adiabatic demagnetization the spin entropy of an assembly of interacting magnetic dipoles, in contact with a low temperature heat reservoir, is reduced by the application of a magnetic field. Subsequent adiabatic, reversible removal of the field (isentropic demagnetization) causes the temperature of the spin system to fall to that at which the same degree of ordering would be produced by the interactions between the magnetic spins alone. The final temperature is given by the well known expression

$$T_f = T_i H_f / H_i$$

where H_f, the final field, is the "internal field" due

to the magnetic spins which is of the order μ/r^3, where r is the separation of neighbouring spins of moment μ, and where T_i and H_i are the temperature and field before demagnetization.

Some paramagnetic salts are sufficiently dilute and the internal field sufficiently small that there is almost complete disorder in the spin system even at 1 ^oK. This disorder can be removed by a magnetic field $\sim$10 KØ and upon demagnetization the temperature falls to between 10^{-3} ^oK and 1 ^oK, according to the strength of the interactions. The very lowest of these temperatures can only be reached by using highly diluted salts with perhaps only one magnetic atom in every thousand. For these salts the available entropy per unit volume, and hence the specific heat, is very small and in general it can be said that few experiments have been performed below 0.003 ^oK for this reason.

Nuclear paramagnetics can be used to obtain very low temperatures for their interactions are also very weak. This is because of the small magnetic moment of nuclei and not because of a large separation, in fact in the most suitable nuclear paramagnetics every nucleus is magnetic. This gives a much higher available entropy

per unit volume than for diluted electron paramagnetics and for a given interaction temperature they have a correspondingly higher specific heat per unit volume.

There are considerable technical difficulties involved in nuclear cooling experiments.

Because of the small magnetic moments of nuclei it is necessary to use strong magnetic fields and very low temperatures in order to remove even a small proportion of the nuclear spin entropy. Present techniques, as described in this thesis, are limited to the use of fields of up to 30 KØ at .012 ^{o}K. Under these conditions it is only possible to remove a fraction of one per cent of the total spin entropy.

In order to obtain these initial conditions it is necessary to use a two stage demagnetization technique using an electron paramagnetic material to obtain a temperature $\sim 10^{-2}$ ^{o}K (generally referred to as the "heat sink"). It must be possible to magnetize the nuclear specimen in a high field without remagnetizing the heat sink. This generally needs a specially designed high powered solenoid.

The most formidible problem is that of thermal contact between the nuclear specimen and the paramagnetic heat sink. Considerable progress has been made by the

pressed fin technique[4] and more recently by using a slurry of the salt in glycerol[5] or other suitable media, but this still remains one of the limiting factors.

It is essential that the material chosen for nuclear cooling experiments has a reasonably small nuclear spin-lattice relaxation time so that the nuclear spins can come into thermal equilibrium with the heat sink during magnetization. Dielectric materials have times of the order of hours at these temperatures although this can be reduced by the addition of electron paramagnetic impurities or F centres.[6] The most suitable substances are metals which have relaxation times of the order of a minute at 10^{-2} ^{o}K due to the hyperfine coupling with the conduction electrons.[7,8]

Of the available metals with large Curie constants many are superconductors or ferromagnetics which are not suitable. Some of the alkali metals having a high Curie constant would be very suitable were it not for the difficulties involved in making a specimen in the form necessary for these experiments. The metal with the most suitable properties is copper and this was used in these experiments and the earlier experiments of Kurti et al.[9]

In order that the demagnetization be adiabatic it is necessary to prevent heat flowing into the nuclear spin system from the heat sink and to prevent any other spurious heat influxes. This is a problem of considerable difficulty, calling for the use of heat switches, thermal shields, and other techniques.

The Thermodynamics of Nuclear Cooling.

Consider an assembly of spins, say unit volume containing N nuclei of spin I and moment μ_n. At high temperatures in zero field the entropy is $Nk \log(2I+1)$ corresponding to the $(2I+1)^N$ states of the assembly. Application of a field H at temperature T reduces the spin entropy and a simple thermodynamic calculation shows that for values of H/T such that Curies' law holds the entropy (neglecting self-ordering) is

$$S = Nk \log(2I+1) - \tfrac{1}{2}\lambda (H/T)^2$$

where $\lambda = N\mu_n^2(I\ \ 1)/3k\ I$ is the Curie constant per unit volume. From this equation can be calculated the reduction in entropy of a nuclear spin system for given initial conditions.

At very low temperatures in zero external field there will be self-ordering due to the interactions, for the $(2I+1)^N$ levels are not completely degenerate but are split into a band of levels of small but finite width.

Suppose these $(2I+1)^N$ levels of the complete assembly of N nuclei be $E_1, E_2 \ldots E_N \ldots\ldots$. Then the partition function is

$$Z = \sum \exp(-E_n/kT)$$
$$= (2I+1)^N + \sum(-E_n/kT) + \tfrac{1}{2}\sum(-E_n/kT)^2 \quad \ldots$$

where the summation is over the $(2I+1)^N$ levels.

At higher temperatures when these levels have almost the same probability density the series converges rapidly. The sum of the levels can be taken to be zero and so to the first approximation

$$Z = (2I+1)^N \left[1 + \tfrac{1}{2}(\overline{E^2}/k^2T^2)\right]$$

where $\overline{E^2}$ is the mean square energy of the $(2I+1)^N$ levels of the N nuclei.

From this it can be shown that the entropy is

$$S = Nk\left[\log(2I+1) - \tfrac{1}{2}(\overline{E^2}/Nk^2T^2)\right]$$

showing that the reduction is entropy by self-ordering in zero field is, to the first approximation, proportional to T^{-2} and the mean square splitting of the energy levels per nucleus.

A more convenient way of describing this average mean square splitting is in terms of a nuclear spin degeneracy temperature θ_n. Spohr used a simplified picture of the zero field splitting in his definition of θ_n.[10] In his

model all nuclei were in an internal field such that the energy difference of adjacent levels was k θ_n. In this case the entropy in zero field is

$$S = Nk \left[\log(2I + 1) - (1/6)I(I + 1)(\theta_n/T)^2\right] .$$

For the sake of continuity the same θ_n will be used in this thesis but it will be defined in terms of the average mean square splitting of the energy levels by

$$I\ (I + 1)(k\ \theta_n)^2 = 3\ \overline{E^2}/N.$$

In these nuclear cooling experiments the value of θ_n is found by finding the relationship between the entropy and nuclear spin temperature in zero field after demagnetization.

The initial reduction in entropy by the field H_i at temperature T_i is

$$\Delta S = \tfrac{1}{2}\lambda\,(H_i/T_i)^2$$

the self-ordering being negligibly small. After demagnetization the final temperature is that at which this reduction in entropy occurs by self-ordering, so that

$$\left[Nk\ I(I + 1)/6\right]\ (\theta_n/T_f)^2 = \left[N\mu_n^2(I + 1)/6kI\right]\ (H_i/T_i)^2$$

giving

$$\theta_n = \mu_n H_i\ T_f\ /kI\ T_i.$$

From this equation and a knowledge of the nuclear constants, the initial conditions and final temperature

the nuclear spin degeneracy temperature, which is a measure of the average mean square splitting of the energy levels in zero field, can be found.

CHAPTER 2

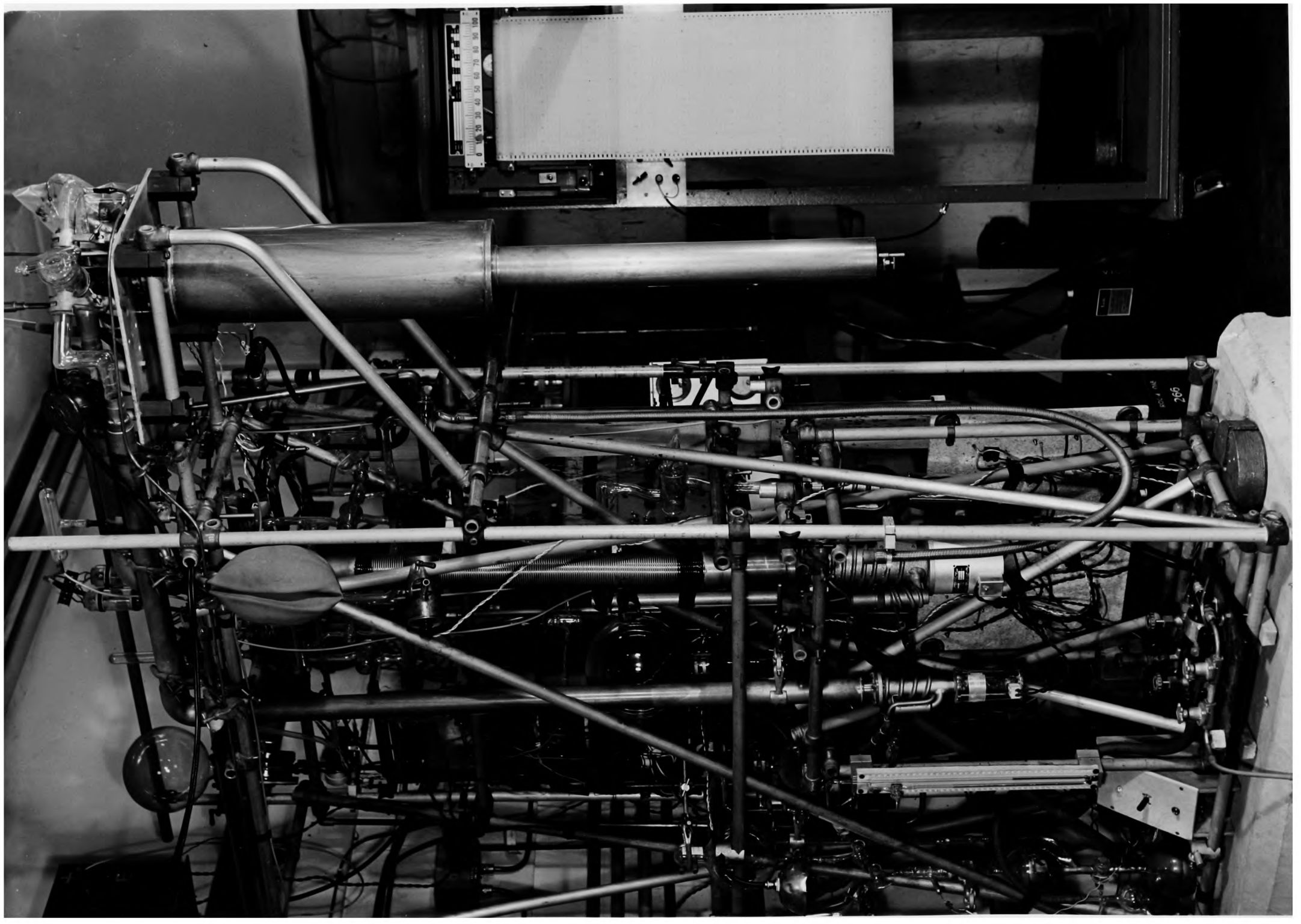
The Apparatus for Nuclear Cooling Experiments

The Anti-vibration Mounting

In this type of experiment it is important to keep the heat leaks into the specimen very small. One serious heat leak which is able to by-pass thermal shields is that due to vibration. The mechanism by which heat is liberated in specimens at very low temperatures is not very well understood although experimentally well known.

For this reason the whole apparatus was mounted on a concrete raft weighing nearly half a ton which was supported on ten helical springs. The natural periods of vibration were of the order of one second. It was hoped that this low-pass filter would remove vibrations from the generator and rotary pumps. All couplings to the apparatus were flexible.

Vibrations were also generated on the apparatus itself. These were due to the bumping of mercury in the three diffusion pumps, the automatic Toepler pump in the



He^3 system and perhaps small vibrations due to the boiling of liquid oxygen and helium in the metal dewar.

To reduce these to a minimum the mercury pumps were mounted on a separate internal framework embedded separately in the concrete raft. Flexible pumping lines were used as far as possible to connect them to the cryostat. The Toepler pump was seated directly onto the concrete. It was hoped that the massive construction of the dewar and cryostat would help reduce the vibrations due to the boiling of the oxygen and helium.

In spite of these precautions however, vibration heating still remained the biggest heat leak into the specimen.

The Helium Dewar

It was decided to use a metal dewar for the liquid helium based on the original idea of Henry." The dewar was fixed to the top plate of the cryostat assembly by three large threaded studs and sealed by an O ring. This ensured that the tail of the dewar was always in correct alignment with the axis of the high powered solenoid. The O ring seal allowed the interior of the dewar to be evacuated during the precooling process.

The liquid oxygen tank held about three litres and this boiled off via one of the three vents running through the centres of the threaded studs. One of these tubes extended to the bottom of the tank to facilitate quick removal of the liquid if this were necessary. This quantity lasted for twelve hours and moreover as the tank itself had a large heat capacity, the temperature of the shield would remain below 200°K for several more hours. This enable the interior of the dewar and cryostat to be kept at a temperate ~ 100°K overnight between experiments. This prevented deterioration of the specimen (see below) and allowed immediate precooling with liquid hydrogen on the following morning with a consequent saving of time. In this way the specimen could be kept cold for several weeks until a new specimen was required.

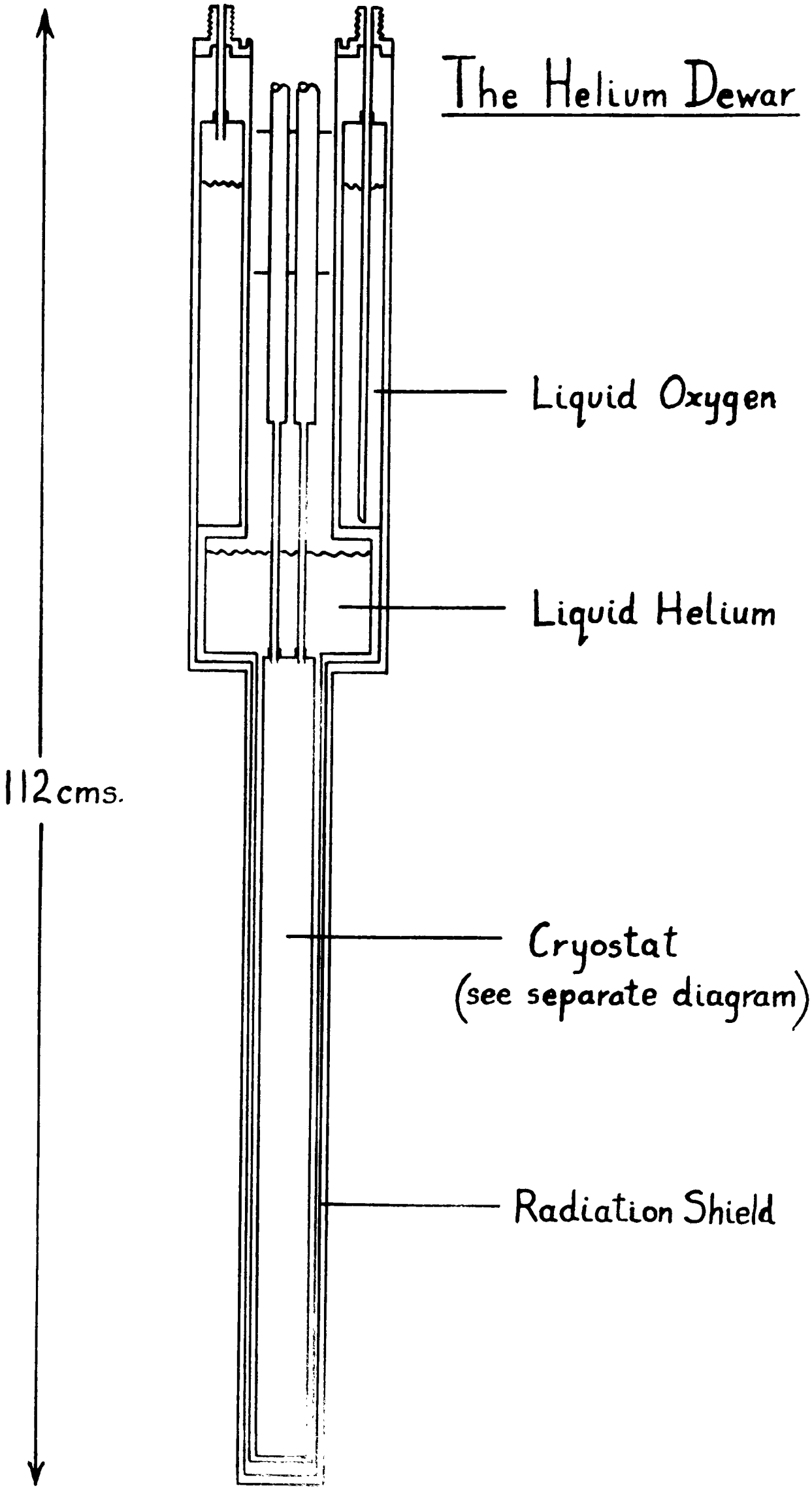
The total mass of metal to be cooled to helium temperatures was of the order 7.5 kilograms and so it would have been quite impracticable to cool this from liquid oxygen temperature with liquid helium. Liquid hydrogen, which has a larger heat of vaporization and is cheaper, was used for precooling from 90°K. This was syphoned directly into the helium dewar, the temperature at the top of the cryostat and at the very bottom of the dewar being monitored using two direct reading carbon resistance thermometers.

Each carbon resistor (LAB 47 ohm ½ watt) was in a Wheatstone bridge circuit exactly balanced at 20°K and giving full scale reading at 90°K. The maximum sensitivity of this theremometer was at the low temperature end where it was needed. A further scale between 20°K and 4.2°K was also available.

With practice precooling could be done in such a way that no free liquid hydrogen remained in the dewar. Any excess liquid could be removed by means of a heater situated within 1 mm of the bottom of the dewar. Temperature equilibrium in the tail was greatly assisted by the thick pure copper ripple shield (see below). The process of precooling with liquid hydrogen took about twenty-five minutes; the final temperature of the tail being about 25°K.

At this point the helium transfer syphon was inserted into the apparatus. This syphon had a needle valve fitted at the outside end. The whole of the interior of the dewar and the syphon up to the valve was pumped free of hydrogen using a rotary pump. The helium transfer vessel was fixed to the syphon and the valve opened to allow a little of the cold helium to enter the evacuated dewar, the pressure rising to ~ 5 mm Hg. After this had mixed with the last traces of hydrogen it was

The Helium Dewar



pumped out and discarded. This flushing action was performed at least three times to ensure that no hydrogen could be returned to the helium gas holder.

By the end of this process the temperature in the dewar rose slightly to about 30°K. The syphon valve was then fully opened and liquid helium allowed into the dewar, a slight overpressure in the transport dewar assisting this process. Cooling from 20°K to 4.2°K was a relatively fast process as the heat capacities were much lower and the thermal conductivity of the ripple shield in the tail was very high. Only about 200 ccs of liquid helium were required to cool 7.5 kilograms of copper and brass. With one full transport dewar of 1400 ccs it was usual to finish with 1000 ccs of liquid in the dewar. This was sufficient for one experiment of twelve hours. Considering the large cryostat and dewar to be cooled this was quite economical. This method was also economical with time; experiments could be started within an hour of the initial precooling.

The evaporation rate from this dewar can be estimated using the following data:

Cross sectional area of the inner inconel tube =

$0.90\ cm^2$

Mean conductivity of inconel (4.2° to 90°K) =

0.051 watts/cm deg.

Cross sectional area of pumping tubes and electrical leads = 0.24 cm^2

Mean conductivity of tubes and leads = 0.12 watts/cm deg.

Specific heat of helium gas, C, = 20.9 joules/deg.mole

Latent heat of vaporization, λ, = 87 jourles/mole

Distance between levels at 90°K and 4.2°K = 30 cm

The differential equation for the conductivity problem is

$$\sum (KA) \frac{d^2\theta}{dx^2} = - \dot{M}C \frac{d\theta}{dx}$$

where $\dot{M}$ is the evaporation rate in moles/sec. This assumes perfect thermal equilibrium at all levels in the inconel tube between the gas and the walls. Integrating and inserting the appropriate boundary condition

$$- \sum (KA) \frac{d\theta}{dx} = \dot{M} \left[C(\theta - 4.2) + \lambda \right]$$

and integrating again

$$- \frac{\sum (KA)}{\dot{M}C} \log \left[\frac{C(\theta - 4.2) + \lambda}{C(90 - 4.2) + \lambda} \right] = x$$

Now $\theta = 4.2°$ when x = 30 cm, and so

$$\dot{M} = - \frac{\sum (KA)}{LC} \log \left[\frac{\lambda}{C(90 - 4.2) + \lambda} \right]$$

With the values given the evaporation rate should be 1.33 moles per hour, i.e. 43 ccs of liquid helium per hour.

The other source of heat leak into the dewar was by radiation from surfaces at 90°K. All surfaces were cleaned by an acid dip; in this way the net flow of heat can be reduced to one or two percent of that for black body surfaces. The heat leak estimated in the case of this dewar was ~ 10 milliwatts which is equivalent to ~13 cc of helium per hour. It might be thought that the extra flow of cold gas would help to reduce the heat conduction into the dewar but by means of an extra term in the foregoing analysis it is found that the effect is very small.

