# THE MAGNETIZATION OF SOME ALLOYS OF NICKEL AND THE COLLECTIVE ELECTRON THEORY OF FERROMAGNETISM

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ABSTRACT

An investigation of the magnetic properties of copper-nickel and chromium-nickel alloys and their relation to the 3d-band has been carried out. Measurements of magnetization at temperatures between room temperature and liquid helium temperatures have been made for a range of compositions near that for which ferromagnetism vanishes. A new technique for measuring magnetizations at these temperatures is described. The method makes use of the fact that the magnetization of a cylindrical sample placed in a uniform field may be completely cancelled out by a current passing through a small pitch solenoid wound on the surface of the sample. A theoretical model, based on the collective electron approach, of the copper-nickel system is analyzed with particular emphasis placed on the spontaneous magnetization at 0°K, the Curie temperature, and the electronic specific heat, all as a function of the composition of the alloys. With the simplest possible assumptions this model gives a consistent account of the thermal and magnetic properties of the ferromagnetic copper-nickel alloys by employing a rectangular density of states curve for the 3d-band. Measurements of magnetization of copper-nickel alloys of 58 and 63 atomic per cent copper and of chromium-nickel alloys of 15 and 20 atomic per cent chromium are reported. The results of our measurements on copper-nickel alloys support the theoretical model presented here. The chromium-nickel data give added information concerning the transition from ferromagnetism to nonferromagnetism in solid solutions.

Measurements of the susceptibility of vanadium at liquid helium temperatures show that a reported anomaly in the specific heat of this metal is the result of measurements in magnetic fields too low to quench the superconductivity.

## I. INTRODUCTION

As a part of a program to investigate the magnetic properties of the transition elements and their alloys in relation to the 3d-band we have studied the alloys of copper with nickel and of chromium with nickel. These two alloy systems are of interest from an experimental point of view because they show a continuous transition from ferromagnetism to nonferromagnetism as a function of the composition of the solid solutions. The copper-nickel system is of particular interest from a theoretical point of view because the simplicity of the phase diagram, the similarities of the copper and nickel atoms, and the straightforward nature of the available experimental information suggest the possibility of explaining the observed phenomena with a rather idealized model.

Some information concerning the transition from ferromagnetism is found in the magnetization data of Alder[35] for copper-nickel and Sadron[48] and Marian[45] for chromium-nickel. From these measurements it has been concluded that the spontaneous magnetization at $0^{\circ}K$ and the Curie temperature are linear functions of the concentration of the alloys and that the spontaneous magnetization vanishes at the same composition for which the Curie temperature goes to $0^{\circ}K$. These conclusions are based on a series of extrapolations from the measured quantities; for example, the spontaneous magnetization at $0^{\circ}K$ is necessarily obtained from measurements at finite temperatures. Previous measurements have been restricted to the temperatures of liquid nitrogen ($\sim 80^{\circ}K$) and above. For alloys with Curie temperatures below room temperature an extrapolation from $80^{\circ}K$ to $0^{\circ}K$ is a doubtful procedure. As the Curie temperature of pure nickel is $\sim 600^{\circ}K$, the previous data for about half of the range of compositions between pure nickel and the critical composition for which ferromagnetism disappears are inadequate.

The data of Alder have formed the basis of an early theory by Mott[58] which interprets the magnetization phenomena in alloys

in terms of simple energy band arguments. These arguments, however, do not consider the influence of the band shape on the predictions of the band model, and furthermore, these arguments are based on the extrapolation of the measurements all the way to the critical composition.

We have made an analysis of a theoretical model of the copper-nickel alloy system using the collective electron approach and have shown that the dependence of the magnetic properties on composition are, in fact, extremely sensitive to the shapes postulated for the bands. From the analysis it is seen that experimental data for the critical range of composition is necessary in order to ascertain more clearly the role of the band shape.

We have developed an apparatus particularly suited for measuring the magnetization of alloys in the range of composition for which ferromagnetism disappears. The details of this apparatus and the results of some measurements at liquid helium temperatures ($\sim$ 2 K) and above are reported here. We have measured copper-nickel alloys of the compositions 58 and 63 atomic per cent copper and chromium-nickel alloys of the compositions 15 and 20 atomic per cent chromium. From a comparison of our theoretical analysis with previous experimental results and our experimental results for the copper-nickel alloys we have concluded that a rectangular 3d-band shape is the only simple band shape for which a simple model agrees with experiment.