The measured evaporation rate was 60($\pm$ 5) ccs per hour - a value slightly larger than that calculated, but close enough to show that the assumptions of good thermal equilibrium between the gas and the walls and of low radiation input are justified.

The Ripple Shield

It can be shown that at frequencies lower than those at which the skin depth becomes comparable with the radius, the rate of eddy current heating in a cylindrical conductor of unit permeability and radius a which is parallel to an alternating magnetic field of amplitude H and frequency ω is

$$Q = \frac{\omega^2 a^2 H^2}{16\rho} \text{ ergs/cm}^3 \text{ sec.}$$

where the resistivity ρ is expressed in e.m.u. (1 e.m.u. = 10^{-9} ohm cm).

The nuclear cooling specimen is composed of pure copper wire of radius .0061 cm and has a total volume of about 5 cm^3. It will be shown that it is absolutely essential that the heat input to the copper during the process of magnetization of the nuclear spin system is kept well below 10^{-2} erg/second. The value of ρ for copper at very low temperatures is about 20 e.m.u. and so it can be seen that for the magnetic ripple components $\sum(\omega H)$ must be kept below 10^2 radians oersted/sec.

For an iron free solenoid being run directly from a generator at a field of up to 30 KØ this is a stiff requirement. In fact for the generator and solenoid used $\sum(\omega H)$ was about 3×10^3 which would put approximately 1000 times the permissible amount of heat into the specimen.

This heating was reduced by the use of a ripple shield, similar to that first used by Spohr[10] in the first nuclear cooling experiment. This was a thick, pure copper tube fitting inside the tail of the helium dewar. Due to the high ratio of inductance to resistance at 4.2°K it acted as a very good filter to magnetic fields at frequencies above a few cycles per second.

The following analysis shows quantitatively the effect of this shield. Consider a long cylindrical tube of cross sectional area A and circumferential resistance R per unit length in a magnetic field $H_o e^{i\omega t}$ parallel to the axis. Then at a point inside the tube the field will be H where

$$\frac{4\pi A}{R}\frac{dH}{dt} + H = H\, e^{i\omega t}$$

We expect to find a solution of the form

$$H = \alpha H\, e^{i(\omega t + \beta)}$$

where α is real and β is a phase angle. Substitution in the differential equation gives

$$\alpha e^{i\beta}(1 + ip) = 1 \quad \text{where } p = \frac{4\pi A \omega}{R}$$

By equating real and imaginary parts

$$\tan \beta = -p$$

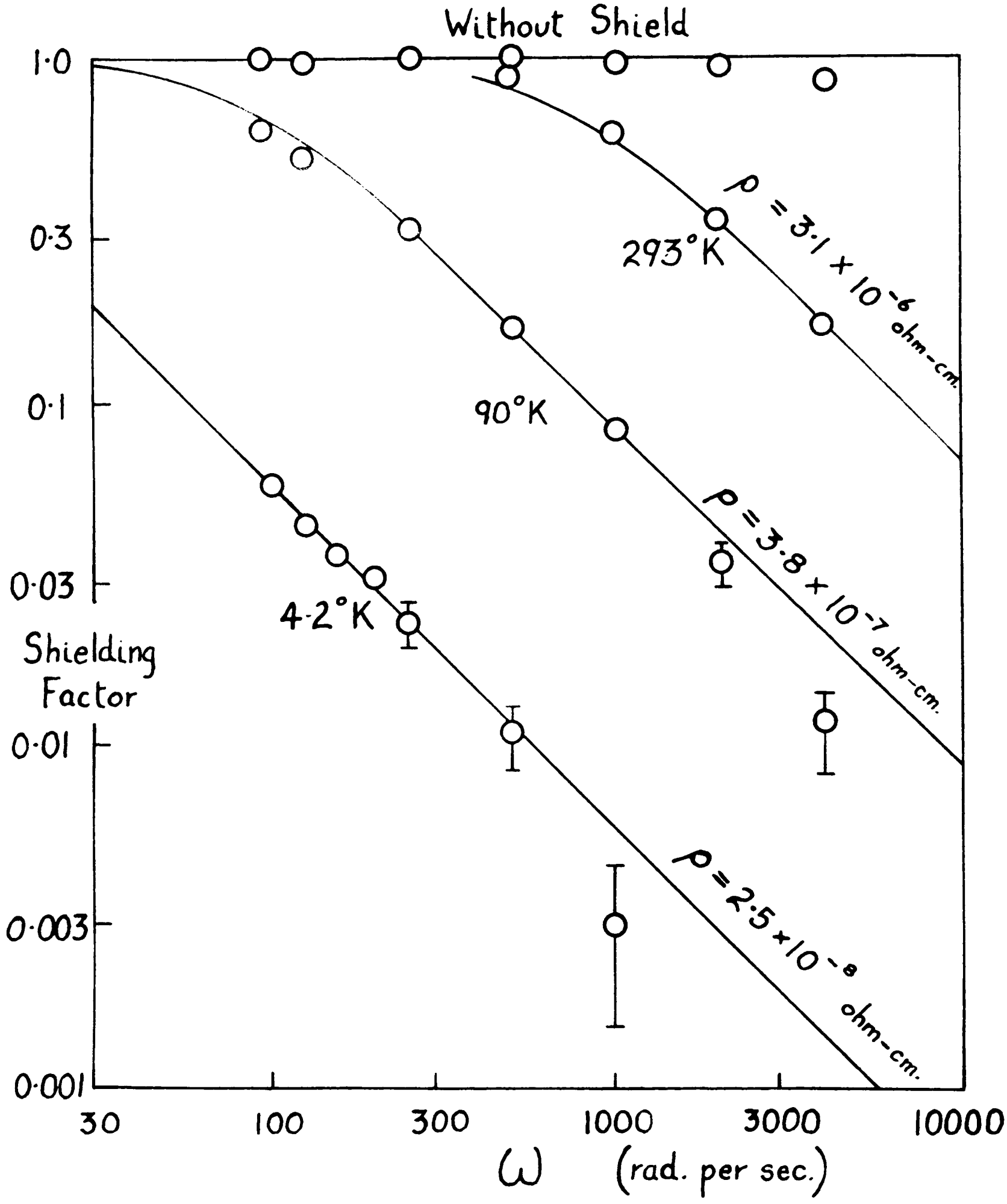
and

$$\alpha = \cos \beta$$

so

$$\alpha = (1 + p^2)^{-\frac{1}{2}}$$

The phase of the field in the tube lags by $\tan^{-1} p$ and the amplitude is reduced by a factor $(1 + p^2)^{-\frac{1}{2}}$. So at high frequencies the shielding factor is inversely proportional to the frequency but will approach unity as the frequency decreases.


Without Shield
1·0
0·3
0·1
0·03
0·01
0·003
0·001
Shielding Factor
293°K
ρ = 3·1 × 10⁻⁶ ohm-cm.
90°K
ρ = 3·8 × 10⁻⁷ ohm-cm.
4·2°K
ρ = 2·5 × 10⁻⁸ ohm-cm.
30
100
300
1000
3000
10000
ω (rad. per sec.)

The ripple shield in this experiment was 60 cms long, 5.3 cms in diameter and 0.2 cm thick and it was drawn from pure electrolytic copper and annealed. In the graph are shown experimental values of the shielding factor together with theoretical curves for the stated value if resistivity. As can be seen the points at 4.2° K and 90°K fit the theoretical curves for values of resistivity expected at these temperatures.

The skin depth in a metal is approximately $\sqrt{\frac{\rho}{\pi\omega}}$ and so for $\omega < 1000$ and $\rho = 20$ e.m.u. the skin depth is < 1 mm. These experimental points fall within the frequency range where the skin depth phenomenon is not important.

The dominant frequencies of the magentic ripple field were between 10 c/s and 500 c/s. By measuring with a pick-up coil inside the shield at 4.2°K it was found that $\sum(\omega H)$, as measured by the peak to peak amplitude of the noise voltage induced in the coil and displayed on a C.R.O., was reduced by the shield from ~ 3000 to ~ 100 at a D.C. field of 30KØ.

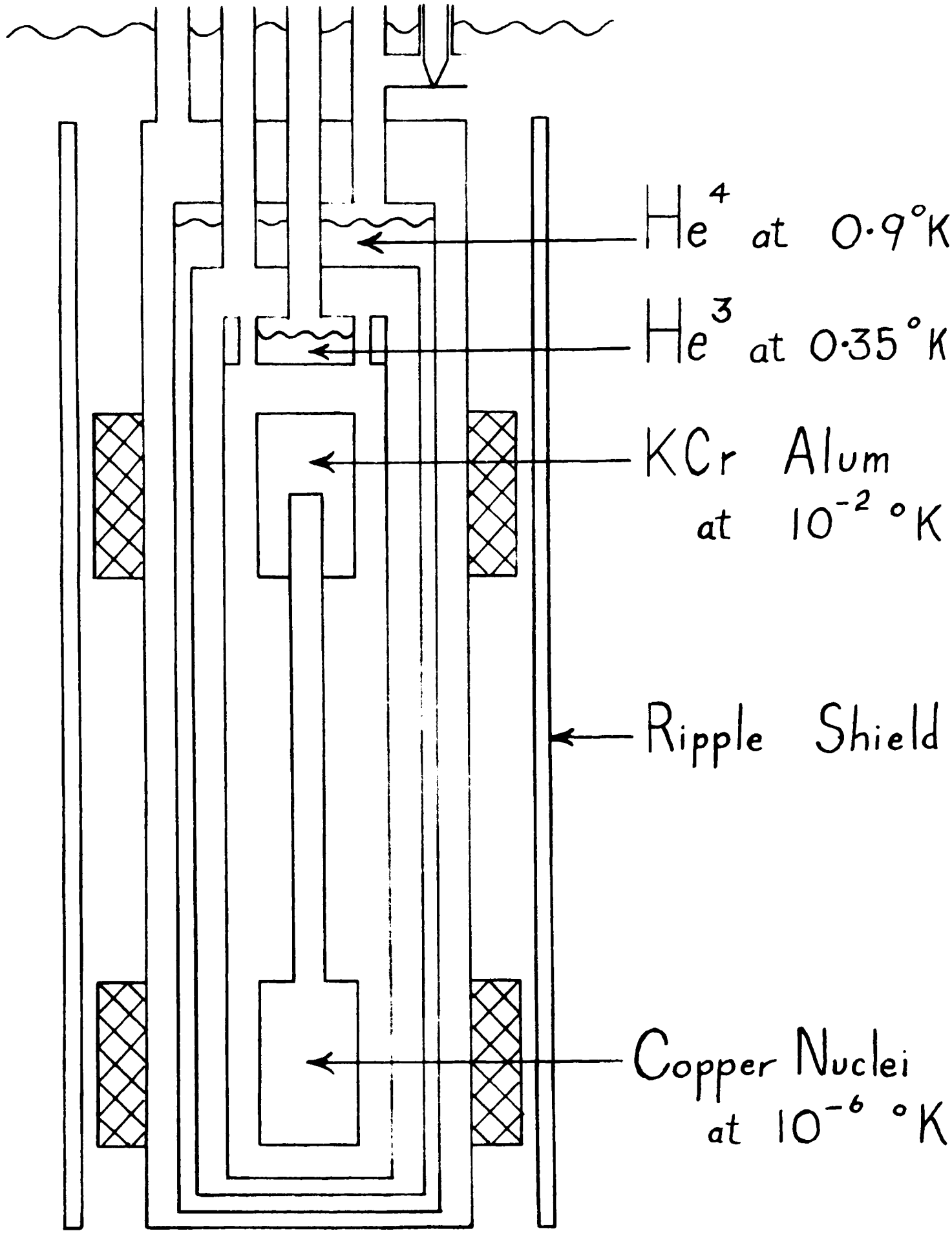
If a steady magnetic field is removed suddenly from this shield the field inside is governed by the equation

$$\frac{4\pi A}{R}\frac{dH}{dt} + H = 0$$

This shows that the field decays exponentially with a time constant of 0.17 seconds in this case, i.e. shorter than any time actually used for magnetizing or demagnetizing.

It should be pointed out that accidental tripping of the generator excitation, which causes the magnet current to drop to zero in about one second, will induce large currents in this shield and liberate heat into the liquid helium. A field of 30KØ dropping to zero in one second would induce sufficient heat to boil off ~ 100 ccs of liquid helium. However it is unlikely that heat transfer to the helium would be sufficiently fast to prevent the temperature of the shield from rising so increasing the resistance and choking back the induced current. Nevertheless in future apparatus where fields of 100KØ may be used with ripple shields of 50 cm^2 cross-sectional area this type of accident may cause trouble.

The ripple shield in these experiments was made very long to cover the whole of the cryostat in the tail of the dewar in order to reduce ripple heating in the metal helium vessel at 0.9°K and the He^3 capsule. Until this shield was employed it was not possible to pump the helium below 1°K when magnetizing.



SCHEMATIC VIEW OF CRYOSTAT

The Cryostat

The cryostat was of all metal construction and consisted of an outer jacket containing a vacuum space in which was suspended a double walled vessel containing helium at 0.9°K. Within this vessel was a vacuum space which could when necessary be filled with helium as exchange gas. Suspended within this space by a 3 mm german silver pumping tube was a He^3 capsule (see Chapter 3) with an attached shield which acted as a thermal shield to the specimen suspended within it. A schematic diagram of the cryostat is shown. The various removable jackets, the shields, and the cradle were made of thin walled telescopic brass tubing with hard soldered joints. The overall length of the cryostat was 60 cms and the clearances between jacket at different temperatures was ~ 1 mm. The small clearances were made possible by the use of fine tufnol star spacers at the bottom of the jackets.

The 0.9°K cryostat was initially filled, via a needle valve operated from above the apparatus, with liquid helium from the dewar. The valve was situated in 4.2°K helium so that there was no problem due to λ leaks. When the valve was closed the helium was pumped to 0.9°K with a 2" mercury diffusion pump and a rotary pump.

Attached to the outer jacket and situated in the liquid helium in the dewar were the two sets of mutual inductance coils for measuring the magnetic susceptibility of the paramagnetic heat sink and that of the nuclear specimen. The former was measured conventionally with a ballistic galvanometer. The mutual inductance coils for the nuclear specimen were larger, having 18,000 turns on the secondary of both the measuring coil and the identical compensator coil. The primaries were wound with extra turns at the ends in order to give a field of 35Ø per ampere uniformly over the nuclear specimen to within ± 2% yet falling off quickly beyond the specimen. This precaution was taken to ensure that any properties depending on the magnitude of the measuring field would not be obscured and at the same time reduce any signal from nuclei not in the specimen itself.

The High Power Solenoid

The iron free, water cooled, high power solenoid used in these experiments was designed by Daniels[12] for fields up to 40KØ at 1 megawatt. In fact it was never used above 700 kilowatts because of the danger of electrical and mechanical breakdown.

The coils in this solenoid were split into two groups. The upper group were used when magnetizing the

paramagnetic heat sink. When the nuclear stage was magnetized most of the current was passed through the lower group of coils but a small fraction (.0224) was fed in a reverse direction through the upper set in order to balance out the stray magnetic field acting on the paramagnetic heat sink to a value well below the internal field of potassium chrome alum (~ 300ø). The current for this balancing circuit was derived from the same generator as that for the lower coils via a water cooled resistor network and the current ratio for the two coil systems should in principle have remained constant at .0224. However the resistance of the coil system changed with the power being dissipated while the water cooled resistor network did not, so changing the current ratio. The resistors were adjusted to give correct balancing at the highest powers used and the field on the paramagnetic salt at lower powers was less than 30 ø. The change in temperature of the heat sink due to this small field was estimated to be less than 3%.

CHAPTER 3

The He^3 System

The upper stage of the nuclear cooling specimen, the paramagnetic heat sink, had to be magnetized with a field of 25KØ at 0.9°K to remove the electron spin entropy of the Cr^{+++} ions. So the specimen was situated within a cryostat at 0.9°K and exchange gas was used to transfer the heat of magnetization. After pumping off this gas the salt was demagnetized to the specific heat anomaly at .012°K. If the immediate surroundings had been allowed to remain at 0.9°K there would have been a heat leak ~ 100 ergs/min by conduction through the specimen supports to the heat sink and a heat leak ~ 20 ergs/min by the adsorption of gases onto the specimen from the walls at 0.9°K.

Such a large heat leak would have had two important consequences. Firstly the large conduction leak into the heat sink would have prevented nuclear magnetizations lasting more than about fifteen minutes, for after that time parts of the heat sink would have been at a

temperature well above .012°K. Secondly the large adsorption heat leak to the nuclear stage would have caused a large temperature drop across the junction of the metal and the paramagnetic salt ($\sim$ .005°K for 20 ergs/min). This would mean that the initial H/T ratio for nuclear magnetization would not have been known accurately.

If a successful heat switch experiment had been accomplished, i.e. if the whole of the nuclear stage had been thermally isolated at 10^{-6}°K, it would have been necessary to keep the adsorption heat leak to the nuclear stage to much less than 0.1 ergs/min because the total heat content would have been only $\sim$ 0.1 erg. So some method of reducing these heat influxes had to be used.

Spohr[9,10], in the earlier experiments, used a shield cooled by manganous ammonium sulphate to surround the specimen but unfortunately this prevented reliable measurement of the temperature of the heat sink.

This difficulty was overcome by the use of a shield cooled by pumping liquid He^3. When this shield was pumped from 0.9°K to 0.35°K the conduction heat leak was reduced by a factor $\sim$ 10. It was presumed (in the absence of any direct evidence) that at this temperature it acted as a good "getter" for any gases desorbed from the cryostat walls at 0.9°K. The temperature of the heat

sink could be found accurately by measurement of the susceptibility.

A liquid He^3 cryostat is a most convenient method for obtaining temperatures in the range 1°K to 0.3°K i.e. well below those obtainable using He^4. The vapour pressure of He^3 is ~ 10^2 times larger than that of He^4 at 1°K and at 0.5°K the ratio is ~ 10^4. It has the advantage that there is no λ film which gives rise to large evaporation rates in He^4 cryostats. Whereas it is difficult to pump He^4 below 50μ Hg it is quite easy to pump He^3 to 5μ Hg with a small pumping system.

Liquid He^3 has a heat of evaporation of~7 x 10^6 ergs/cm^3 at 0.35°K.[13] (By way of comparison it should be noted that demagnetized manganous ammonium sulphate can only absorb 5 x 10^4 ergs/cm^3 below this temperature.) About 10% of the liquid is evaporated in cooling the other 90% from 1°K to 0.35°K.

Several types of He^3 cryostat have been used but in general they all use the continuous refrigeration method[14,15] or the single shot condensation method.[14,16] The vapour pressure of He^3 at 1°K is 8.6 mm Hg and so it is quite easily condensed from a low pressure gas handling system or from the high pressure side of a diffusion or rotary pump (as in the continuous method). In this apparatus the single shot condensation was used.

The capsule itself was made of brass and heavily constructed because of the poor thermal conductivity of this material at 0.3 °K (~0.5 milliwatts/cm deg). A large surface area (13 cm^2) was allowed for attaching the shield, which surrounds the specimen, using Wood's metal. It was feared that the thermal resistance of this soldered joint would be high, the Wood's metal being superconducting and well below the transition point.

The shield would not have been satisfactory if made of thin brass tube for with the expecte. heat leaks the temperature difference between the top and bottom would have been ~0.1 °K. The use of copper tube of similar thickness would have introduced difficulties due to eddy current heating during the raising and lowering of the magnetic field even if it were slotted. As the thermal conductivity of pure copper is ~1000 times that of brass at these temperatures, it was decided to use thin brass tubing with a thin layer of copper on the outside surface. This was deposited by a bright copper plating process until it was 0.1 mm thick; the copper was not brittle and amorphous but shiny and soft. Assuming the thermal conductivity at 0.3 °K to be ~0.5 watts/cm deg and that all the heat leak into the capsule came from the lower end (the worst possible

case) the temperature drop along the shield would be $\sim 10^{-3}$°K.

An experiment was performed with an auxiliary carbon resistance thermometer situated at the very bottom of the shield. It was found that any temperature difference between this and the capsule was less than the experimental uncertainty of the thermometers ($\sim 10^{-2}$°K), so showing that the shield and the Wood's metal joint were, thermally, quite satisfactory.

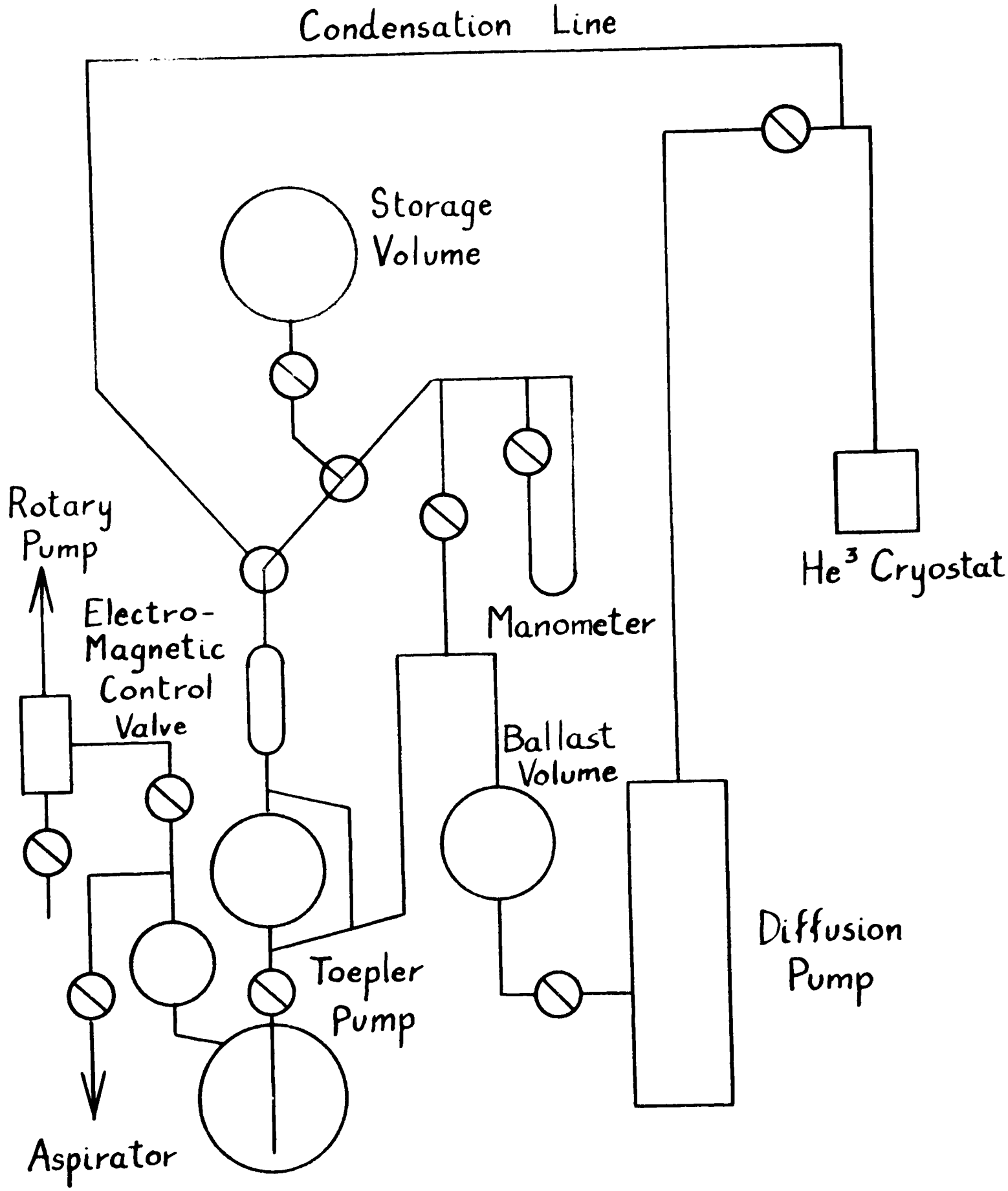
The temperature of the bottom of the shield was also measured during a typical nuclear demagnetization when 20KØ was reduced to zero in 30 seconds. Heavy induced currents were prevented by a longitudinal slit 0.2 mm wide running the whole length of the shield. However smaller eddy currents were set up in the walls which caused a slight rise in temperature to 0.5°K which fell back to 0.35°K in a few seconds. It was hoped that any desorption of gas from the shield due to these induced currents would come from the outside copper plated surface where most of the heat is produced and not from the inside brass surface. The capsule was suspended from the 0.9°K cryostat by the 3mm german silver pumping tube, 2.5 cms long. From the data of Berman[17] on the thermal conductivity of german silver at these temperatures it was calculated that the conduction heat leak

would be 15 ergs/second. A substantial reduction of this figure might be expected due to the heat capacity of the evaporating gas between 0.35°K and 0.9°K. There would also be a heat influx to the shield due to the "gettering" of desorbed helium from the walls at 0.9°K. This was estimated to be ~ 5 ergs/second (~1 erg/cm^2 sec).

In fact the steady state gas flow as measured over several hours (no other experiments being performed) showed that the heat leak was 20 ergs/second (0.1 cm^3 of gas at N.T.P. per minute). Under these conditions the He^3 would have lasted for twenty hours.

The temperature of the capsule was measured using a carbon resistance thermometer (Aerovox 470 ohm ½ watt) attached by low temperature varnish (General Electric 7031). The characteristics of these thermometers in the range down to 0.25°K have been extensively studied by other workers[18] and their reliability proved. In this experiment the actual temperature of the shield was not important as long as it was well below 0.5°K.

The resistance was measured using a potentiometer. Four 47 s.w.g. constantan wires were used for current and potential leads and these were taken down the inner vacuum space pumping line. The measuring current was 0.8 microamps, the resistance being ~ 5000 ohms.



The He^3 System

An experiment was performed using two carbon resistance thermometers on the He^3 capsule to find how the temperature of one varied with the power being dissipated in it by the measuring current; the temperature of the capsule remained virtually constant. From this experiment it could be estimated that the thermometer read 0.01°K too high at 0.35°K when the measuring current was 0.8 microamps. The apparent change of temperature with power dissipation was 5 deg/microwatt. Incorrect temperature measurements can easily be made by using too large a measuring current.

In another experiment the temperature of the He^3 capsule was measured as a function of extra power input above that due to conduction, etc. It was found that the temperature rose from 0.37°K to 0.43°K at 50 ergs/second and 0.47°K at 100 ergs/second.

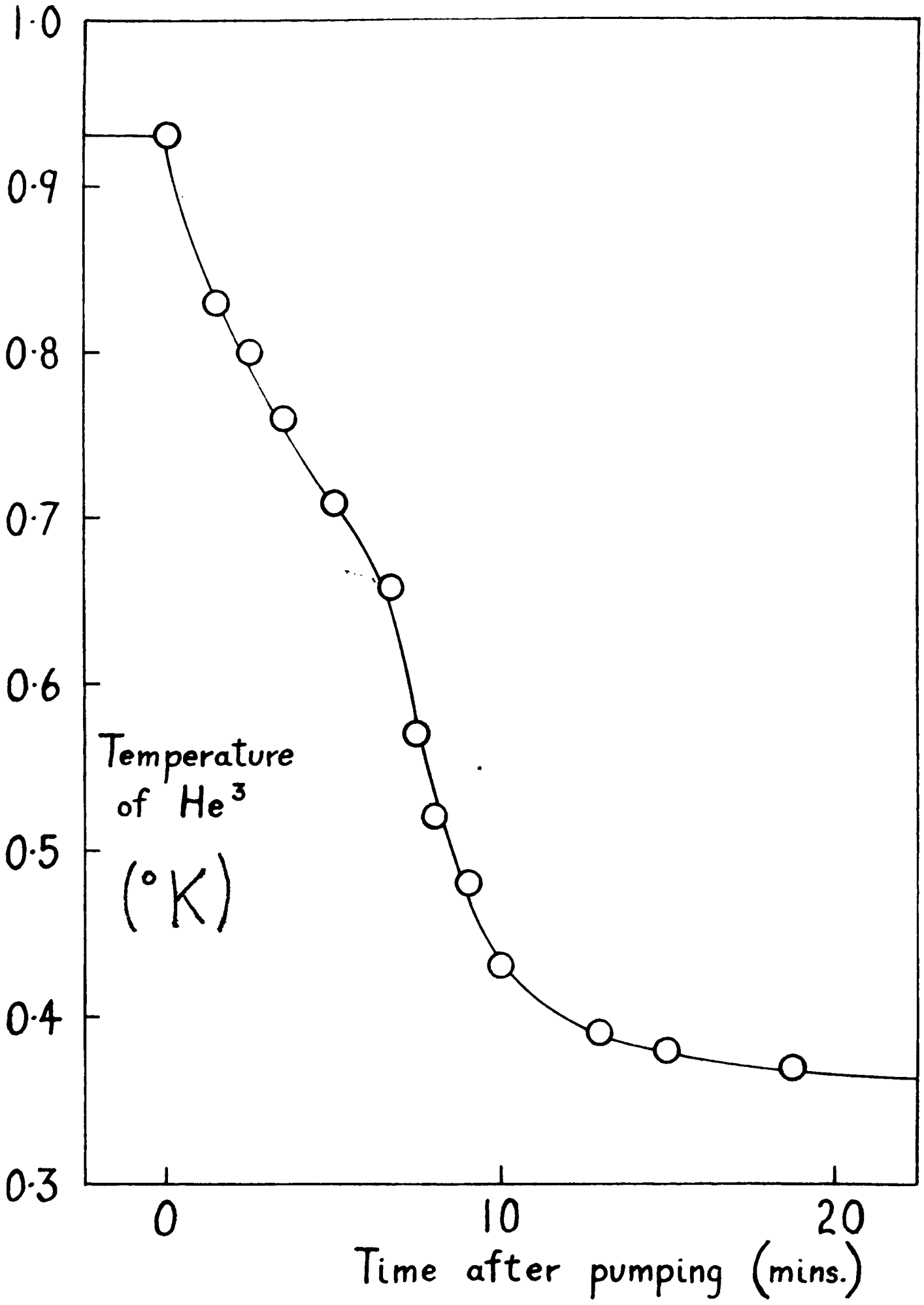
A diagram of the He^3 gas handling system is shown. It was a closed circuit system for single shot condensation and pumping. In the storage volume was kept 150 cm^3 (at N.T.P.) of He^3 gas at a pressure of about 10 cms Hg, the pressure being measured by the capillary manometer. The gas was fed via the condensation line and pumping tube to the capsule which was at 0.9°K. The gas condensed into the capsule until the

capillary manometer read 5 mm Hg (the vapour pressure at 0.9°K), approximately 80% of the gas being in the form of liquid, occupying 0.2 cm^3.

The heat of magnetization of the heat sink was removed by the 0.9°K temperature bath and not by the He^3. The He^3 was not pumped until the heat sink was being demagnetized, the respective temperatures being reduced from 0.9°K to 0.35°K and .012°K simultaneously.

The He^3 was pumped from the capsule by a 1" diameter mercury diffusion pump and an automatic Toepler pump back into the storage volume. The diffusion pump needed a backing pressure of less than 4 mm Hg and as 10% of the liquid as well as the gas in the pumping tubes had to be removed it took about five minutes for the Toepler pump to reduce the pressure sufficiently for the diffusion pump to come into operation. The overall time to pump to 0.35°K was about ten minutes.

The Toepler pump was of the mercury in glass type with a displacement of 350 cm^3. The cycling period was 45 seconds giving a pumping speed ~ 500 cm^3/min. This was quite satisfactory for dealing with the normal evaporation rate but was responsible for the initial time taken to reduce the temperature to 0.35°K.


1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
Temperature of He³ (°K)
0
10
20
Time after pumping (mins.)

CHAPTER 4

The Measurement of Nuclear Susceptibility

In the experiments of Kurti et al[9] in 1956 the nuclear susceptibility was measured using a ballistic galvanometer system with large susceptibility coils having secondaries with 15,000 turns and with a measuring field of 8 oersted. Before measurements could be taken after a demagnetization a moveable ripple shield situated in the liquid hydrogen dewar had to be lifted away from the susceptibility coils to avoid large eddy current kicks in the galvanometer when the measuring field was reversed. It was not until 15 seconds after demagnetization that the first measurements could be made and then only once every six or seven seconds. The susceptibility decayed to a value below the threshold of observability in 60 seconds, the measurements on the average being ~ 10 times larger than the probable error. Due to the reliance on manual dexterity and human judgement of the galvanometer

deflections and the time the method was unavoidably prone to error.

It was later shown that the measuring field used in these experiments was nearly three times greater than the internal field of the nuclear spins in copper metal. In this type of experiment it is desirable to have the measuring field very much less than the internal field. A reduction of the measuring field by a factor 10 would have reduced the size of the deflection to a magnitude comparable to residual deflections due to fluctuating thermal e.m.f.s, etc.

The decay of the nuclear susceptibility could have been due to the conduction electron-nuclear spin relaxation process or alternatively, if the conduction electrons were at the same temperature as the spin system, it could have been controlled by the rate at which heat flowed into nuclear stage. In the former case an exponential decay would be expected but in the latter a linear decay, for a constant heat leak, due to the $1/T^2$ form of the specific heat. The results of the 1956 experiments were not sufficiently accurate to enable a firm conclusion to be drawn though it was suspected that the conduction electrons did cool with the nuclei and

that the subsequent warm up was controlled by the rate at which heat entered the nuclear stage from the paramagnetic heat sink.

For these new experiments it was decided that a better susceptibility measuring device would have to be devised. More sensitivity, to enable smaller measuring fields to be used, and great precision were required. In order that the form of the decay could be studied many more measurements during each decay were necessary beginning about two seconds after demagnetization rather than fifteen seconds. This would also allow more accurate extrapolation to the instant of demagnetization.

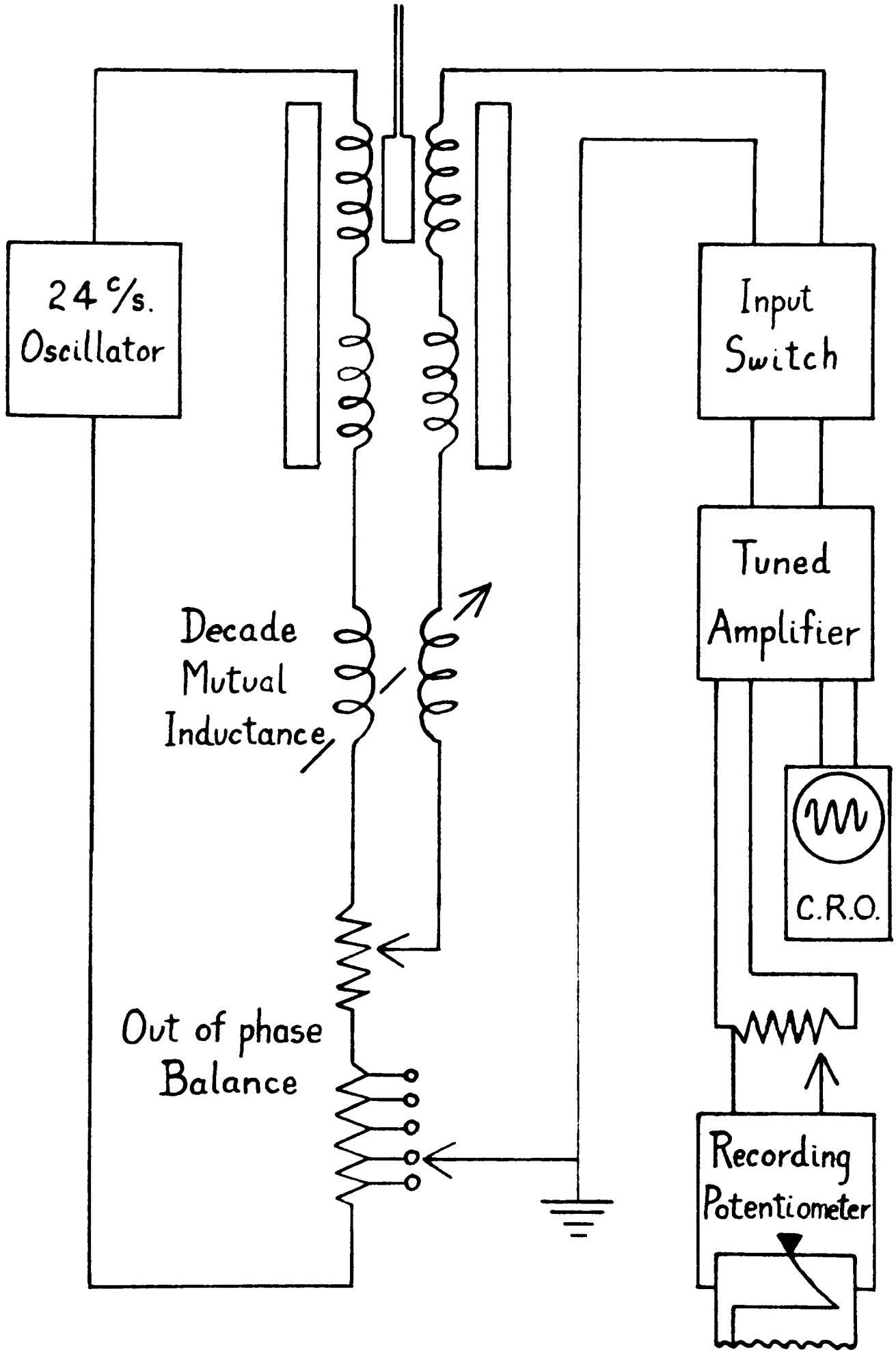
One of the most undesirable features of the previous apparatus was the moveable ripple shield. It took too much time to move after a demagnetization and caused considerable vibration of the cryostat. It frequently became stuck in the wrong position.

It was quite well established that there was no prospect of using a better ballistic system (such as a ballistic galvanometer amplifier) with the ripple shield in situ. No satisfactory way of balancing the powerful eddy current kicks has been found. Even if this were possible the ballistic system although reliable is very slow.

An A.C. method of susceptibility measurement devised so that the ripple shield could remain in place was the obvious suggestion but this has several disadvantages.

Firstly a continuous alternating magnetic field on the specimen causes induction heating. The use of measuring fields ~ 1 oersted at ~ 100 c/s (as used in A.C. bridges for measuring paramagnetic salts having volumetric susceptibilities of the same order of magnitude as that of copper nuclei in copper at a few microdegrees K) would completely warm up the spin system in ~ 1 second. The rate of heating is proportional to $\omega^2 H^2$ but the signal induced in a mutual inductance secondary by a paramagnetic specimen is proportional to ωH, so that the use of low frequencies is advantageous.

The second difficulty is that of balancing the bridge as the signal decays to obtain measurements. If this were done manually it is likely to give even fewer measurements than the ballistic method. It could in principle be done by a feed-back method but due to difficulties with phase relationships (see below) this idea was not pursued.



Recording A.C. Bridge

Thirdly there is the difficulty due to the presence of metal in the cryostat. The use of metal in a conventional cryostat having an A.C. bridge is to be avoided for this causes the χ' and χ'' components of susceptibility to be shifted in phase with respect to the in phase and out of phase balance controls (see below). This apparatus was entirely of metal and the mutual inductance coils were to be surrounded by a thick copper ripple shield at 4.2°K.

A susceptibility measuring system was devised which operated in the presence of this metal and which gave a continuous pen recording of the susceptibility as a function of time, with the absolute minimum of human effort and consequent errors, from within two seconds of demagnetization.

A schematic diagram of the bridge is shown. A low frequency (24 c/s) oscillator fed the primary with a current ~ 10 milliamps giving a measuring field at the specimen ~ .03 oersted. The bridge consisted of similar measuring and compensating mutual inductances within the dewar, and an external decade mutual inductance and variable resistor (~ 0.1 ohm). The latter was common to primary and secondary circuits as shown.

The signal from the secondary was amplified by a 24 c/s tuned amplifier by a factor 6×10^4 and displayed on a C.R.O. The rectified signal was smoothed and fed to a continuous strip chart recording potentiometer. A switch was fitted between the bridge and the amplifier and this was actuated by the high powered solenoid, being closed only when the solenoid was fully lowered after a demagnetization. This prevented the amplifier seeing the large transients due to the removal of the strong magnetic field, which would have made the amplifier inoperative for several seconds.

The amplifier was of the type originally described by Sturtevant[19] and later improved by Brown[20] as a thermocouple amplifier. It had two directly coupled twin-T amplifiers in series, each with a gain ~ 250. They were stagger tuned to give a slightly flattened frequency responce but the overall Q could be made as high as 100. In practice it was adjusted to give a Q of about 70.

These amplifiers were very unstable and adjustment for optimum performance was not easy. They were prone to burst into oscillation as valve or component characteristics changed and for that reason were run continuously. Fluctuations in mains voltages such as those produced by the adjustment of the loading of heavy electrical plant

in the same building, thunder storms, desk calculating machines (to name a few of the known ones) caused the amplifier to burst momentarily into oscillation. If the amplifier was adjusted with Q at about 70 it took ~ 1 second for these oscillations to die out. These bursts of oscillation sometimes occured as frequently as once a second. More valuable experimental time was lost in this way than any other. A modern commercial version of this amplifier acquired after these experiments were performed does not show this defect.