The work is divided into a theoretical analysis of the copper-nickel alloys (part II), an experimental section giving methods and results (part III), and, finally, discussions of the results for copper-nickel (part IV), for chromium-nickel (part V), and for vanadium (part VI).

The theoretical analysis of the copper-nickel alloys places particular emphasis on the spontaneous magnetization at $0^{0}$K, the Curie temperature, and the electronic specific heat as a function of the composition of the alloys. We start with the simplest possible assumption as to the dependence of the exchange energy on magnetization. For definiteness a one parameter family of band shapes

which contains as particular cases a rectangular band shape and a parabolic band shape is assumed. Keeping all our assumptions as simple as possible, we show that only with the rectangular band shape are we able to find agreement with experimental data available prior to the measurements which form the basis of this thesis. With more complicated assumptions, Wohlfarth[26] has been able to explain the same data using a parabolic band shape. However, additional experimental information on the spontaneous magnetization at $0^0$K as a function of composition and on the field dependence of the magnetization at $0^0$K should discriminate between the predictions of the rectangular band model and those of Wohlfarth's parabolic band model. The indicated measurements are those which are reported here, i.e. magnetization of several copper-nickel alloys in the composition range near 60 atomic per cent copper at temperatures of liquid helium. Better agreement is obtained using the rectangular band shape, with the simpler assumptions of our model, than with the parabolic band shape, even considering the more complicated assumptions of Wohlfarth's model.

In the experimental part details are given of a method of measurement which makes use of a principle which has not been sufficiently exploited heretofore, namely that the magnetization of a cylindrical sample placed in a uniform field may be completely cancelled out by a current passing through a small pitch solenoid wound on the surface of the sample. The current necessary for complete cancellation measures the magnetization and restores the uniformity of the applied field. A complete description of our apparatus which uses this principle for measurements at liquid helium temperatures is given.

The results for the copper-nickel alloys are considered with the aim of extracting the quantities to be compared with the theoretical analysis. The extraction is complicated by parasitic paramagnetism, a paramagnetism superimposed on the spontaneous magnetization, an effect which in the alloys remains equal to the effect in pure nickel, but, because of the decrease in spontaneous

magnetization of the alloys, becomes relatively more important in the analysis of the alloy data. A criterion for the presence of ferromagnetism is discussed, and a method of determining the spontaneous magnetization from the data is given. Consideration is also given to the possible influence of inhomogenities in the samples on the observed magnetizations, and it is concluded that inhomogenities, if present, are within the limits for which the results will not be altered.

From the temperature dependence of the susceptibility of the two different compositions of the chromium-nickel alloy system it is concluded that the magnetic properties of the alloys of copper and chromium with nickel are quite similar.

We have used our apparatus to measure the susceptibility of vanadium at liquid helium temperatures in order to check a reported anomaly in the specific heat of this metal below $2^{0}$K. No anomaly was found in the susceptibility in fields sufficient to quench the superconductivity, but by measuring this field as a function of temperature it became evident that much higher fields than previously supposed are required to quench the superconductivity and that the specific heat measurements were made in too low a field.

# II. COLLECTIVE ELECTRON FERROMAGNETISM AND THE COPPER-NICKEL ALLOYS

## A. Introduction

A big step toward the understanding of the behavior of ferromagnetic materials was made by Pierre Weiss* when he postulated the existence of regions of uniform spontaneous magnetization called domains. Many of the interesting properties of ferromagnetic materials arise because they are aggregates of domains whose directions of magnetization are apt to differ one from another. A problem of fundamental interest, however, is to explain the spontaneous magnetization of the individual domains, that is, to give an atomic origin for the magnetic moments and to account for the cooperative alignment among the atomic moments. Extensive experiments on the gyromagnetic effect and the discovery of electron spin by Goudsmit and Uhlenbeck showed that the origin of the magnetic moment is that associated with the electron spin. The cooperative effect was treated phenomenologically by Weiss by postulating an intense internal molecular field. The quantum explanation of this internal molecular field has followed along two different lines which reflect two different ways of approximating the solution of the Schrodinger equation for electrons in crystals, namely, the Heitler-London-Heisenberg or atomic point of view, and the collective electron or band approach due primarily to Bloch, Slater, and Stoner.