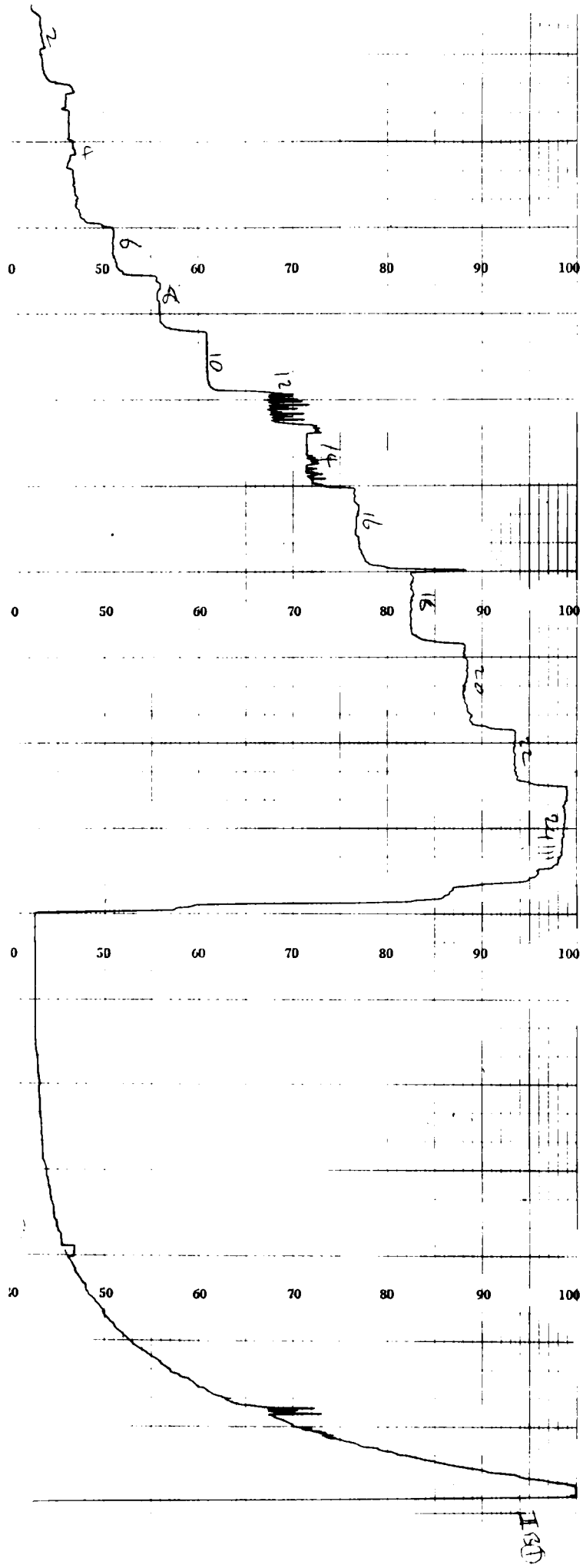
The output impedance of the secondary circuit at 24 c/s was 1500 ohms and it would probably have been advantageous to match this to the amplifier with a high quality shielded transformer. It would be necessary to use a transformer of high inductance at this low frequency and magnetic shielding would have been essential. This would have increased the signal strength with respect to the noise being generated within the amplifier. However as the amplifier performed well enough for these experiments with direct coupling and as a suitable transformer was not immediately available direct coupling was used.

The output from the amplifier was displayed on a C.R.O. so that the bridge could be balanced. The output was also fed via a cathode follower to a thermionic diode rectifier and after smoothing fed to the recorder.

The recorder was a Honeywell-Brown instrument with a span of 1 millivolt and a pen speed of 1 second for full scale. The chart speed was four inches per minute.

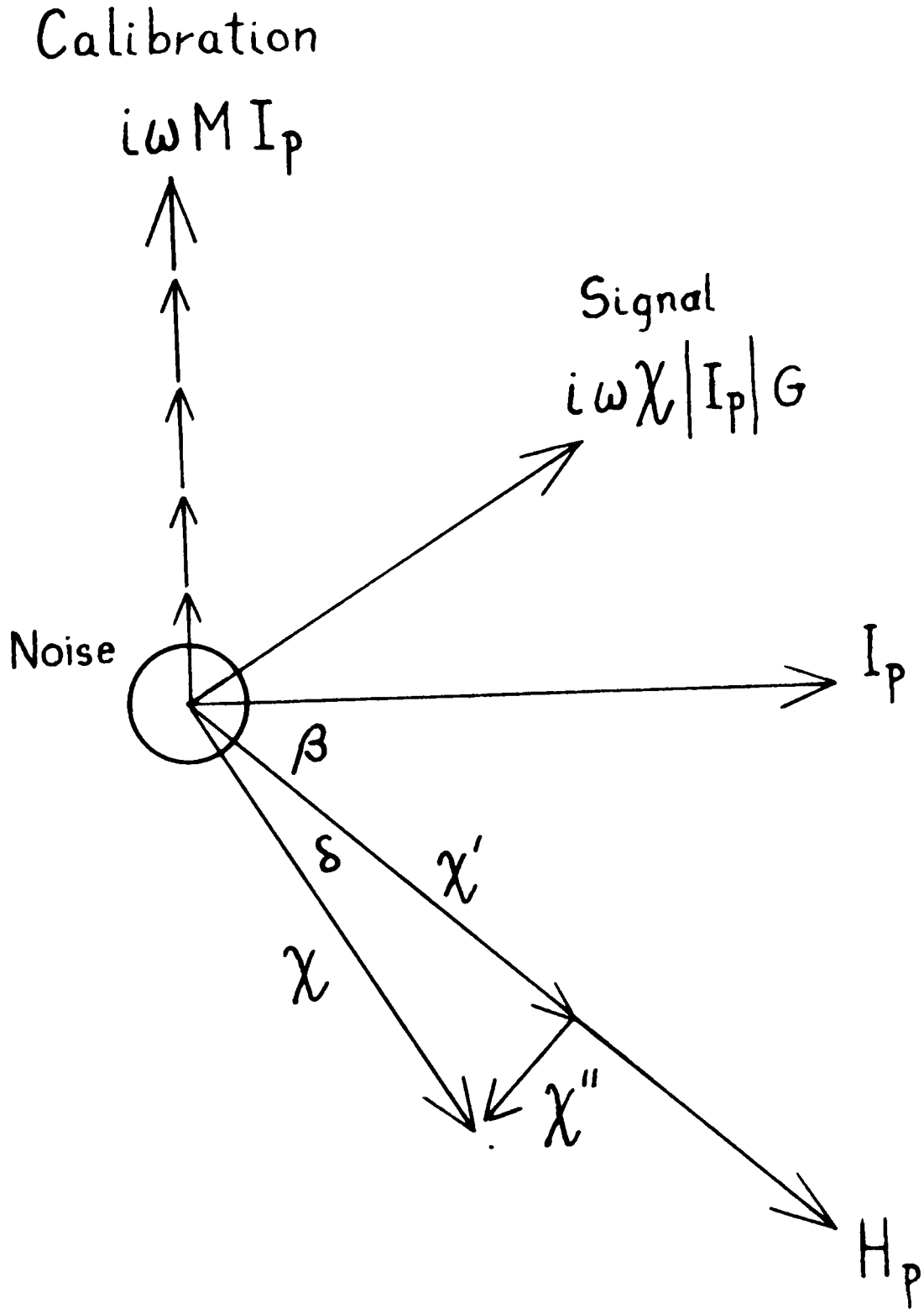
The time constant of the amplifier was ~ 0.5 seconds with $Q \approx 70$. At higher values of Q the time constant became too large and showed a peculiarity in that the output would "bounce" in response to a change in the input signal. The optimum adjustment of recorder and amplifier gave an overall response time a little less than one second.

Copper metal has a nuclear Curie constant of 4.5×10^{-3} emu/cm^3 deg and it was expected that a temperature of the order 10^{-5}°K would be reached. The susceptibility at this temperature would be 4.5×10^{-3} emu/cm^3. The specimen was long and thin having a cross sectional area ~ 1 cm^2. The number of turns on the secondary of the mutual inductance was 18,000 and the angular frequency of the measuring field was $\omega = 150$. From this data it could be estimated that with a measuring field of .03 oersted the signal strength would be ~ 50 microvolts i.e. 10 times greater than the internal noise of the amplifier. In fact temperatures of ~ 10^{-6}°K were reached thus enabling smaller specimens to be used.


0
50
60
70
80
90
100
2
4
6
8
10
12
14
16
18
20
22
24
0
50
60
70
80
90
100
0
50
60
70
80
90
100

The bridge was used in the following manner. When the heat sink and the copper nuclear stage were at .01 °K and the He^3 shield was at 0.35 °K the bridge was balanced using the C.R.O. to detect the null. The nuclear susceptibility at this temperature is so small that it was negligible. When the nuclear stage had been demagnetized to a very low temperature where the susceptibility was high there was an off balance signal which decayed back to zero as the spins warmed up. This signal after amplification and detection was recorded as a measure of the nuclear susceptibility.

After this signal had decayed to a very small value (after 100 seconds the signal was well below the noise) the amplifier and recorder were calibrated by altering the decade mutual inductance in steps from the balance condition up to the maximum size of the signal. A reproduction of an actual trace is shown and the calibration steps can be seen. By reading across from the steps to the decay curve the times at which the nuclear signal corresponded to a given value of mutual inductance could be found. In this way the size of the signal was found during the warming up by reference to a vector not in phase with the original vector. A vector diagram will make this more clear.



Nuclear Susceptibility Bridge.

Vector Diagram.

Let the reference vector be Ip, the primary current. The field on the nuclear spin system is Hp lagging by some large angle β (see Chapter 2). The susceptibility is at some small angle δ to this vector being composed of the χ' and χ'' components. The signal from this susceptibility is $i\omega\chi |I_p| G$, where G is a geometrical factor depending upon the mutual inductance coils.

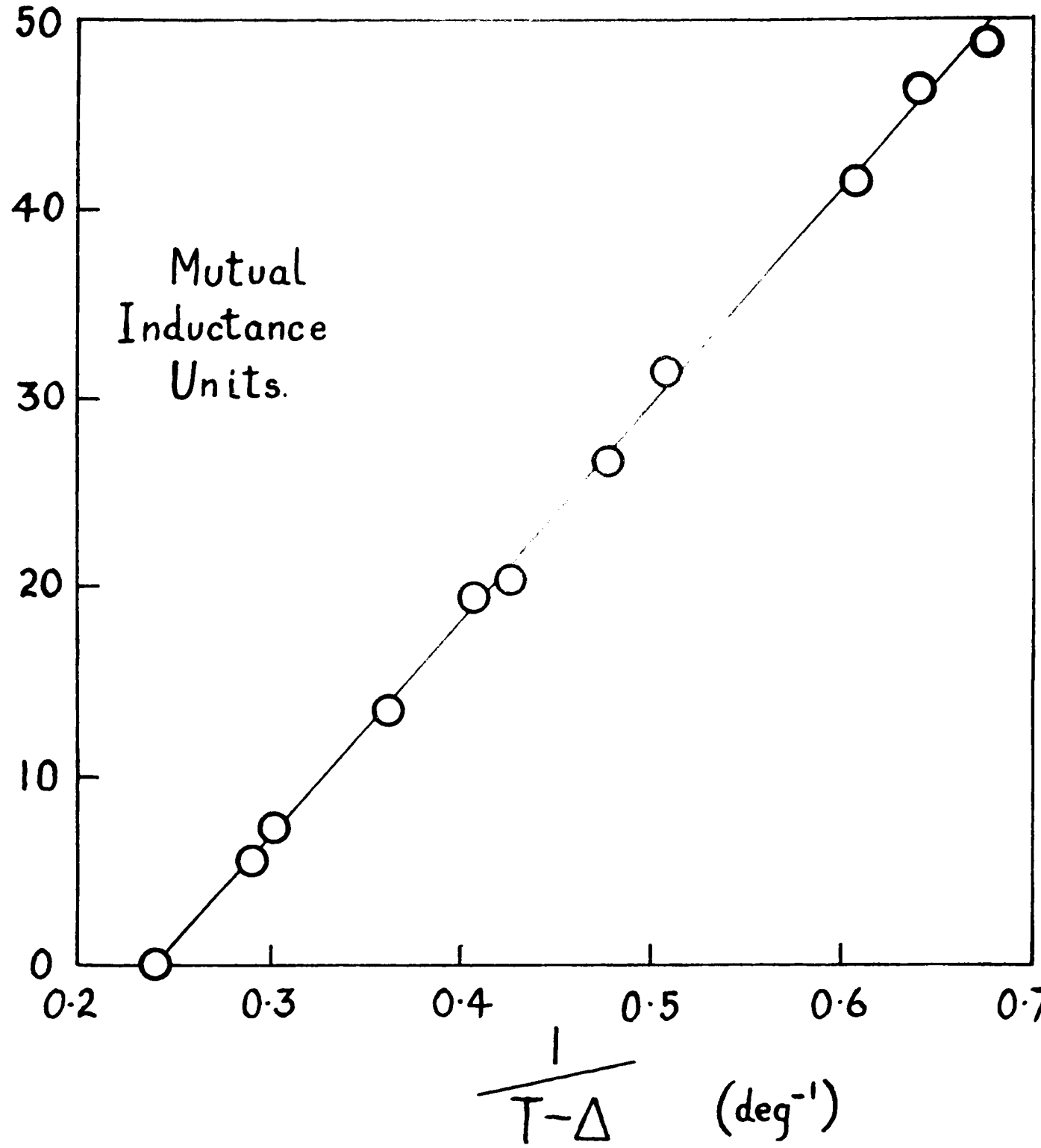
It is the magnitude of this vector which was recorded by the amplifier and recorder. When it had fallen to zero the amplifier and recorder were calibrated in steps by the external decade mutual inducance M which gave rise to the vector $i\omega IpM$. If it had been attempted to balance the nuclear signal as it decayed it would have been necessary to use both external balance controls. This method relies on the fact that the amplifier is not phase sensitive. The noise can be represented by a circle at the origin of the vector diagram and as the phase was random affected signal and calibration equally.

Nuclear Curie constants are so small that it was impossible to calibrate the mutual inductance bridge by varying the temperature of the nuclear stage in the region of 10^{-2}°K. As there is a factor of 10^4 in the susceptibility at 10^{-2}°K and 10^{-6}°K this can be well understood. Apart from considerations of stability and

sensitivity of the bridge the nuclear susceptibility would be ~ 100 time smaller than that due to electron paramagnetic impurities and pick up from the paramagnetic heat sink.

The absolute calibration of the nuclear susceptibility coils was made using a pill of manganous ammonium sulphate of the same shape and size as the nuclear stage and placed in exactly the same position as that normally occupied by the copper. The volumetric susceptibility of this salt in the helium range is of the same order of magnitude as that of copper in the micro-degree range.

By balancing the bridge when the salt was at 4°K and then reducing the temperature to various values in the range 4°K to 1°K a signal was produced due to the increase in susceptibility. This signal was equated to mutual inductance units by allowing the salt to warm back to 4°K (balance) and then producing signals of equal magnitude with the decade mutual inductance. In this way a calibration equation relating mutual inducance units and temperature for manganous ammonium sulphate was found. Knowing the Curie constants for the salt and the copper a similar equation was derived relating the nuclear signal (in mutual inductance units) to the temperature.



Susceptibility Calibration Curve
for Manganous Ammonium Sulphate

In this way the calibration equation for the copper specimen containing 0.68 gram atoms was found to be

$$T - \Delta_1 = \frac{150}{M} \text{ microdegrees Kelvin}$$

and for the smaller specimen containing .17 gram atoms

$$T - \Delta_2 = \frac{39}{M} \text{ microdegrees Kelvin}$$

the units of M being the units of the decade box (1.70 microhenries). The small difference in the calibration constant per gram atom is due to a correction made for pick up from the lower end of the thermal link.

Δ_1 and Δ_2 are the corrections due to the internal field of the specimen and the demagnetization due to the shape of the specimen. Calculation shows that $\Delta_1 = 0.14$ microdegrees K and that $\Delta_2 = 0.15$ microdegrees K, assuming a Lorentz type internal field. This is, however, a small correction for all temperatures actually measured.

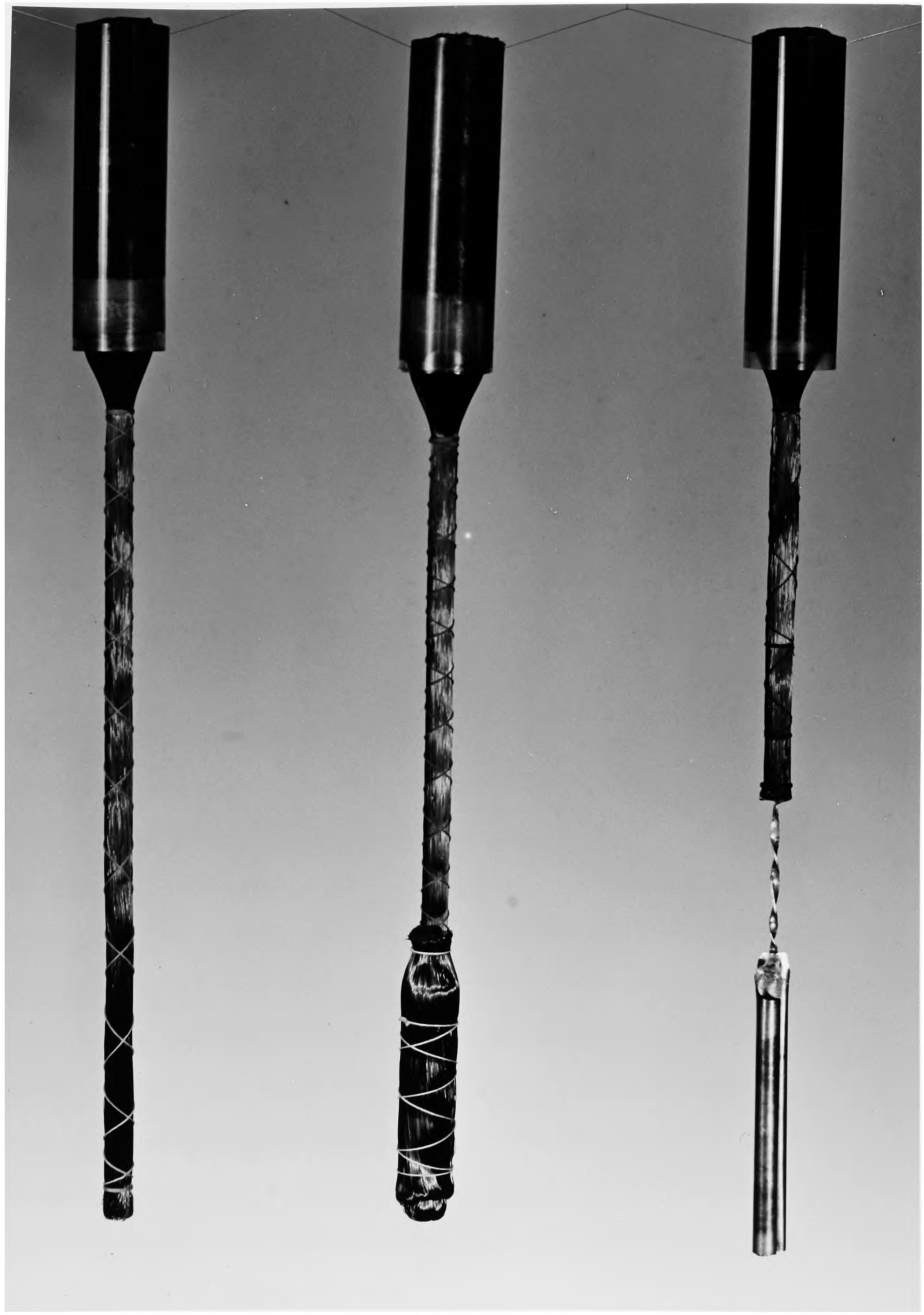
CHAPTER 5

Preliminary Nuclear Cooling Experiments

The Specimen and Supports

The construction of the specimen for two stage demagnetizations with copper metal as the second stage was based on the method due to Spohr[10] which was developed from the fin technique using glycerol slurries due to Robinson.[5]

The upper stage (the "heat sink") was composed of finely ground potassium chromium alum, produced by mechanical crushing and sieving, mixed into a slurry with a solution composed of 70% glycerol and 30% water. This was held in a thin perspex case of 23 mm diameter and 80 mm length. Within this slurry were embedded 1640 No. 40 s.w.g. single enamel covered copper wires. The slurry was introduced into the case and between the wires by means of a hypodermic syringe using a filtration technique. The top stage contained 27 grams of potassium chromium alum, i.e. .055 gram ions.



The purpose of the glycerol-water-salt slurry was to form a glass-like substance at low temperatures to obtain better thermal contact between the wires and the crystals. The composition of the slurry was very important. With 30% of water the slurry was quite effective and even 40% of water was tolerable but 50% mixtures formed a micro-crystalline substance with very poor thermal properties. A mixture using less than 30% of water was too viscous for the filtration technique. The area of contact between wires and slurry was 400 cm^2.

The copper wires embedded in the paramagnetic slurry formed the link to the nuclear stage and also the nuclear stage itself. The centre of the nuclear stage was 23 cms from the centre of the heat sink and was formed by folding the wires four times to make a bundle 65 mm long and 14 mm diameter. It contained .68 gram atoms of copper and is shown in the centre of the photograph of specimens. Due to the abrupt falling off of the primary measuring field, the sharp falling off of the magnetizing field and the fall off of the sensitivity of the secondary coils it was calculated that the signal from the thermal link during a nuclear cooling was ~ 1% of that from the nuclear stage itself. Allowance for this was made in the calibration equation (Chapter 4).

In other experiments the wires were not folded and the nuclear stage consisted of the single bundle of 1640 wires containing .17 gram atoms of copper as shown on the left of the photograph. In this case the pick-up from that portion of the bundle beyond the lower 64 mm was 4% of the total signal. Allowance was also made for this in the calibration equation.

In the earlier experiments the specimen was supported by a framework of fine glass rods and tubes which held the perspex case. This followed the example of the experiments of Kurti et al.[9] In later experiments this was replaced by a cotton fibre support which held the perspex case within the cradle (as shown in the photograph) which fitted inside the He^3 shield. This support was less fragile and more easily assembled.

The heat leak into the potassium chrome alum was found to vary approximately as $T^{2.4}$ where T was the temperature of the He^3 shield (in the range 0.35°K to 1.6°K) when using the glass supports which suggests that the heat was largely by conduction. With the cotton fibre supports the heat leak increased very little in this range and this leak was attributed to vibration heating. This is in agreement with other work which has shown that the use

of stiff glass supports reduces the vibration heating but due to their greater cross sectional area, compared with thin fibres, increases the conduction heating. Both types of support gave a heat leak ~ 40 ergs/min when the He^3 shield was at 0.35°K.

This heat leak was not small but could be tolerated for experiments requiring that the heat sink should remain at .012°K for up to two hours. In fact the longest magnetization time used was one hour.

Experimental Procedure

The procedure for precooling and transferring liquid helium into the Dewar has been described in Chapter 2.

The needle valve was opened and the inner cryostat, initially evacuated, filled with liquid helium from the Dewar. The outer vacuum space was pumped to ~ 10^{-5} mm Hg and the inner vacuum space filled with helium exchange gas at .03 mm Hg. On closing the helium valve the inner cryostat was pumped from 4.2°K to 1.5°K with a rotary oil pump. During this process ballistic measurements were made of the susceptibility of the potassium chromium alum heat sink at temperatures determined by the helium vapour pressure. These measurements enable a calibration equation to be derived which allowed the temperatures

obtained after demagnetization of the heat sink to be measured. The data of Daniels and Kurti[21] were used to calculate thermodynamic properties of the heat sink and to relate T and T*.

The He^3 gas was then allowed access to the capsule. The temperature of the inner cryostat was reduced to 0.9°K using a mercury diffusion pump, and the He^3 condensed in the capsule, the vapour pressure falling to 6 mm Hg. Under these conditions the pressure in the inner vacuum space was ~ 10^{-4} mm Hg.

The solenoid was raised and the paramagnetic heat sink magnetized, the field being taken up to 22 kØ in about four minutes. During this process the specimen warmed up and the exchange gas pressure rose to ~ 10^{-2} mm Hg. The He^3 vapour pressure measuring the temperature of the inner cryostat rose to ~ 20 mm Hg, corresponding to 1.2°K.

Within ten minutes this fell back to 6 mm Hg and the exchange gas pressure to ~ 5 x 10^{-4} mm Hg. The exchange gas was then pumped away from the inner vacuum space for ten minutes until the pressure was reduced to ~ 10^{-4} mm Hg.

The heat sink was then demagnetized to zero field, the temperature falling to .012°K, (slowly, in order to

absorb the heat of the conduction electrons in the copper as reversibly as possible). The He^3 was pumped from 0.9°K to 0.35°K during the demagnetization. The heat sink was usually brought to a temperature just below the susceptibility maximum, i.e. just below the large specific heat anomaly.

With the magnet fully lowered so that the switch between the bridge and the amplifier was closed, the nuclear susceptibility bridge was balanced. This could be done to one or two tenths of a mutual inductance unit under the best conditions. The primary current was set at the required value and the sensitivity of the recorder adjusted so that the expected signal would utilise most of the scale.

The magnet was raised, the switch opening, and the nuclear stage was magnetized. This was done slowly so that the magnetization should be performed as reversibly as possible. After sufficient time had been allowed for the nuclei to come to the temperature of the heat sink the field was reduced to zero.

The field on the nuclei was reduced to zero in 30 seconds in almost all cases. By control of the generator excitation the field was reduced to 300 oersted as linearly as possible in 28 seconds. At 30 seconds precisely the

solenoid was dropped away from the specimen, the switch to the amplifier closing at about 31 seconds. The recorder, which was synchronised with the laboratory clock would then move across the chart and record the decay of nuclear susceptibility. Useful results were usually obtained from 3 seconds after demagnetization; before this the recorder was recovering from the initial transient. When the signal had decayed well below the noise the whole system was immediately calibrated (as described in Chapter 4).

Preliminary Experiments

The first nuclear cooling experiments performed on this apparatus were with a copper specimen having 0.68 gram atoms in the nuclear stage. The nuclear susceptibilities were at first observed using the ballistic method used by Kurti et al[9] in the 1956 experiments.

Experience soon showed this to be unsatisfactory and the A.C. method was devised (Chapter 4). This was at first used with a critically damped galvanometer and readings were taken every three seconds using a metronome. However the visual and aural coordination of the experimenters was not sufficiently accurate and so a recording potentiometer was obtained.

Magnetizations were performed with fields of up to 15.2KØ with the heat sink at .012°K. The field was increased to the desired magnitude over a period of one to five minutes and allowed to remain at that strength for a period up to 60 minutes. The times allowed for these processes will be discussed later.

It was found that the nuclear susceptibility decayed exponentially and not linearly. When the decay curves were plotted as a function of time on logarithmic paper they gave lines which were almost straight and which could be extrapolated to the instant of demagnetization quite accurately to give M_o the mutual inductance at this instant. The slope of the decay curves on this graph gave the relaxation time constant τ which was usually in the range 10-25 seconds.

The experiments were not very consistent but it could be seen that the intercepts M_o were proportional to H_i, the initial field, for fields up to about 8KØ but beyond this the proportionality broke down and M_o tended towards a limit.

This had two possible explanations, the first being that the entrory of the copper nuclei in the temperature range attained was not of the form

$$S/R = \log(2I + 1) - \frac{b}{T^2}$$

as would be expected from the simple theory of a non-ideal paramagnetic at temperatures well above that associated with the splitting of the energy levels. This would imply that some cooperative phenomenon was causing the entropy to fall faster than that predicted by the previous formula. However as only ~ 0.25% of the nuclear spin entropy was removed in these experiments this would seem rather unlikely.

The second more mundane and probable reason for M_o not being a linear function of H_1 was that the initial temperature of the spin system before demagnetization from the higher fields was not the same as the temperature before demagnetization from the lower fields. Unfortunately in this type of experiment the initial spin temperature before demagnetization cannot be measured. It can only be inferred from circumstantial evidence such as the temperature of the heat sink before and after the nuclear magnetization and demagnetization, calculation using data (often of doubtful value at these temperatures) on heat conductivities, thermal capacities, heat transfer coefficients, etc., and such data as the linearity of the M_o with H_1 (which is open to the criticism that there is no direct evidence that the entropy has the simple form $(2I + 1) - b/T^2$ quoted above). The relaxation time

also gives an indication of the temperature as will be shown.

Experiments were performed over some weeks with this specimen and it was found that the values of M_o became lower and that the relaxation became somewhat faster. This was finally attributed to deterioration of the potassium chromium alum slurry even through this was kept almost continuously at 90°K between experiments.

The deterioration seemed to be due to removal of water molecules from the Cr^{+++} ions by the glycerol used in the slurry, for when a pure glycerol water solution was forced through the perspex case under pressure the solution dripping through was found to be bright green in colour and not the usual faint pink. This indicated that the Cr^{+++} ions had lost one or more of their six water molecules with which they are usually surrounded.

A fresh but otherwise identical specimen gave results with exactly the same behaviour as the first results of the original specimen, i.e. M_o was not proportional to H_i above 8KØ.

The heat capacity of the heat sink, which contained .055 gram ions of potassium chromium alum, after demagnetization from 22 KØ and 0.9°K to 0.12°K up to the point at which the temperature begins to rise above that

of the specific heat anomaly at .012°K was about 1.5×10^4 ergs. The heat of nuclear magnetization for this specimen with a field of 15.2KØ at .012°K was 2×10^3 ergs. This figure is calculated using the nuclear Curie constant and is for reversible magnetization. If the magnetization were adiabatic followed by cooling to .012°K in the field the heat of magnetization would have been $\sim 4 \times 10^3$ ergs but in practice the field was applied at such a rate that the situation would have been closer to the isothermal case. Heat leaks into the potassium chromium alum over a period of an hour were ~ 2000 ergs. So the total heat input to the heat sink after magnetization at 15.2 KØ for an hour would be ~ 4000 ergs. So it seemed that the temperature of the heat sink should not rise above .012°K during this experiment.

Measurement of the temperature of the heat sink after such an experiment showed, at first sight, that the temperature was indeed .012°K.

It was thought that perhaps not enough time had been allowed for the spin system to come to the temperature of the sink. Calculations using the data of Spohr[10] on the heat transfer at the copper-slurry boundary showed that with a field of 15.2KØ the spin temperature should fall to within $\sim 10^{-3}$°K of that of the heat sink within thirty

minutes. Experiments seemed to support this for there was little increase in M_o for magnetization times greater than 20 minutes.

The possibility of the spins coming to some steady temperature above that of the heat sink due to some steady heat input depending on the magnitude of the field had little to recommend it for the only conceivable phenomenon that could cause this was ripple heating. This had been reduced by the ripple shield to a value far smaller than could account for this.

Experiments were performed to find how reproducible the nuclear decay curves were for demagnetizations from 7.6KØ with the heat sink at .012°K. As the heat of nuclear magnetization was much less than the heat capacity of the heat sink several nuclear magnetizations were possible before it was necessary to remagnetize the top stage. At first the reproducibility was poor. A scatter of 20% in M_o and between 15 and 25 seconds was usual.

As the technique of reducing and removing the field was improved it became clear that the first nuclear demagnetization after cooling the heat sink usually gave the highest value of M_o and τ. Initially this was thought to be due to the fact that the temperature of the sink was slightly below .012°K for the first nuclear cooling.

However it was suspected that there might be temperature inhomogeneities within the heat sink. The top stage after a nuclear demagnetization experiment was remagnetized very slowly (~ 5 minutes) to 5KØ which raised the temperature to ~ o.25°K. The field was kept at this value for ~ 5 minutes and then slowly reduced to zero. At all times the He^3 was pumped below 0.4°K. The specimen would not have become warm enough to liberate exchange gas from its surface.

After this reversible magnetization and demagnetization it was found that the overall susceptibility of the salt had fallen considerably, apparently indicating that hot spots had been evened out by raising the temperature to a region where the thermal conductivity of the slurry was much higher. These hot spots could have been regions in the immediate neighbourhood of each embedded wire.

An hypothesis of this sort could also explain why M_o did not increase linearly with H_i above 8KØ as might be expected. The heat of magnetization for fields above this value might have been sufficiently great to heat that part of the slurry localised about each wire to a temperature above that of the specific heat anomaly at .012°K.

The tentative conclusions drawn from these preliminary experiments were:

1. That as the nuclear susceptibility decay was almost exponential and not linear (the small deviation from exponential will be discussed later) it was most probable that the conduction electrons were not cooled to micro-degree temperatures as had previously been supposed and that the warming up of the spins was governed by the nuclear spin-conduction electron relaxator process, the conduction electrons being at the temperature of the heat sink. It was known that this relaxation process in copper ought, on the basis of the theories of nuclear relaxation in metals, to be of the order of magnitude of those found in these experiments. In fact a straightforward calculation on the basis of the Korringa[8] theory which relates this relaxation time and the size of the Knight shift predicted a relaxation time of 100 seconds for conduction electron temperatures of .012. It was not known at this stage whether the smaller relaxation time actually measured (~ 20 seconds) was due to the fact that the conduction electrons were at a temperature greater than the sink or whether it was due to the presence of electron paramagnetic impurities in the metal.

2. That the thermal contact between the copper and the bulk of the heat sink was not sufficiently good to allow it to absorb heat of magnetization greater than ~ 500 ergs while remaining at .012°K.

CHAPTER 6

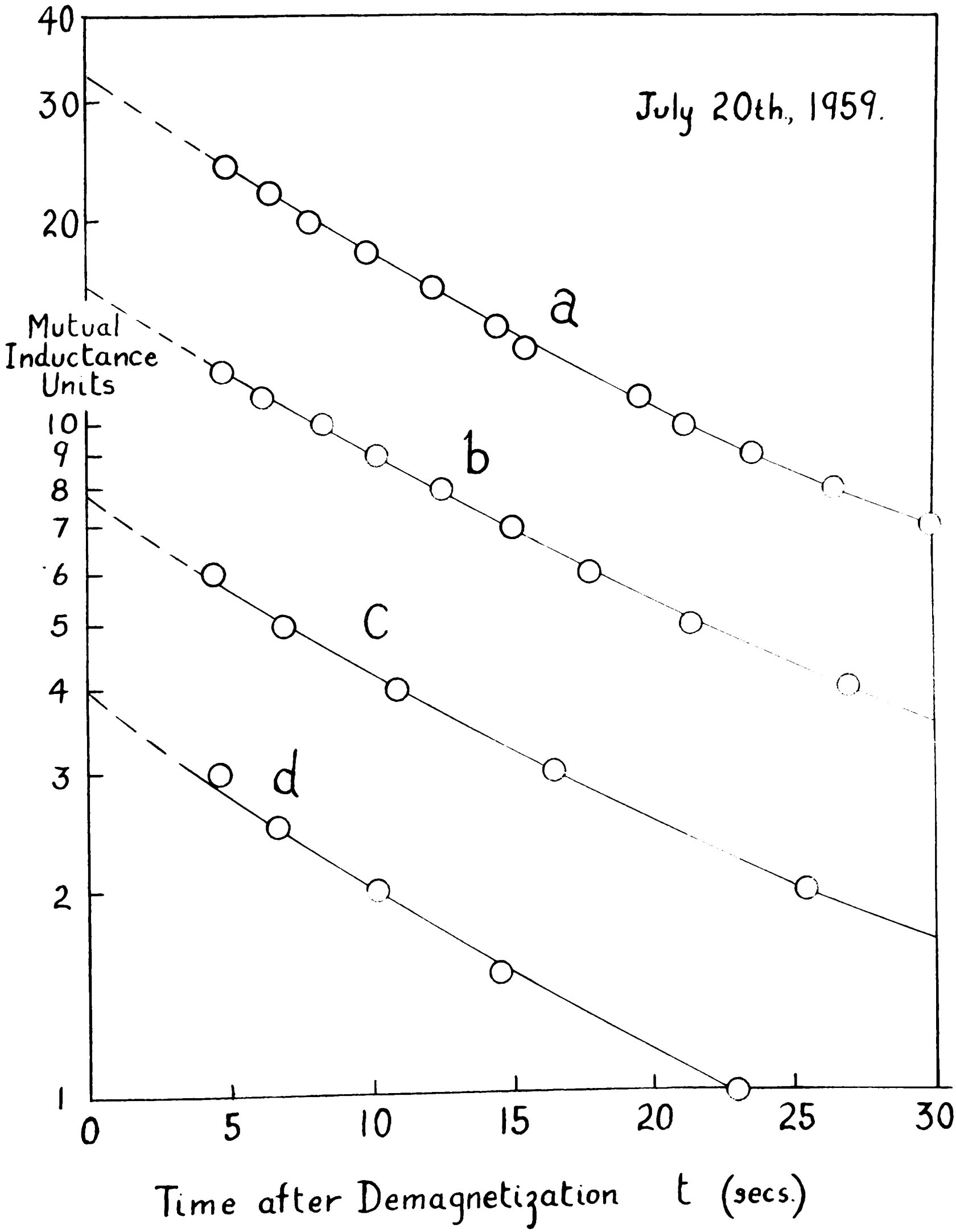
FURTHER NUCLEAR COOLING EXPERIMENTS

Experiments Using a Specimen Having a Smaller Nuclear Stage.

To overcome the problem of local overheating in the top stage of the specimen when using fields greater than about 8 KØ a specimen was made identical in all respects to those used previously except that the nuclear stage was reduced from .68 gram atoms to .17 gram atoms of copper. This specimen is described at the beginning of chapter 5 and is shown on the left hand side of the photograph of specimens.

This reduction by four allowed the magnetic field to be increased by a factor two for the same heat of magnetization. It was indeed found that the final temperatures reached after demagnetization were inversely proportional to the magnetizing field up to about 15 KØ.

In an attempt to improve the thermal contact and conductivity within the heat sink a 70% glycerol -30% water solution saturated with potassium chrome alum was forced through the perspex case of this specimen under pressure. The solution was more viscous than that used during the initial manufacture of the specimen.


July 20th., 1959.
Mutual Inductance Units
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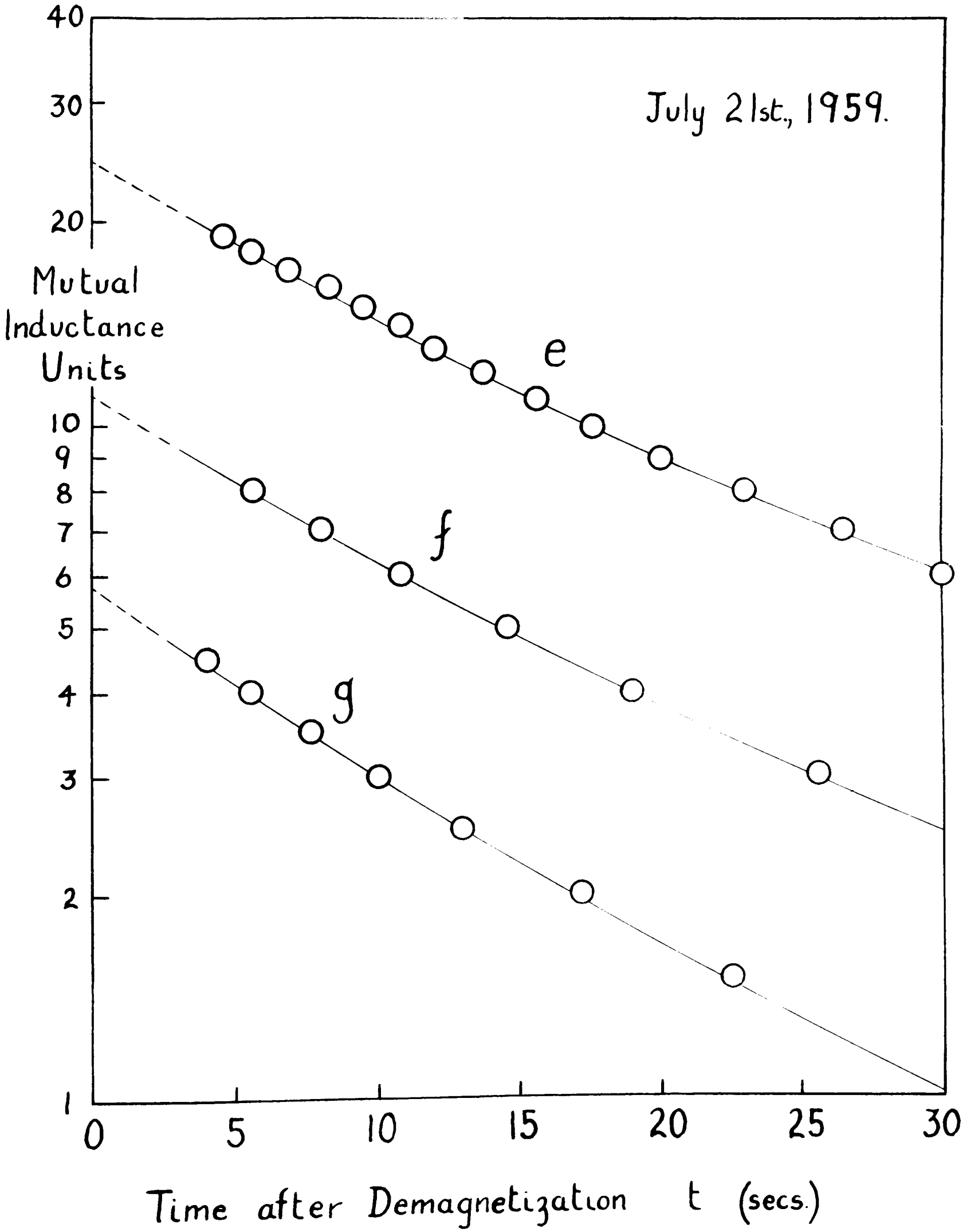
Time after Demagnetization t (secs.)