1. The Band Model - In this work we will consider some** of the magnetic properties of electrons in metals and alloys using the band model***. The starting point for this model is the solution

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*Several interesting review articles are listed as such in the bibliography[5-8].

**Diamagnetic contributions will not be considered.

***For a fuller discussion of the band model see Seitz[4].

of the eigenvalue problem for one electron in a potential well. The assumption is made that the valence electrons in a metal will distribute themselves among the eigenstates of the one electron problem; the energy of the system being the sum of the eigenvalues of the individual eigenstates. The effects of the electrons on one another are neglected except that, as they have spin 1/2, they must obey Fermi-Dirac statistics. The lowest energy state of the system then is the state in which the N electrons find themselves with an electron of each of the two possible spin directions in each of the N/2 one electron states of lowest energy. Such a state of the system is clearly nonmagnetic as the spins and hence the associated magnetic moments cancel in pairs.

The problem of what happens when an external magnetic field is applied to a metal is attacked by considering that all the electrons of one spin direction form a gas which can trade electrons with a gas formed of all the electrons of the opposite spin direction. The electrons with their moments in the direction of the field will have their energies lowered while those of the opposite spin direction will have their energies raised by the application of the field. The energy of the system can be lowered by the transfer of electrons from one gas to the other as this will decrease the magnetic energy, but the transferred electrons must undergo an increase in kinetic energy because all available states have a higher zero field energy than the zero field energy of the states from which these electrons came. Electrons will be transferred until the two effects balance. The important quantity in the treatment of this equilibrium is the density of states per unit energy range. This may be seen by considering the transfer of one electron after a few, say n, have already been transferred. In this case the decrease in the magnetic energy will be given by $2\mu H$, where $\mu$ is the magnetic moment of the electron, H is the applied field, and the factor 2 occurs because it is the net change in spin which is effective. The accompanying increase in the kinetic energy is given by $n/\frac{\partial n}{\partial E}$ where $1/\frac{\partial n}{\partial E}$ is the rate of increase of energy of the single spin system per electron added. Clearly for weak fields the process must stop when $n = 2\mu H \left(\partial n/\partial E\right)$. For strong

fields, if more than just a few electrons are transferred it will be necessary to know in detail the density of states per unit energy range as a function of energy. It is possible to discuss completely the magnetic and thermal properties of this model, if it is assumed that: The density of states curve is unaffected by the way in which the electrons are distributed among the possible eigenstates of the one electron Schroedinger equation.

The model is more sophisticated than implied at the start of this discussion because the interaction of the electron with the smeared out field of all the other electrons in the band is considered as well as the influence of the periodic potential of the lattice. The field of all the other electrons and the periodic potential affect the form of the density of states curve markedly, but do not alter the basic concept of the one-electron picture. The above assumption is equivalent to saying that the smeared out field of all the other electrons in the band is independent of the group of eigenstates which they occupy.

Certain ranges of eigenvalues are excluded as solutions of the Schroedinger equation with a periodic potential; hence the density of states goes to zero for these ranges and the available states lie in the so-called allowed energy bands. In an insulator the available states in a given band are either all filled or none of them are occupied; in a conductor at least one band contains fewer electrons than eigenstates. Calculations of the distribution of electrons among the available states of a conduction band as a function of temperature and external magnetic field using the above assumption have succeeded in explaining the temperature independent paramagnetism and the contribution to the specific heat linear in the temperature found for most conductors.