July 21st., 1959.
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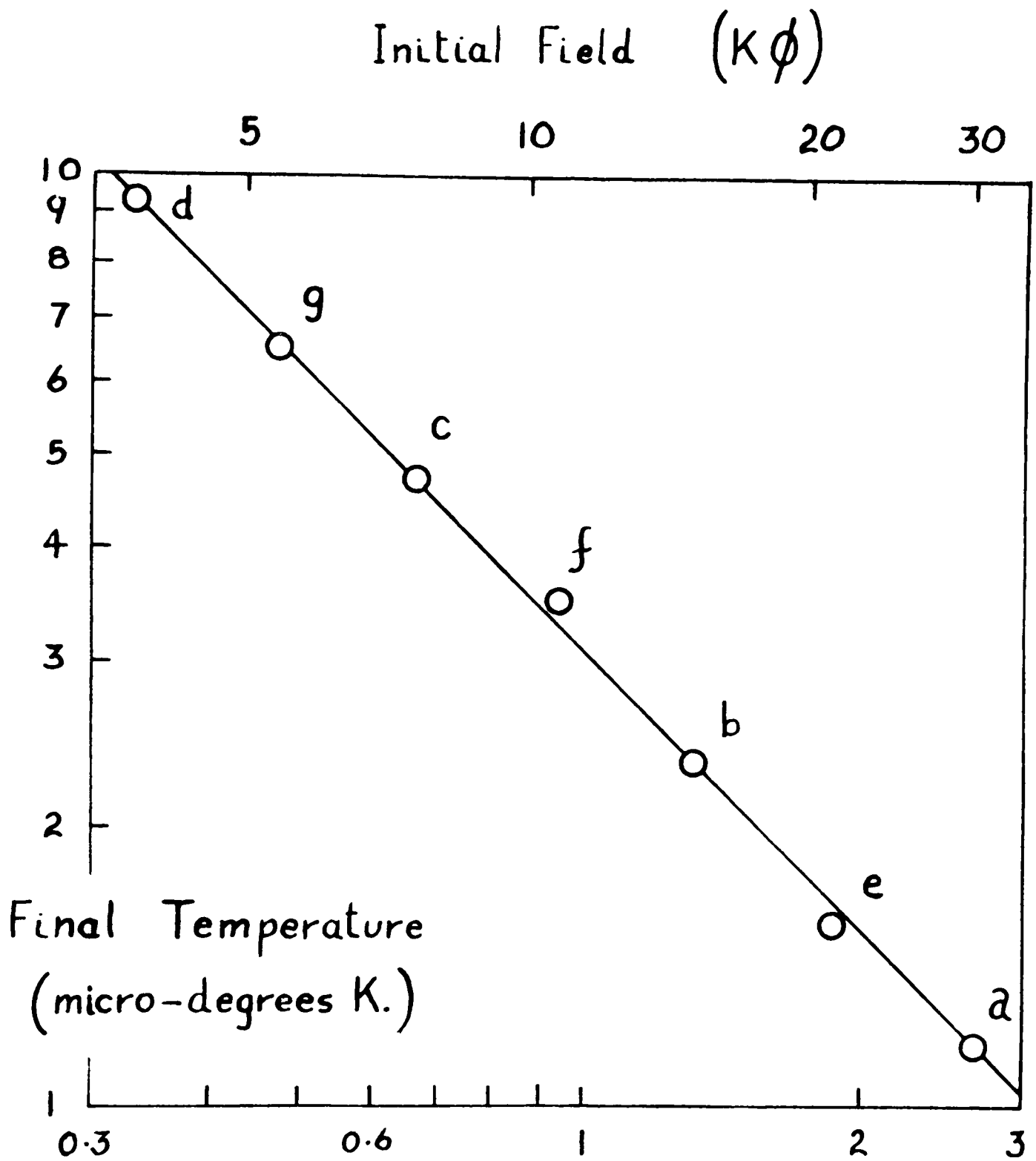
Time after Demagnetization t (secs.)



Demagnetizations from ·012°K and various fields.

DEMAGNETIZATION OF COPPER

4.2A

	H_i	TIME	T_i	$(H/T)_i$	M_o	T_f	θ_n
	A/	secs	^oK	A/^oK	units	μ^oK	μ^oK
a)	30.4	2400	.0126	2.42	32.5	1.32	.175
b)	15.2	1200	.0119	1.28	16.2	2.50	.177
c)	7.6	600	.0117	0.65	8.0	4.90	.177
d)	3.8	300	.0116	0.33	4.1	9.45	.175
e)	21.6	1800	.0121	1.79	24.1	1.73	.172
f)	10.8	900	.0118	0.92	10.8	3.67	.167
g)	5.4	450	.0117	0.46	5.8	6.70	.173

An immediate improvement was noticed in the next experiment for the final temperatures reached were inversely proportional to the field up to 30.4 Kø, the maximum permissible field for the solenoid. The constant of proportionality was equal to that found in the early experiments at low fields. That this linear relationship of H_i and $1/T_f$ should have been extended to the highest field available by these various methods shows that the foremost difficulty had been that of heat contact with the sink, i.e. ensuring that T_i was at the temperature of the main body of the sink in each case.

Nuclear susceptibility decay curves obtained on two consecutive days are shown, the magnetizing fields ranging from 30.4 Kø to 3.8 Kø. These decay curves have been extrapolated to the instant of demagnetization and the corresponding nuclear spin temperatures calculated from the calibration equation referred to in chapter 4. The lowest spin temperature was 1.5×10^{-6} °K.

The final temperatures T_f are shown plotted as a function of the initial field H_i and also of the initial H_i/T_i on the assumption that the initial temperatures T_i in these particular experiments were that of the heat sink i.e. .012°K. The validity of this assumption will be

examined in chapter 7. The probable values of T_i, corrected by a small quantity on the basis of the conclusions of chapter 7, are given in the table.

From these data the interaction temperature θ_n, as defined in chapter 1, has been calculated from the expression

$$\theta_n = (\mu_n / kI)(H_i T_f / T_i).$$

These results give a mean value of $\theta_n = 1.75 \times 10^{-7}$ °K. The uncertainty of these individual values of θ_n due to errors in extrapolation, timing, etc., are of the order ± 3%. It is thought that any systematic error due to inaccurate magnet calibration, errors in the calibration equation for the nuclear specimen, etc., will also be of the order ± 3%.

An Experiment Using a Specimen Without a Nuclear Stage.

To check that the susceptibility bridge was not picking up spurious signal from some unsuspected source an experiment was performed using a specimen without a nuclear stage. This experiment was conducted in a similar manner to the other experiments previously described. The "nuclear stage" was magnetized at 15 KØ for ten minutes, the heat sink being at .012 °K.

This experiment was repeated several times and in each case only a small transient was observed which decayed with the response time of the amplifier (~2 seconds). After 5

seconds from the instant of demagnetization there was nothing observable above the noise (i.e. less than 2% of the signal usually obtained when a nuclear stage was used). It may be concluded that all of the signal normally observed is due to the paramagnetism of the nuclear stage.

A Gamma-Ray Heating Experiment.

In order to test the hypothesis that the conduction electrons remained at the temperature of the sink during the nuclear spin relaxation after demagnetization, a γ-ray source was placed very close to the tail of the Dewar, at the level of the nuclear stage, when the signal had fallen to about 50% of the maximum value. It was found that the rate of decay of the nuclear susceptibility was not affected.

A subsequent calibration showed that the amount of heat being fed into the nuclear stage due to the γ-rays was $\sim$ 1 erg/sec. If the conduction electrons had been at the temperature of the spins and the nuclear spin warm-up had been governed by the rate at which heat was leaking into the nuclear stage then the signal would have decay to zero in $\sim$1 second. As this did not happen it would seem to confirm that the conduction electrons were in good thermal contact with the top stage and that this heat was passed into it. Reference to the thermal junction equation in chapter 7 shows that the electrons would only warm $\sim 10^{-3}$ deg. above that

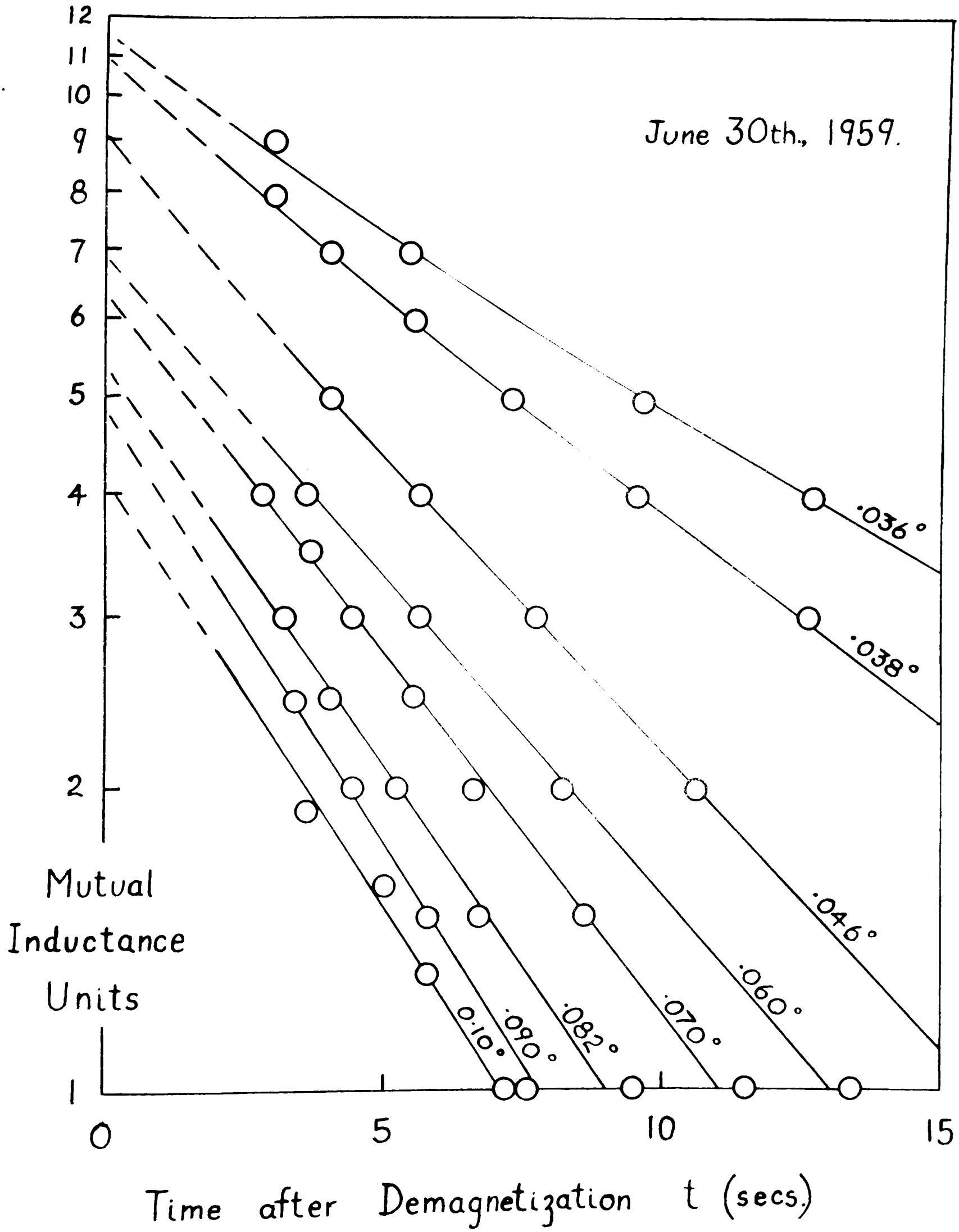
ofthe sink. This would reduce the relaxation time by a few per cent, which would probably not be detectable.

Experiments at Higher Initial Temperatures.

The experiments previously described have shown that the nuclear susceptibility decay was governed by the nuclear spin-conduction electron relaxation process. The theory of this relaxation in metals, proposed initially by Heitler and Teller[7] and subsequently developed by Korringa,[8] suggests that the relaxation time is inversely proportional to the conduction electron temperature. Nuclear resonance experiments between 1 °K and 300 °K have shown this to be true within experimental error.

Nuclear cooling experiments were performed with potassium chrome alum in the heat sink at temperatures between .012 °K and 0.10 °K. The actual values of the temperature were derived from a calibration equation using the T-T^* relationship of Daniels and Kurti.[21] The nuclear stage was of the same size as that used in the preliminary experiments, i.e. .68 gram atoms of copper. The magnetizations were all at 7.6 μ, a relatively small field, because of the small heat capacity of the heat sink in this temperature range.

The size of the signal in these experiments was small due to the high spin temperatures, and the relaxation times


June 30th., 1959.
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Mutual Inductance Units
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Time after Demagnetization t (secs.)
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·070°
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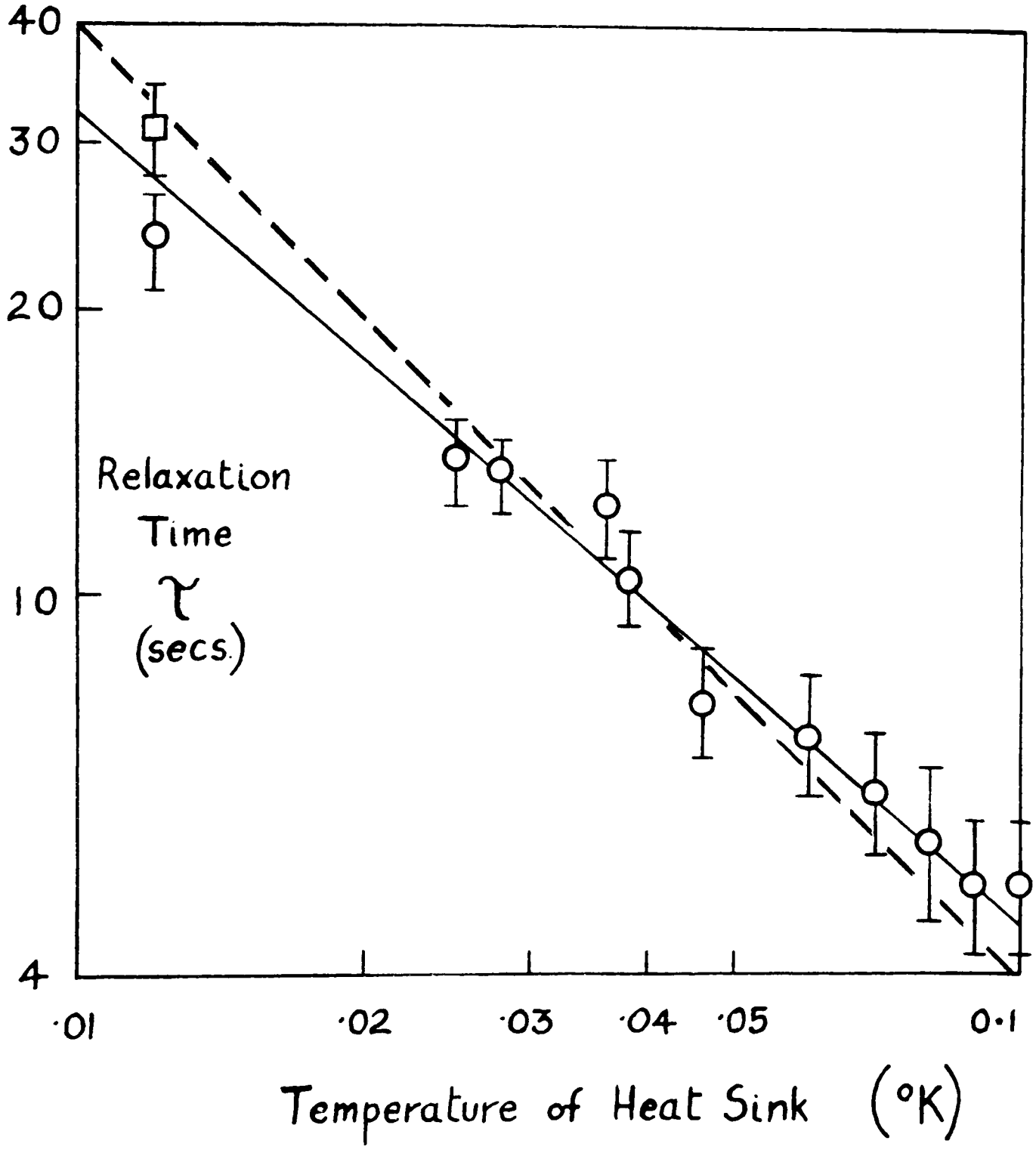
40
30
20
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4
Relaxation
Time
τ
(secs.)
·01
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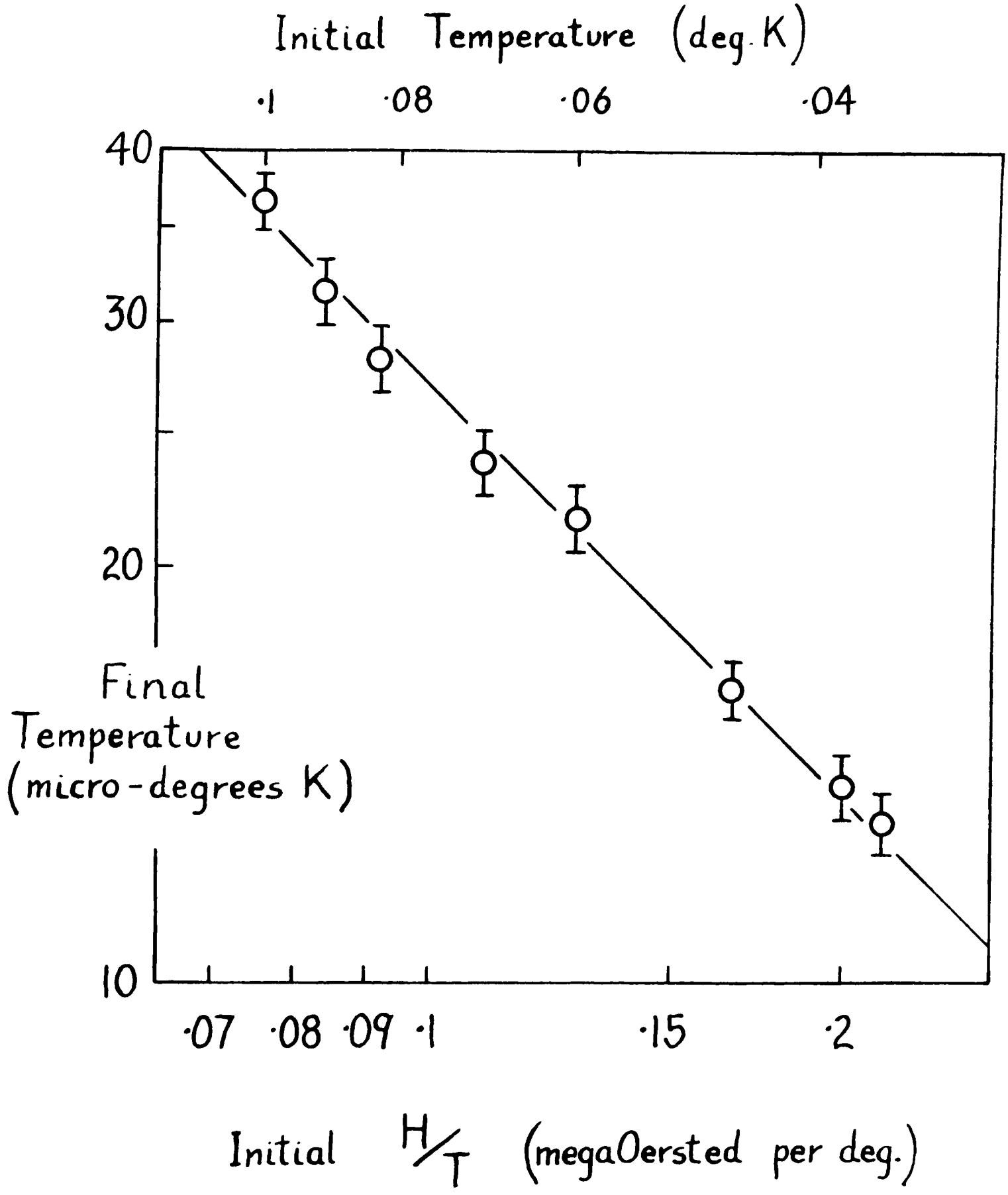
·03
·04
·05
0·1
Temperature of Heat Sink (°K)



Demagnetizations from 7·60 Kϕ and various temperatures.

were smaller than in previous experiments. A figure shows the decay curves for the various heat sink temperatures, the time scale in this case being 0-15 seconds.

As can be seen from the next figure the relaxation times, τ, were approximately inversely proportional to the heat sink temperature. At the higher temperatures τ became comparable with the response time of the amplifier and recorder ($\sim$ 2 seconds) and so these values may be slightly greater than the true nuclear spin relaxation time. The value of τ at .012 ^{o}K is 24 seconds but, as explained in chapter 7, this appears to be dependent on the magnitude of the measuring field. A crude extrapolation to zero measuring current indicates a value of $\tau \approx 32$ seconds. This is plotted on the figure as $\boxdot$.