2. Ferromagnetism in the Band Model - The above model cannot account for such cooperative phenomena as superconductivity and ferromagnetism. For this there must be a more direct interaction between pairs of electrons than is indicated by the smeared out potential. An interaction disregarded above follows from the requirement that the wave-function of the system must be

antisymmetric for the exchange of the coordinates of any two electrons. This leads to a correlation of the positions of pairs of electrons having parallel spin direction. If this correlation tends to separate electrons in the same spin state, the energy from coulomb repulsion will be less between electrons of parallel spins than between electrons with antiparallel spins. The presence of an excess number of spins in one direction, which would increase the number of pairs of electrons with parallel spins, would then tend to decrease the energy of the system. This decrease in energy, given the name exchange energy, has not been considered in the above form of the model. If it were considered, it would have to be weighed against the increase in kinetic energy of the electrons which necessarily accompanies an increase in the net number of spins in one direction. Clearly this presents the possibility of the lowest energy state in the absence of an external field being one in which there is a net number of spins in one direction. The presence of such a spontaneous magnetization is by definition ferromagnetism. The inclusion of the exchange energy into the band model was originally proposed by Slater[15] and as developed by Stoner[17-25] is given the name "Collective Electron Ferromagnetism."*

To treat quantitatively the problem of ferromagnetism on the basis of the band model it is necessary to know the density of states as a function of energy and the way that the exchange energy depends on the number of parallel spins. Once these are known, then the application of Fermi-Dirac statics to the system (consisting of a gas of electrons of plus spin and a gas of electrons of minus spin which are free to trade electrons) gives the degree of magnetization as a function of temperature and applied field.

3. Application to the Transition Metals - The comparison with experiment is to be found in the ferromagnetic elements, nickel,

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*A list of pertinent papers in the development of Collective Electron Ferromagnetism is given as a group in the bibliography[9-31].

cobalt, iron, and gadolinium and in alloys containing one or more of the elements of the first transition series of the periodic table. Nickel, cobalt, and iron come at the end of the first transition series. Some knowledge of the density of states as a function of energy is found from the calculations of Slater[14,15] and Krutter[11] for copper which follows nickel in the periodic table. The density of states curve shows two overlapping bands, one made up of wave functions of primarily "s" character and the other made up of wave functions of primarily "d" character. The latter, the so-called d-band, has a high density of states, containing enough states for 10 electrons per atom in a range of energies small compared to the range of energies available in the low density of states s-band. In copper, the d-band is filled and there is one electron per atom in the s-band. It has been suggested that the band shapes for nickel are the same as those calculated for copper. The difference between nickel and copper is that there is one less electron per atom. Then in nickel the s-band will have only a fraction of an electron per atom and the d-band will have less than 10 electrons per atom. This is equivalent to saying that there are holes in the d-band. For nickel the number of holes in the d-band must be equal to the number of electrons in the s-band. Mott[58] has suggested that the holes in the d-band account for the ferromagnetism of iron, cobalt, and nickel. The magnetic moment found for nickel is 0.6 Bohr magnetons per atom. If it is assumed that all the holes in nickel are of one spin direction, it follows that there are 0.6 holes per atom in nickel. Furthermore, it has been pointed out by Mott that the data of Alder[35], showing that the magnetic moments of copper-nickel alloys decrease by one electron moment for each nickel atom replaced by copper, gives evidence that an effect of alloying is to decrease the number of holes in the d-band. This leads to an attempt to apply the collective electron theory to the number of holes in the d-band in order to treat theoretically the ferromagnetism of the transition elements and their alloys*.

In applying the collective electron theory to the copper-nickel alloy problem we assume:

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* The ferromagnetism of the alloys is discussed in a review article by Goldman[57].

1. The number of electrons in the d-band is independent of field and temperature, despite the presence of an overlapping s-band.

2. The density of states curve is unaffected by the way in which the electrons distribute themselves among the various states.

3. The density of states curve is unaffected by the total number of electrons in the band.

4. The exchange interaction is the same for all pairs of electrons with parallel spin directions.*

5. The exchange interaction between any pair of electrons with parallel spin directions does not change with composition.

6. The density of states $\nu(\epsilon)$ versus energy $\epsilon$ is given by an expression of the form

$$\nu_p(\epsilon) = C\,\epsilon^p \qquad p \geq 0 \tag{1}$$

This expression includes the rectangular band ($p=0$) and the parabolic band ($p=1/2$) as part of a whole family of band shapes.

In what follows we first treat the equilibrium of electron gases of opposite spin direction using assumptions 1, 2, 4, and 6. A general expression for the magnetization as a function of field and temperature is given with particular attention focussed on the magnetization at $0^{\circ}K$ and the Curie temperature as a function of two variables -- the band shape and the exchange interaction between any pair of electrons with parallel spin direction. The model is then applied to the alloy problem using all the above assumptions. The magnetization of the alloys is found explicitly in terms of the number of holes in the d-band. The variation of the number of holes in the d-band with fractional copper concentration is discussed for the case where electrons enter the s-band as well as the d-band on alloying. The theory is compared with previously available experimental data and it is shown that the rectangular band shape ($p=0$) gives a consistent picture of the ferromagnetic copper-nickel alloys. It is pointed out that Wohlfarth[26] has been able to give a consistent picture of the ferromagnetic copper-nickel

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*A second order correction to this assumption is also considered.

alloys on the parabolic band model by introducing complications not present in the rectangular band model. However, we show that his treatment predicts a field dependence of the magnetization at $0^{\circ}K$. We have tested this prediction by a suitable experiment, and in part IV after considering the data of part III we conclude that the parabolic band picture of Wohlfarth is not consistent with our new data whereas the rectangular band model as described in this part of the work with very simple assumptions is shown to give a consistent description of not only the magnetic but also the thermal properties of the ferromagnetic copper-nickel alloys.

## B. Equilibrium of Electrons of Opposite Spin Directions

1. Magnetization at $0^{\circ}K$ - The arguments presented here are based on the statement that, for two gases of electrons of opposite spin directions which are free to trade electrons, the equilibrium state at $0^{\circ}K$ is the one in which the total energies of the electrons in the highest occupied energy states of each gas are equal. The energy of an electron in the ith energy state is given by the sum of $\epsilon_i$, the kinetic energy of the electron in the ith state, plus the energy from the interaction of the electron moment, $\mu$, with the applied field (or the interaction of the moment with an internal field).

The kinetic energy of the electron in the highest occupied energy state for the band of $\uparrow$ spin is given by $\epsilon_o^{\uparrow}$ in the expression

$$N^{\uparrow} = \int_0^{\epsilon_o^{\uparrow}} \nu(\epsilon)\, d\epsilon \qquad (2)$$

where $\nu(\epsilon)$ is the density of states curve for the band and $N^{\uparrow}$ is the number of electrons of $\uparrow$ spin. There is a similar expression for the band of $\downarrow$ spins. For density of states curves of the form of assumption (1), equation (2) becomes

$$N^{\uparrow} = \frac{C}{p+1} (\epsilon_o^{\uparrow})^{p+1} \qquad (3)$$

with a similar expression for the band of spins. It is useful to describe the band in terms of an energy parameter $\epsilon_o'$, the kinetic energy of the highest occupied state in the absence of any field.

$\epsilon_0'$ is given by $$\frac{N}{2} = \frac{C}{p+1}(\epsilon_0')^{p+1} \tag{4}$$

where $N = N^{\uparrow} + N^{\downarrow}$ is the total number of electrons in the whole band. Elimination of C between equations (3) and (4) gives

$$N^{\uparrow} = \frac{N}{2}\left(\frac{\epsilon_0^{\uparrow}}{\epsilon_0'}\right)^{p+1} \tag{5}$$

with a similar expression for $N^{\downarrow}$.

The above relations, particularly equation (5), will be used in applying the condition of equilibrium to electrons; first in the presence of an external magnetic field; next in the presence of an exchange field, but without the external field; and finally to the combined external and exchange field.

The total energy of an electron in the presence of an external magnetic field, H, is given by $\epsilon_i - \mu H$ for electrons whose moments are in the direction of the field and by $\epsilon_i + \mu H$ for electrons whose moments are opposite to the direction of the field. Our condition of equilibrium then gives

$$\epsilon_0^{\uparrow} - \mu H = \epsilon_0^{\downarrow} + \mu H \tag{6}$$

where, as will be recalled from above, $\epsilon_0^{\uparrow}$ and $\epsilon_0^{\downarrow}$ are the kinetic energies of the highest occupied states of $\uparrow$ spin and $\downarrow$ spin respectively. From equations (5) and (6) we may obtain the number of electrons in each gas as a function of field, namely

$$\frac{\mu H}{\epsilon_0'} = \frac{1}{2}\left(\frac{2N^{\uparrow}}{N}\right)^{\frac{1}{p+1}} - \frac{1}{2}\left(\frac{2N^{\downarrow}}{N}\right)^{\frac{1}{p+1}}$$