The points on this figure lie approximately on the line $\tau T = 0.4$ secs. deg. ; any divergence can be fairly explained on the basis of the arguments given above and by the experimental error.

This result adds further weight to the hypothesis that the electrons are at the temperature of the heat sink for this is the type of relationship expected for nuclear spin-conduction electron relaxation.

The value of τT found by other workers[22,23] at higher tem-

peratues, by nuclear resonance techniques, is about 1.2 secs. deg., i.e. about three times larger than in these experiments. Their value agrees well with that obtained from the Korringa relation,

$$\tau T = (\hbar/\pi k)(I \mu_B/\mu_n)^2 \quad (H/\Delta H)^2$$

which expresses the relaxation time in terms of the Knight shift. Using the best available resonance line shift data, andmaking small corrections to the above expression for electron correlation, $\tau T = 1.3$ secs. deg.

It has recently been shown, however, that the Korringa theory of nuclear spin relaxation is not applicable to relaxation in small magnetic fields i.e. τT is in fact field dependent. A new theory of nuclear spin relaxation in metals by Redfield[24] shows that τT, as calculated using the Korringa[8] theory, should fall by a factor two when the applied magnetic field is less than the internal field.

Nuclear resonance experiments by Anderson and Redfield[23] have shown that this does indeed occur, although in some metals, e.g. copper and aluminium, the factor is about three. They have found that at fields below 1 oersted $\tau T = 0.45$ secs. deg. for copper in good agreement with the figure obtained in these experiments at temperatures a factor 100 times lower.

By way of a further check on the applicability of the Redfield theory to this relaxation process an experiment was performed in which a transverse magnetic field of 5 oersted was applied to the nuclear stage immediately after a nuclear demagnetization. The application of the field raised the spin temperature and so reduced the signal but the relaxation time increased from 24 seconds to about 45 seconds which is also in accord with the results of Anderson and Redfield.[23]

By extrapolation of the decay curves obtained in these experiments the values of T_f at the instant of demagnetization were found. These are shown plotted as a function of H_i/T_i and T_i. The experimental uncertainty of these points is considerably greater than in the experiments described at the beginning of this chapter due to the small signals and rapid relaxation. The mean value of σ_n derived from these points is $\sim 1.5 \times 10^{-7}$ o.K.

CHAPTER 7

CONCERNING THE TIME REQUIRED FOR MAGNETIZATION AND OTHER TOPICS

The Time Required for Raising the Magnetic Field

The entropy of copper between 10^{-2}°K and 1°K is given by

$$S = R \log (2I+1) - \tfrac{1}{2} \lambda_m (H/T)^2 + \gamma T$$

where $\lambda_m = 3.21 \times 10^{-7}$ e.m.u./gram atom and $\gamma = 7500$ ergs/gram atom deg^2.

Initially the copper is at .012°K. As the magnetic field is applied the temperature rises and heat is absorbed by the sink. In view of the limited capacity of the heat sink it would be desirable that the field be raised so that the input to the heat sink is as small as possible.

Consider two extreme cases. For very slow isothermal magnetization the heat evolved is $T\Delta S$ where $\Delta S = \tfrac{1}{2}\lambda_m (H/T)^2$. On the other hand removal of the entropy by cooling in the field H (following adiabatic magnetization) gives rise to a larger heat evolution. For values of H/T used in these experiments it can be shown that the heat evolved is twice that of the isothermal case.

Robinson[5] and Spohr[10] have shown that the rate of heat transfer from copper at temperature T to the slurry used in these experiments at temperature T_1 is given by

$$Q \approx 10^3 (T^3 - T_1^3) \text{ ergs/cm}^2 \text{. sec.}$$

A calculation for magnetization a) described at the beginning of chapter 6, i.e. with 30.4K ø, shows that in order to keep the heat of magnetization to only 25% more than the isothermal case it would be

necessary to raise the field over fifty minutes keeping HdH/dT constant.

This condition could not be fulfilled as only a hand control of the 2000 Kwatt generator was available. Even if it had been possible to magnetize in this way the advantage would be offset by the ordinary heat leak into the heat sink during this long period.

In the experiments at high fields described in this thesis the field was increased over a period of two to five minutes depending on the final magnitude. A rough calculation shows that the total heat input to the sink was about 75% greater than the ideal case and that little better can be achieved.

The Temperature Ti of the Nuclear Stage before Demagnetization

When the field has been raised to the required magnitude it is necessary to allow time for the nuclear stage to cool towards the temperature of the heat sink. It is interesting to calculate, on the basis of the data on thermal properties of the system that is available, how close the nuclear spin temperature comes to that of the sink after a given time, for it is this temperature which determines the entropy before demagnetisation.

From the specific heat of the spin system and the thermal junction equation

$$(\lambda H^2/T^2)\, dT/dt = 10^3 A\, (T^3 - T_1^3)$$

which reduces to

$$d\theta/dt = [10^3 A\, \theta^2\, (\theta^3 - 1) T_1^4]\, \lambda H^2,$$

where $\theta = T/T_1$ and A is the contact area of the junction.

By integration of this equation it is possible to find the time necessary for θ to fall to a given value. The upper limit of θ is not important above 1.5. From this anlysis the values of Ti given in the table of data are calculated. It will be seen that the time necessary to reach a given value of θ depends upon H^2/T_1^4 and so this problem will become increasingly more difficult as attempts are made to use higher fields and lower sink temperatures.

The Loss of Signal due to Relaxation During Demagnetization

It has been assumed until now that the demagnetisation process is isentropic though the nuclear stage remains in thermal contact with the heat sink. It is necessary to enquire how much of the increase in spin ordering is lost during demagnetisation.

If the field were reduced linearly over a period equal to that taken for magnetisation the process would approximate to isothermal demagnetisation with no cooling. In principle if the field were removed instantaneously there would be no increase in entropy.

An exact analytical calculation of the increase in entropy as the field is reduced linearly to zero would be very complex and unwarrented in view of the uncertainty of some of the factors involved. Such a solution would have to take into account the thermal junction equation of Robinson and Spohr, the relaxation of nuclear spins and conduction electrons which depends upon the temperature and the field, and the specific heats of the two systems which depend upon the temperature and field in different ways.

There are two "bottlenecks" for the transfer of heat, firstly across the junction and secondly between the conduction electrons and nuclear spins. These two act in series and it is possible to find an upper limit

to the entropy gain by considering the worst of these two.

If it is assumed that the restriction is between the nuclei and the conduction electrons, i.e. if the conduction electrons remain strongly coupled to the heat sink and the relaxation is that between nuclei and electrons at .012°K it can be shown that the final temperature T_f of the spin system is given by

$$T_f / T_f' = (td/\tau)\left[1 - \exp(-td/\tau)\right]^{-1}$$

where T_f' is the final temperature which would have been reached by isentropic demagnetization. In these experiments τ = 100 seconds and td = 30 seconds. So T_f/T_f' = 1.15 and is independent of the initial field Hi.

Alternatively it is possible that under certain circumstances the heat flow is limited by the copper-slurry junction. From the transfer equation it can be seen that there is a maximum flow rate $\dot{Q}$ for a given heat sink temperature. In the specimens used in these experiments this is ~ 0.5 ergs/second.

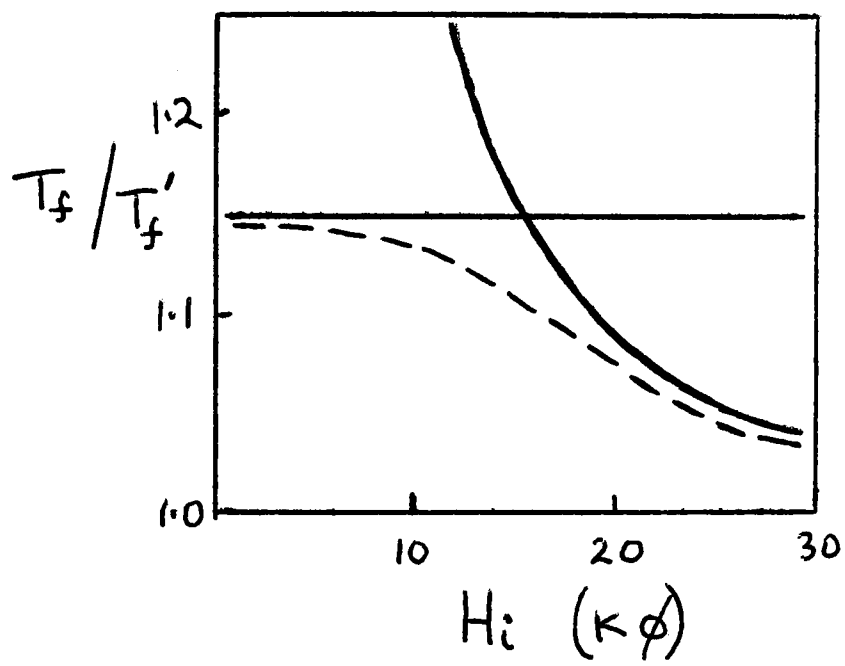
It can be shown that the fractional decrease of the initial spin ordering during demagnetization is

$$(2\dot{Q}td T_1/\lambda H_i^2) \log (H/H_i)$$

when the field has been reduced from H_i to H. If the final field is taken as the internal field H′ of the specimen then it can be shown that

$$T_f/T_f' = 1 + (\dot{Q}td T_1/\lambda H_i^2) \log (H_i/H').$$

If the expressions obtained in these two limiting cases are plotted as a function of H_i for T_i = .012°K and for H′ = 3.0 ϕ the following is found.



As heat must pass across the boundary and also between the conduction electrons and the nuclei the actual values of T_f/T_f' must lie below both of these curves. This sets an upper limit to T_f/T_f'.

In an actual demagnetisation from, say, 15Kø it is likely that the conduction electrons are cooled by the nuclear spin system during the initial stages of the demagnetisation. When $H/H_i \approx 0.3$ the spin system can no longer keep the conduction electron temperature down and in the last ten seconds of the demagnetisation it will rise to .012°K, the loss of spin ordering being governed by the relaxation process. An approximate calculation for this behaviour show $T_f/T_f' = 1.10$. A similar calculation for $H_i = 30$ Kø shows $T_f/T_f' = 1.03$. It is thought that the dotted curve is a good representation of actual T_f/T_f' in these experiments.

The data in chapter 6 have not been individually adjusted for this effect in view of the uncertainty of the actual values of T_f/T_f'.

However it is quite likely that the value $\theta_n = 1.75 \times 10^{-7}$°K is too high by about 9%; i.e. it is quite probably that $\theta_n = 1.6 \times 10^{-7}$°K.

On the basis of this analysis it is quite inexplicable why the value $\theta_n = 1.5 \times 10^{-7}$°K should have been obtained from the results of the experiments performed at higher temperatures, described at the end of chapter 6. This analysis predicts that the ordering should have been reduced by a factor of the order two. The only conceivable explanation is that the Robinson-Spohr formula does not hold in the temperature range .03 - o.1°K.

Experimental Evidence Concerning Demagnetization Times

Demagnetizations from 7.6K and .012°K showed that increasing the time taken for demagnetization to one minute gave rise to ~30% less signal. Decreasing the time to 15 seconds gave an increase of ~5% and to 7 seconds an increase of ~10%. This is in fairly good agreement with the foregoing analysis which predicts the figures 15%, 7% and 10% respectively.

An attempt to demagnetize in ~1 second by tripping the generator excitation gave 15% less signal than normally obtained. This is due to the considerable heat input to the nuclear stage due to eddy current heating.

Calculation shows the heat induced to be ~20 ergs. The internal equilibrium time within the nuclear stage and thermal link is ~0.1 seconds and this heat would be passed quickly to the heat sink, the temperature of the copper rising to about .04°K. The demagnetization over, the conduction electrons would cool back to .012°K very quickly. The extra loss of signal is that due to relaxation for ~2 seconds with the conduction

electron temperature at ~.04°K.

The Shape of the Nuclear Susceptibility Decay Curves

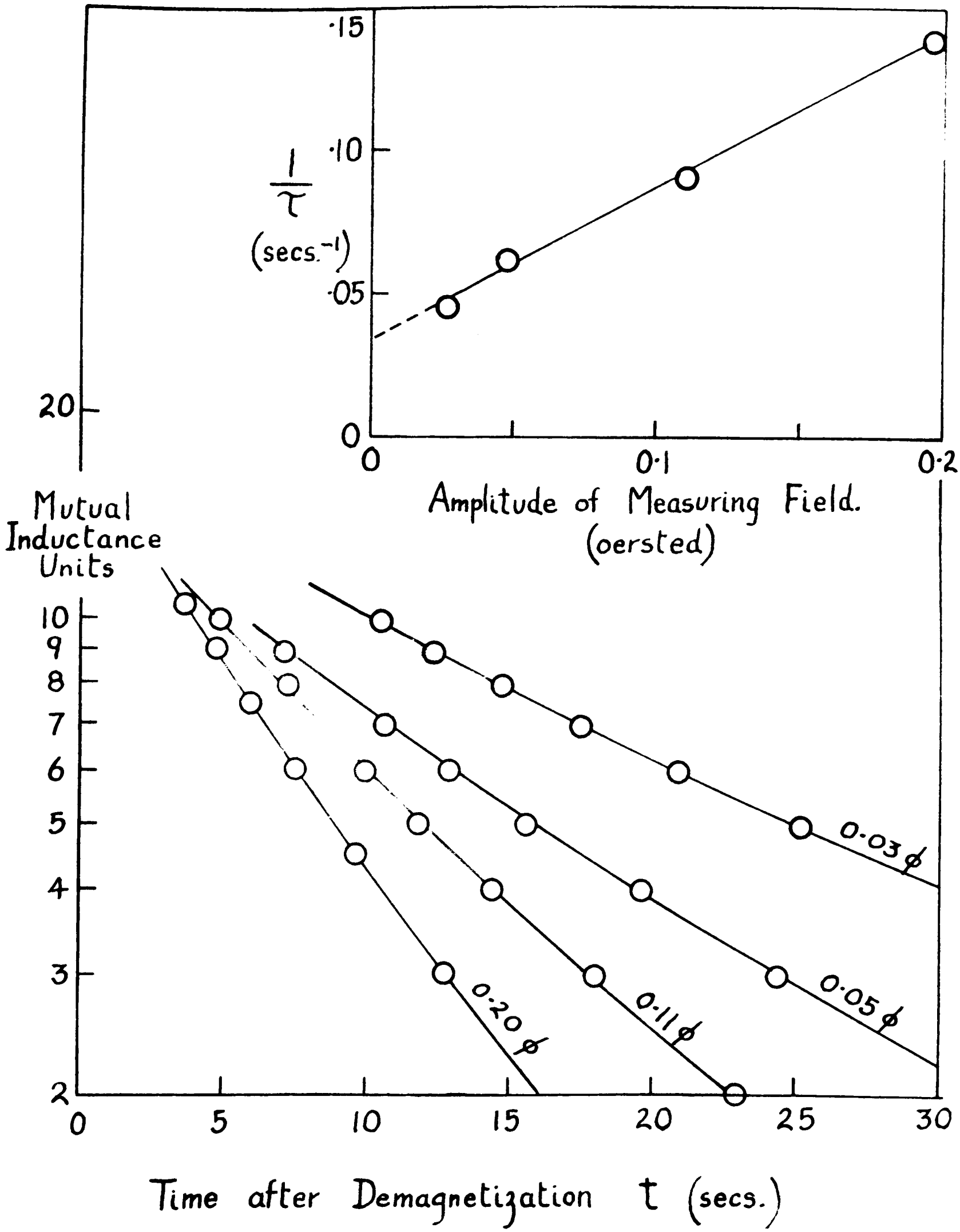
The nuclear susceptibility decay curves, plotted on logarithmic paper, are almost straight lines. There is a slight curvature. This departure from true exponential decay is inexplicable.

The Korringa[8] theory of relaxation shows that the relaxation time depends upon the inverse square of the nuclear moment for a given element. Copper contains two isotopes in the natural state. There is 69% of Cu^{63} with moment 2.23 n.m. and 31% of Cu^{65} with moment 2.38 n.m. The spin in both cases is 3/2. Calculation of the combined effects of these two isotopes, considered to be relaxing independently, gives the right type of curvature to the decay curve but not enough to explain the experimental results.

Another interesting phenomenon is the dependence of the relaxation time on the magnitude of the measuring field used in the bridge. Some curves are shown for demagnetisations from .012°K, the amplitude of the measuring field being shown. Inset is shown how the reciprocal of the relaxation time depends on the measuring field. It might be possible to infer that the relaxation time for zero measuring field is ~ 32 seconds.

This phenomenon cannot be the effect of eddy currents raising the temperature of the conduction electrons for calculation shows the heat input to be only ~ 10^{-3} erg/sec.

A tentative explanation for these two phenomena could be that at the lowest temperatures, although well above any ferromagnetic Curie point, there may be a small amount of long range order which gives


·15
·10
·05
0
$\frac{1}{\tau}$
(secs.$^{-1}$)
0
0·1
0·2
Amplitude of Measuring Field.
(oersted)
20
Mutual
Inductance
Units
10
9
8
7
6
5
4
3
2
0·03 ϕ
0·05 ϕ
0·11 ϕ
0·20 ϕ
0
5
10
15
20
25
30
Time after Demagnetization t (secs.)

rise to hysterysis and an out of phase susceptibility component. So the curvature may be due to the fast decay of the out of phase component of the total susceptibility and the dependence of the relaxation time on the measuring field may be due to hysterysis.

Chapter 8

SUPERCONDUCTING HEAT SWITCH AND OTHER EXPERIMENTS

The experiments described in the previous chapters have shown that although it is possible to obtain nuclear spin temperatures of a few microdegrees the conduction electrons remain at the temperature of the heat sink. If it were possible to sever the thermal connection between the two stages just before demagnetization it would be possible to cool the conduction electrons to microdegree temperatures, for the specific heat of the spin system during demagnetization is much greater than that of the conduction electrons. It might be thought that the relaxation time at microdegree temperatures would be $\sim 10^6$ seconds but Kittel[25] has pointed out that this is the time characteristic of energy transfer between nuclei and an infinite conduction electron heat bath at this temperature. In this case, where the electronic specific heat is very small compared with that of the spins, the time is $\sim 10^{-1}$ seconds for the electrons to come into equilibrium with the spins.

There are two advantages to be obtained by the use of a thermal switch. If the conductivity of the switch in the open state and other heat leaks are sufficiently small, the warming up of the spin system would be governed

by the residual heat leak rather than the spin lattice relaxation time, and it would be possible to keep the specimen cold for a longer period, allowing time for more elaborate experiments. Also, cooling the conduction electrons into equilibrium with the spins would be the first step towards cooling another body to microdegree temperatures by contact.

It is interesting to note that the nuclear susceptibility of a demagnetized specimen, isolated from the heat sink, would decay linearly for a constant heat leak, due to the T^{-2} form of the specific heat. When the decay is governed by the nuclear spin-conduction electron relaxation process, it is exponential.

The only heat switch that has been used successfully at temperatures below 1 ^{o}K is the superconducting heat switch. This relies on the difference in thermal conductivity in the normal and superconducting phases of a metal. The superconductor can be switched from the normal to superconducting phases by the removal of a strong magnetic field; this is a very convenient switch with no moving parts but easily controllable from outside the apparatus. At very low temperatures in the normal state (i.e. in a field greater than the threshold field) the thermal conductivity is almost entirely due

to the conduction electrons. This conductivity is directly proportional to the temperature, the scattering of the electrons being due to impurities. For a typical pure metal such as tin the conductivity is $K_n \approx 10^7$ T ergs/cm deg. which is of the same order of magnitude as that of copper.

In the superconducting state at very low temperatures the thermal conductivity is due to phonon conduction. The number of phonons available is proportional to T^3 but the mean free path is that set by the imperfections and crystal boundaries in the metal and is constant. This conductivity is comparatively small and for tin is $K_s \approx 10^6 T^3$ ergs/cm deg. The ratio of the two conductivities for tin is

$$K_n/K_s \approx 10/T^2.$$

It can be seen that as the temperature becomes lower this ratio becomes very great, being $\sim 10^5$ at 10^{-2} °K.

It can be seen that by inserting a length of a metal such as tin in the thermal link of a nuclear cooling specimen is ought to be possible to make a very effective switch. Furthermore it could be arranged so that the superconductor is situated at such a position in the link that the stray field of the main nuclear magnetizing field just makes it normal. As soon as the

nuclear stage is demagnetized the switch reverts to the superconducting state. The switch should be placed so that it is normal during most of the demagnetization of the top stage, to allow the copper to cool to $\sim 0.1\ ^{o}K$. If this were not allowed the large electronic heat content of the copper at $1\ ^{o}K$ (~ 3000 ergs for these specimens) would flow into the top stage as soon as the bottom stage was magnetized and the switch made normal. These restrictions on the position of the switch make it impossible to do experiments over a wide range of magnetic fields.