It is more informative to put this expression in terms of the magnetization, $\mu(N^{\uparrow}-N^{\downarrow})$. For simplicity we work with the reduced magnetization $\zeta = (N^{\uparrow}-N^{\downarrow})/N$, hence we get

$$\frac{\mu H}{\epsilon_0'} = \frac{1}{2}(1+\zeta)^{\frac{1}{p+1}} - \frac{1}{2}(1-\zeta)^{\frac{1}{p+1}} \tag{7}$$

If we inquire as to the field necessary to align all the holes in one spin direction, we find, setting $\zeta = 1$, that

$$\frac{\mu H}{\epsilon_0'} \geq 2^{-\frac{p}{p+1}} \tag{8}$$

which gives for the rectangular band ($p = 0$) that $\frac{\mu H}{\epsilon_0'} \geq 1$ for complete alignment and for the parabolic band, ($p = 1/2$) that $\frac{\mu H}{\epsilon_0'} \geq 2^{-\frac{1}{3}} = .794$ for complete alignment.

The step necessary to introduce ferromagnetism is the inclusion of the "molecular" field, that is, an exchange effect which acts as an internal field. The simplest possible assumption is that the exchange introduces a term in the energy of the whole system which

depends quadratically on the net magnetization, i.e., a term of the form $-\frac{J}{4}(N^{\uparrow}-N^{\downarrow})^2$. In order to apply the condition of equilibrium we consider the transfer of one electron from one gas to the other. The change of this quadratic term in the total energy of the gas will be

$$\frac{\partial}{\partial(N^{\uparrow}-N^{\downarrow})}\left[-\frac{J}{4}(N^{\uparrow}-N^{\downarrow})^2\right]\cdot 2 = -J(N^{\uparrow}-N^{\downarrow})$$

The factor 2 appears because $N^{\uparrow}-N^{\downarrow}$ changes by 2 on transferring one electron. This change in the energy of the system as a whole is considered to be part of the total energy of the individual electron transferred.* The total energy of the electron in the occupied state of highest energy in the gas with the larger number of electrons will be $\epsilon_0^{\uparrow} - J(N^{\uparrow}-N^{\downarrow})$. The total energy of the electron in the occupied state of highest energy in the gas of fewer number of electrons will be $\epsilon_0^{\downarrow}$. The equation for equilibrium becomes

$$\epsilon_0^{\downarrow} = \epsilon_0^{\uparrow} - J(N^{\uparrow}-N^{\downarrow})$$

If we wish to introduce the exchange energy in slightly different words we could also get

$$\epsilon_0^{\downarrow} - JN^{\downarrow} = \epsilon_0^{\uparrow} - JN^{\uparrow}$$

or

$$\epsilon_0^{\downarrow} + \frac{J}{2}(N^{\uparrow}-N^{\downarrow}) = \epsilon_0^{\uparrow} - \frac{J}{2}(N^{\uparrow}-N^{\downarrow})$$

Since we have not introduced an external field in dealing with the exchange, any magnetization which results from the application of these equations is a spontaneous magnetiz ation. We introduce the symbol $\zeta_0$ to denote the reduced spontaneous magnetization, giving

$$\epsilon_0^{\downarrow} = \epsilon_0^{\uparrow} - JN\zeta_0 \qquad (3)$$

It follows from equations (5) and (9) that

$$\frac{JN}{2\epsilon_0'}\zeta_0 = \frac{1}{2}(1+\zeta_0)^{\frac{1}{p+1}} - \frac{1}{2}(1-\zeta_0)^{\frac{1}{p+1}} \qquad (10)$$

For convenience in describing the band shape we have again introduced the parameter, $\epsilon_0'$, which has the meaning of the energy of the highest occupied state in the absence of any exchange or applied field.

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*The approach followed here is essentially that of Stoner [23]. A fuller treatment of this point is found in the work of R.S. Smith [16] and in Appendix i.

The values of $\frac{JN}{2\epsilon_0'}$ large enough to obtain complete spontaneous magnetization, that is $\zeta_0 = 1$, are

$$\frac{JN}{2\epsilon_0'} \geq 2^{-\frac{2}{p+1}} \tag{11}$$

which for p = 0 gives $JN/2\epsilon_0' \geq 1$

and for p = 1/2 gives $JN/2\epsilon_0' \geq 2^{-\frac{2}{3}} = .794$

The values of $\frac{JN}{2\epsilon_0'}$ sufficient to cause one electron to flip its spin direction, that is $\zeta_0 = \frac{2}{N}$ are

$$\frac{JN}{2\epsilon_0'} = \frac{1}{p+1} \tag{12}$$

which for p = 0 gives $JN/2\epsilon_0' = 1$

and for p = 1/2 gives $JN/2\epsilon_0' = \frac{2}{3} = .667$

This shows one important difference between the rectangular and the parabolic band, namely that there is no value of the parameter $JN/2\epsilon_0'$ which for the rectangular band will give an incomplete spontaneous magnetization at 0°K. The value of $\zeta_0$ for a rectangular band is either 0 or 1, whereas for the parabolic band (and all value of p>0) $\zeta_0$ may take values from 0 to 1 as the parameter $JN/2\epsilon_0'$ goes between the limits given by

$$\frac{1}{p+1} \leq \frac{JN}{2\epsilon_0'} \leq 2^{-\frac{p}{p+1}} \tag{13}$$

The general expression for the magnetization at 0°K follows by combining the above arguments for the external field with those for the exchange field. The condition for equilibrium becomes

$$\epsilon_0^{\downarrow} + \mu H = \epsilon_0^{\uparrow} - \mu H - JN\zeta \tag{14}$$

from which it follows using (6) that

$$\frac{\mu H}{\epsilon_0'} + \frac{JN}{2\epsilon_0'} = \phi_p(0,\zeta) \tag{15}$$

where

$$\phi_p(0,\zeta) \equiv \tfrac{1}{2}(1+\zeta)^{\frac{1}{p+1}} - \tfrac{1}{2}(1-\zeta)^{\frac{1}{p+1}}$$

2. Magnetization as a Function of Temperature - The above relations apply to 0°K. In order to discuss $\zeta$ for T > 0°K it is necessary to minimize the free energy of the system rather than the internal energy as was done above. The magnetization as a function of temperature is treated in Appendix i; the result is that the magnetization is given by

$$\frac{\mu H}{\epsilon_0'} + \frac{JN}{2\epsilon_0'}\zeta = \phi_p\left(\frac{kT}{\epsilon_0'}, \zeta\right) \tag{16}$$

where the functional form of $f_p\left(\frac{KT}{\epsilon_0'}, \zeta\right)$ depends only on the band shape parameter p. We have already evaluated $f_p(0, \zeta)$ explicitly in equation (15). At the higher extreme of temperature, we must approach Boltzman statistics; hence as $\frac{KT}{\epsilon_0'}$ becomes large compared to unity

$$f_p\left(\frac{KT}{\epsilon_0'}, \zeta\right) \longrightarrow \frac{KT}{\epsilon_0'} \tanh^{-1} \zeta$$

The spontaneous magnetiz ation will be given by setting H = 0 and solving for $\zeta$ as a function of temperature and the exchange parameter. In particular we are interested in the Curie temperature, the temperature at which the spontaneous magnetization goes to zero. This is given by $T_c$, the temperature for which

$$\lim_{\zeta \to 0} \frac{1}{\zeta} \cdot f_p\left(\frac{kT_c}{\epsilon_0'}, \zeta\right) = \frac{JN}{2\epsilon_0'} \qquad (17)$$

In general this relation must be given in tabular form. However, we note that as ferromagnetism disappears when $\frac{JN}{2\epsilon_0'} \to \frac{1}{p+1}$, $T_c$ must go to zero as $\frac{JN}{2\epsilon_0'} \to \frac{1}{p+1}$ . For $\frac{KT}{\epsilon_0'} > 1$ we get $\frac{JN}{2\epsilon_0'} = \frac{KT_c}{\epsilon_0'}$.