The successful use of superconducting heat switches has been reported by several workers.[26] Heer and Daunt used tin at temperatures above $0.3\ ^{o}K$ and extrapolation of their data indicates that K_n/K_s should be $\sim 10^5$ at $10^{-2}\ ^{o}K$. Rollin et al[27] reported the first successful two stage demagnetization using paramagnetic salts and a heat switch, the upper stage being at $.25\ ^{o}K$. They reduced the heat leak into the lower stage to a few ergs per minute.

Nuclear cooling experiments using superconducting heat switches have been performed concurrently with the series of experiments without switches described in previous chapters. Lead, tin, and indium were tried in various shapes, sizes, and positions in the link, with

different methods of support and attachment.

In the initial stages the total heat content of the spin system was estimated from the data of Spohr[10] ($\theta_n = 7 \times 10^{-7}\ ^{o}K$) as being several ergs, so that the successful operation of a switch seemed possible.

It was immediately found that the use of any superconducting alloy for attaching the switch to the copper gave large heat pulses when the field was removed, large enough to be detected by warming of the heat sink. A technique was devised for soldering onto the ends of the 1640 No. 40 s.w.g. wires using the same material as the switch, except in the case of lead which has a high melting point (327 ^{o}C) and oxidises easily.

However in practically all experiments no nuclear susceptibility signal was observed. In a few cases using tin switches with a large are/length ratio (~ 1 cm) a small signal was observed which decayed in ~ 10 seconds.

At first it was thought that the characteristics of the switch were not suitable and experiments were performed with Cerium Magnesium Nitrate (CMN) crystals replacing the copper in the second stage, in order to find the conductivity of the switch, and also to see if there were any irreversible heating effects. However the large heat capacity of the CMN crystals and the poor thermal con-

tact of these crystals with the link made the experiment somewhat difficult; little more could be deduced than that the thermal conductivity in the superconducting state was falling rapidly with temperature in the region of 0.1 ^{o}K.

At about this time the other experiments began to show that Θ_n was in fact some four times less than Spohr had estimated, making the specific heat some sixteen times smaller. In fact with values of H/T that could be used with the larger type of nuclear stage (.68 gram atoms of copper) the total heat content of the spin system was less than 1 erg.

The interpretation of the failure to achieve a successful heat switch experiment is that the nuclear spin system was very quickly warmed up either by irreversible heat pulses from the switch during the demagnetization or large leaks to the nuclear stage by vibration. It should be noted that the heat of demagnetization of a superconductor at temperature T is

$$Q = (1/2\pi)(H_o/T_c)^2 \quad \text{ergs/cm}^3$$

where H_o is the critical field at 0 ^{o}K and T_c is the critical temperature in zero field. This is $\sim$ 0.5 ergs/cm^3 under these conditions and as the volume of the switch is $\sim$ 0.1 cm^3 the heat of demagnetization is not negligible.

One possible source of irreversible heating in the switches was that due to eddy currents in the material of the switch when in the normal state especially at the point where it is soldered to the wires of the nuclear stage. Several schemes were tried to reduce this, one of which is shown on the photograph of specimens. The nuclear stage in this case was made of coiled, annealed, copper strip with the connection to the switch much reduced in size. However no nuclear cooling was observed.

In the cases where a small nuclear susceptibility signal was observed it is probable that the thermal contact between the two stages was sufficiently good that the conduction electrons in the nuclear stage remained at about the temperature of the heat sink. Any abnormal heat leak would then have been passed into the heat sink ratherthan the nuclear spin system, the whole experiment approximating to the conditions without a switch.

In reviewing these experiments ,the problems of irreversible heating and stray heat leaks may be appreciated. The minimum requirements for successful operation of a heat switch in these circumstances are that heat produced in the switch must be less than 0.1 erg and heat leaks must be less than 10^{-2} erg/minute.

Nuclear Demagnetization of Silver.

Natural silver contains nearly equal proportions of Ag^{107} and Ag^{109} each with spin ½ and nuclear moments of -0.113 and -0.130 n.m. respectively. Because of these small moments the Curie constant per unit volume is ~ 250 times smaller than that of copper.

However, if the nature of the nuclear spin interaction is similar to that of copper (i.e. magnet dipole interaction) then it might be expected that the interaction temperature is ~ 30 times smaller than that of copper. There is some evidence that indirect exchange interaction is important in silver so that the interaction temperature may be only ~ 10 times smaller.

For demagnetizations from the highest available H/T in these experiments a temperature ~ 10 times smaller than that with copper might be attained. As the Curie constant is ~ 250 times smaller, about 4% of the signal from copper might be expected.

A calculation for silver using the Korringa relation and Knight shift data indicates that at 10^{-2} °K the nuclear spin-conduction electron relaxation time should be ~ 500 seconds.

A specimen was made with 10% pure silver No. 39 s.w.g. wires folded five times to form the nuclear stage containing 0.40 gram atoms of silver, the upper stage being potassium

chrome alum slurry. This was magnetized at 24 KØ and .012 °K for ten minutes. The heat of magnetization under these conditions is only ~ 10 ergs, the Curie constant being so small. The time of relaxation was determined by the expected nuclear spin-conduction electron relaxation time.

The sensitivity of the bridge was such that although a smaller measuring field (~ .01 Ø) was used the expected signal should just have been observable. In fact no definite signal could be seen.

The reasons may be that the relaxation time is longer than expected, the interaction temperature is greater than predicted by theory, the earth's magnetic field is of the same order as the internal field of copper, and that the effect of the measuring field warms the spin system up.

Nuclear Free Precession Experiments.

Hahn[29] has proposed the detection of nuclear free precession in metals at very low temperatures for direct measurement of nuclear spin temperatures and various relaxation times.

The principle of the experiment is as follows. A magnetic field $H_X \approx 100$ oersted is applied to a nuclear spin system in the X direction. Suppose the

nuclei have spin $\frac{1}{2}$. The nuclear spin levels are split and there will be a net magnetic moment in the X direction of $\lambda H_X/T$ where λ is the Curie constant and T is the spin temperature.

A rectangular pulse is used to provide a field H_Z in the Z direction equal in magnitude to H_X, for a length of time that is one half of the Larmor precession frequency of the nuclei in the magnetic field (the vector sum of H_X and H_Z). The effect of this pulse is to turn the nuclei from the $\pm$ X direction to the $\pm$ Z direction and allow them to precess in the X = 0 plane in the field H_X with the appropriate Larmor frequency. A signal from the rotating magnetic moment of the spins is then picked up by an untuned coil system, with axis in the Y direction, amplified, and photographically recorded.

The precessional frequency of a nucleus depends upon the nuclear g-factor and the field at the nucleus. The field at a given nucleus will be H_X plus the fluctuating internal field H'. So after approximately H_X/H' radians dephasing of the spins in the X = 0 plane takes place. Alternately it can be said that spin-spin relaxation dephases the spins. By observing the rate at which the signal decays the spin-spin relaxation time can be measured. For copper nuclei the Larmor

period in 100 Ø is ~ 8μ seconds, and as H' ≈ 3 Ø approximately 10 cycles should be observable. If more cycles could be obtained it should in principle be possible to see the interference of the signals from the two isotopes whose nuclear moments differ by about one part in fifteen.

It should also be possible to measure the spin lattice relaxation time, i.e. measure the rate at which the already dephased spins in the X = 0 plane, return to the X direction. This can be done in principle by applying a second H_z pulse at known intervals and measuring the magnitude of the observed signal which depends directly on the number of spins in the X direction.

In conjunction with Hahn preliminary experiments were carried out to observe these phenomena in copper at 1^{-2} ^{o}K, with a view to the development of a nuclear free precession thermometer for the direct measurement of nuclear spin temperatures. The apparatus was modified so that the 0.9 ^{o}K cryostat had double glass walls surrounding the nuclear stage of a normal copper specimen. On the glass tail were mounted the pulse coil and receiver coil with an earthed screen between them. The field H_x was applied to the system by a Helmholtz pair outside the

Dewar.

The heat sink was demagnetized to .012 °K and attempts were made to observe the free precession of copper nuclei at this temperature. Although care was taken to balance the receiver coil for minimum pick-up from the transmitter coil, the final assembly of metal jackets upset this balance. The large pick-up paralysed the amplifier for so long that no free precession could be observed. It was found that a large quantity of heat (~100 ergs) was put into the specimen by the pulsed field. Although this would not affect a single measurement, it would be quite unsatisfactory for most experiments.

These experiences have shown the difficulties of performing this type of experiment at very low temperatures especially in a metal apparatus.

A similar experiment has since been performed at liquid helium temperatures by Hahn[30] at Berkeley and also by Wheatley[31] at Illinois using an all glass apparatus.

CHAPTER 9

NUCLEAR INTERACTIONS AND RELAXATION IN METALS

The development of the theory of nuclear magnetic interactions and relaxation in solids has been stimulated primarily by the development of nuclear magnetic resonance. Nuclear magnetic interactions are so weak that macroscopic non-resonant effects of these interactions cannot be observed at temperatures obtainable by the conventional techniques. Only recently have nuclear cooling experiments allowed direct measurement of these interactions by observing the thermodynamic properties of a solid state spin system at microdegree temperatures.

It is, therefore, of interest to compare the experimentally determined interactions with those of theory and also with those obtained by resonance experiments.

Magnetic Dipole Interaction

The Hamiltonian for magnetic dipole interaction can be expressed as

$$\mathcal{H}_d = g^2\beta^2 \sum_{j>k} \left[r^{-3}\, I_j \cdot I_k - 3r^{-5} (R \cdot I_j)(R \cdot I_k) \right]$$

where R is the vector between the j th and k th nucleus, of length r. It is entirely analagous to classical dipole interaction.

Indirect Exchange Interaction

Ruderaann and Kittel[28] have proposed an interaction between nuclear moments via electrons in the conduction band of a metal. This interaction bears no resemblance to exchange interaction in ferromagnetics which is concerned with the overlap of electronic wave functions and the Pauli principle. Nuclear wavefunctions do not overlap; the exchange interaction takes place via the hyperfine coupling with the conduction

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In the free atom of a metal such as copper the hyperfine splitting is given by the Fermi or contact interaction.

$$\mathcal{H} = -(16\pi\mu_n\mu_B/3I)\,|\psi(0)|^2\, I\cdot S$$

where $|\psi(0)|^2$ is the probability density of the valance electron at the nucleus. The non-contact term is identically zero for an S state.

In the metal the valance electrons become the conduction-band electrons but retain to a large extent their S wave character. The probability density at the nuclei is slightly reduced in the metal by the spreading of the wave function.

The interaction between conduction electrons and nuclei gives an effective interaction between nuclei. A nuclear spin can scatter an electron from the region of the Fermi surface to an unoccupied level from which it can be scattered back by another nucleus. This is a virtual scattering process in which the momentum of the electron does not change.

Evaluation of this interaction involves integration over filled and empty momentum states. Rudermann and Kittel have evaluated these integrals and with several simplifying assumptions it can be shown that the interaction, having the form of an isotropic exchange interaction, is

$$\mathcal{H}_e = \sum_{j>k} A_{jk}\, I_j\cdot I_k$$

where

$$A_{jk} = \frac{\Omega^2\, m^*\, \nu^2}{2\pi\,(2I+1)^2\, r^4}\left[2kr\cos(2kr) - \sin(2kr)\right]$$

and Ω is volume associated with each atom.

m^* is the effective mass at the Fermi surface.

k is the momentum at the Fermi surface.

ν is the hyperfine splitting as modified in the metal.

Pseudo-Dipolar Interaction

This interaction[32] arises from the coupling of the nuclear moment with p-wave conduction electrons. This is a non-contact term and hence is much weaker than the indirect exchange interaction even for strong p wave concentrations. The form of the interaction turns out to be that of magnetic dipole interaction.

It is however negligably small for most of the better metals and is only of importance for heavier metals with high valancy, complicated band structure and large p-wave concentration.

Quadrupole Interaction

This is not strictly an inter-nuclear coupling, but it does affect the distribution of energy levels of the spin system. This is an interaction between the electric quadrupole moment of the nucleus and any electric field gradient at the nucleus.

For a perfect cubic metal this coupling should vanish. For a cubic metal containing defects and dislocations there will be some nuclei which experience such a coupling, but it is extremely difficult to make any numerical estimates of the overall effect.

The Thermodynamic Properties of a Spin System with Interactions

It is necessary to derive the thermodynamic properties of a theoretical nuclear spin system in a metal, on the basis of the foregoing theoretical interactions, before a comparison with experiment can be made.

The Hamiltonian for unit volume containing N nuclei of spin I in a field H can be written

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_e + \mathcal{H}_Z$$

where $\mathcal{H}_Z$ is the Zeeman term $-\sum g\beta \mathbf{I}\cdot\mathbf{H}$ and where quadrupole and pseudo-dipolar interactions have been neglected. In principle this should be solved to give the energy levels of the complete assembly of N spins. The thermodynamic properties could then be derived from a knowledge of these levels.

The solution of this problem for zero external field is prohibitively difficult. However to obtain the thermodynamic properties it is only necessary to know the partition function. This is the trace of the operator $\exp(-\mathcal{H}/kT)$ and this is invariant for any orthogonal representation describing the states of the assembly. This property allows the use of the representation which diagonolises the Hamiltonian for an assembly of non interacting nuclear spins.

This trick, due to Van Vleck[33] and Waller,[34] allows approximate evaluation of the partition function Z by expansion as a power series. For

$$Z = Tr\left[\exp(-\mathcal{H}/kT)\right]$$

$$= (2I+1)^N - Tr[\mathcal{H}]/kT + Tr[\mathcal{H}^2]/2k^2T^2$$

This allows the partition function to be evaluated at high temperatures by taking the first few terms of this series.

By symmetry $Tr[\mathcal{H}] = 0$. The largest temperature dependent term is the quadratic term. Van Vleck has shown that for magnetic dipole interaction with a small amount of isotropic exchange interaction

$$Tr[\mathcal{H}^2] = (1/6)\, N g^4 \beta^4 I^2 (I+1)^2 \sum r^{-6} (2+v^2)$$

where $v = \dfrac{A r^3}{g^2 \beta^2}$ is the small term

allowing for a small amount of isotropic exchange.

When this is evaluated for a face centred cubic lattice, neglecting exchange except for nearest neighbours, and the entropy is calculated from the partition function it is found that at high temperatures

$$S = Nk\left[\log(2I+1) - (1.2 + v^2/2) N^2 g^4 \beta^4 I^2 (I+1)^2 / k^2 T^2\right]$$

Comparison with the entropy equation in chapter 1 shows that the interaction temperature θ_n is given by

$$(1/6)\, I(I+1)(\theta_n/T)^2 = (1.2 + v^2/2) N^2 g^4 \beta^4 I^2 (I+1)^2 / k^2 T^2$$

$$\theta_n^2 = (7.2 + 3v^2) N^2 g^4 \beta^4 I(I+1) / k^2$$

For copper $v \approx 0.2$ showing that the Rudermann Kittel interaction is comparitively small. Evaluation of θ_n for copper gives a value 1.89×10^{-7} °K using the expression above.

Nuclear Resonance Line Broadening

Lines obtained by nuclear resonance in solids have a certain amount of broadening due to the effect of the interactions between the spins. In a crude way it can be considered that this is due to the fluctuating internal field and that the mean square splitting of the energy levels is approximately

$$g^2 \beta^2 I(I+1) \langle (\Delta H)^2 \rangle_{av}$$

In this case, however, we are interested in the mean square splitting of the energy levels of the nuclear spin system in zero field. In general there is no direct relationship between nuclear resonance line widths and the splitting of the energy levels of the nuclear spin system in zero field; nuclear resonance experiments and nuclear cooling experiments yield different information which cannot be compared unless the form of the interaction is known.

In the particular case of pure dipole interaction a comparison may be made. Van Vleck[35] has shown that for magnetic dipole interaction the mean square line width in zero external field is given by

$$h^2 \langle \nu^2 \rangle_{av} = 2 g^4 \beta^4 I(I+1) \sum r^{-6}$$

being 10/3 times that of the mean square line width of the primary resonance line in a strong external magnetic field. The mean square splitting of the energy levels in zero field is

$$\overline{E^2}/N = h^2 \langle \nu^2 \rangle_{av} I(I+1)/6$$

Exchange interaction gives rise to additional splitting of the levels in zero field but makes no contribution to the second moment of the resonance line.

In copper it is very likely that interactions other than magnetic dipole interaction are very small and so it is of interest to find the splitting of the levels as computed from resonance data.

Gutowsky and McGarvey[36] have made accurate measurements of the second moments of the Cu^{63} and Cu^{65} resonance lines. Making allowance for spin lattice relaxation they found that the observed line widths were 6.3 $gauss^2$ and 5.0 $gauss^2$ respectively. It can be shown that if θ_n is

defined as in chapter 1 in terms of the mean square energy level splitting then for pure dipole interaction it is related to the second moment of the resonance line in an external field by

$$(k\theta_n)^2 = (5/3)\, g^2 \beta^2 \langle (\Delta H)^2 \rangle_{av}$$

Using a mean value of 5.5 gauss^2 these resonance experiments give $\theta_n = 1.7 \times 10^{-7}$ °K.

Nuclear Spin Relaxation in Metals

The first estimate of nuclear spin relaxation times in a metal was made by Heitler and Teller[7] in 1937. They showed that the relaxation at low temperatures would be due to the hyperfine coupling with the conduction electrons, and they derived an approximate expression showing that it would be inversely proportional to the conduction electron temperature.

Korringa[8] has derived essentially the same expression on a quantum mechanical basis obtaining

$$_1T = 4\hbar E_f^2/9\pi a^2 k$$

where T is the conduction electron temperature, E_f is the Fermi energy and a is the hyperfine energy splitting as modified for the metallic wave function. For copper this expression gives a value $_1T = 1.35$ sec. deg.

The Korringa theory applies to a system of nuclei in a strong external field when the interaction energies are comparitively small. Redfield[24] has shown that this theory will not apply when the interactions are stronger than the coupling with the external field; for in a strong external field the energy depends upon the sum of terms such as $g\beta I \cdot H$ and

the energy relaxes as fast as single spins, but in zero external field the energy depends upon the sum of terms such as $g^2 \beta^2 I_i \cdot I_j$ and the energy relaxes at twice the rate for single spins.

Redfield shows that for relaxation induced by uncorrelated random fields at neighbouring lattice sites due to the conduction electrons at the Fermi surface, having a wavelength much smaller than the lattice spacing, the relaxation time in zero field should be twice that found by Korringa for strong fields. For correlated relaxation (i.e. when nearest neighbours see approximately the same fluctuating field) the ratio is somewhat different depending on the type of interaction. In the case of pure dipole interaction between spins the relaxation should be a factor three times faster than in a strong field.

Copper with mainly magnetic dipole interaction should fall between these two extremes. Experimentally it is found that $rT = 0.4$ sec.deg. which is a factor three times smaller than the experimentally determined relaxation time in strong external fields.

Nuclear "Ferromagnetism"

At some temperature of the order of θ_n the nuclear spin system will lose a considerable amount of entropy due to spontaneous long range ordering. It is of interest to consider the nature of this ordered state and the temperature at which it will occur.

The power series method for calculating the entropy as a function of temperature breaks down when $T \simeq \theta_n$ for so many terms are required in order to get useful information. As these terms become progressively much more difficult to compute the method is of little value in predicting the Curie point.

There are several "internal field" models, such as that using the Lorentz internal field, which predict a "ferromagnetic" Curie point. In this particular case "ferromagnetism" spontaneously arises when $T_c = 4\pi\lambda/3$ where λ is the volumetric Curie constant. In the case of copper $T_c = 1.9 \times 10^{-7}$ °K. However in view of the crude nature of the model this cannot be considered to be any more than an order of magnitude calculation.

Fröhlich and Nobarro[37] have proposed a theory of nuclear "ferromagnetism" in metals where the ordering arises from the hyperfine interaction with polarised conduction electrons. Using the best available data for the electron spin susceptibility, etc., this theory predicts a Curie point also at 1.9×10^{-7} °K, but again this theory is crude and cannot be expected to give a reliable figure.

The nature of dipole systems at the absolute zero has been investigated theoretically[38 39 40] by calculation of the free energies of the various configurations. These calculations were made with electron paramagnetics in mind but the results can be carried over to nuclear paramagnetics.

It is found that the "ferromagnetic" state has the lowest free energy if the dipoles are in certain prefered directions and if the shape of the specimen conforms to special requirements. This latter is one of the less fortunate results of the long range nature of magnetic dipole interaction. In an actual substance it is very likely that the ordered state will depend upon the crystallographic nature of the substance and its magnetic history.

With the $(H/T)_i$ available in these experiments only 0.9% of the spin entropy was removed and so only the first temperature dependent term in the entropy equation was found, corresponding to short range

ordering. With $(H/T)_i$ values an order of magnitude larger it should be possible to remove a substantial proportion of the spin entropy, so enabling temperatures of the order of the Curie temperature to be reached where the nature of the ordered state may be investigated.

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