3. The Exchange Term - The exchange effect was introduced above by stating that the total energy of the system contains a term quadratic in the magnetization, namely $-\frac{J}{4}(N^{\uparrow} - N^{\downarrow})^2$. This expression follows from the assumption that there is an exchange interaction between all pairs of mutually parallel electrons which is the same for all pairs and represents a decrease in the energy of the system. If this interaction between each pair is given by -J, then the total interaction will be

$$E_J = -J\left(\frac{N^{\uparrow}(N^{\uparrow}-1)}{2} + \frac{N^{\downarrow}(N^{\downarrow}-1)}{2}\right)$$

neglecting one against N and rewriting gives

$$E_J = -\frac{J}{4}\left[(N^{\uparrow}+N^{\downarrow})^2 + (N^{\uparrow}-N^{\downarrow})^2\right]$$

The first term is a constant and the second term gives the dependence of the total energy on the magnetization. Hence

$$E_J = \text{const} - \frac{J}{4} N^2 \zeta^2 \qquad (18)$$

where as before N is the total number of electrons in the band.

A justification of the assumption of the equality of the exchange interaction between all pairs of electrons has been attempted by Wohlfarth[31] based on the "tight binding" approximation. The arguments involve overlap integrals whose properties can only be

surmised, but it is his contention that the equality is a good first approximation and that the inclusion of a term in $\zeta^4$ gives an even better approach to reality.

This would then require an expression of the form

$$E_s = -\frac{J}{4} N^2 \zeta^2 \left(1 + \frac{A}{2}\zeta^2\right) \tag{19}$$

When put into the general expressions equation (10) becomes

$$\frac{JN}{2\epsilon_0'}\zeta_0(1+A\zeta_0^2) = \tfrac{1}{2}(1+\zeta_0)^{\frac{1}{p+1}} - \tfrac{1}{2}(1-\zeta_0)^{\frac{1}{p+1}} \tag{20}$$

It may be seen on examination that $\zeta_0$ may be double-valued for certain values of $JN/2\epsilon_0'$ and A. . The value of A will not influence the condition on $JN/2\epsilon_0'$ for flipping one electron's spin from the unmagnetized state, but it will change the condition on $JN/2\epsilon_0'$ for complete alignment. The condition for complete alignment becomes

$$\frac{JN}{2\epsilon_0'} \geq \frac{2^{-\frac{p}{p+1}}}{1+A} \tag{21}$$

In order that there be no values of $JN/2\epsilon_0'$ such that there is incomplete alignment at $0^\circ$K it is necessary [see equation (11) that]

$$\frac{2^{-\frac{p}{p+1}}}{1+A} \leq \frac{1}{p+1}$$

or

$$A \geq (p+1)2^{-\frac{p}{p+1}} - 1 \tag{22}$$

this gives for $p = 0$ $\quad A \geq 0$ as we already knew,

and for $p = 1/2$ $\quad A \geq .19$

C. Model for the Copper-Nickel Alloys

The above is a formal treatment of a gas of electrons. The problem of interest is the study of ferromagnetic transition elements with their overlapping s- and d-bands. In order to make the jump from the formal to the physical it is necessary to assume that the above results are applicable directly to the electrons in the d-band of a transition metal. In so doing we assume that the presence of the s-band determines the number of electrons in the d-band as a function of the temperature, magnetization, or field or exchange parameter for a given composition.

The d-band of the ferromagnetic metals is almost filled, hence it is convenient to treat the holes in the d-band as the carriers of the magnetic moment. The above arguments are directly applicable to the holes; it is understood that the energies are measured from the top of the band downwards.

The process of alloying copper to nickel increases the number of electrons in the d-band or can be said to decrease the number of holes. Hence we will be interested in N(c), the number of holes in the d-band, as a function of c, the fractional copper concentration. The similarity of the atoms of copper and nickel makes plausible the following further assumptions as a first approximation:

1. $\nu(\epsilon)$, the density of states curve is unchanged on alloying.

2. $J$, the exchange interaction between a pair of parallel electrons is unchanged on alloying.

A complete discussion of the alloy problem follows from these assumptions once N(c) and $(JN/2\epsilon_0')_c$ are known. $\epsilon_0'(c)$ is the energy of the electron in the highest occupied energy state in the absence of applied or exchange field as a function of concentration. With a fixed band shape constant C, $\epsilon_0'(c)$ is a simple function of N(c). It follows from equation (4), that

$$\epsilon_0'(c) = \epsilon_0'(0)\left[N(c)/N(0)\right]^{1/(p+1)} \tag{23}$$

where c = 0 refers to pure nickel. Hence $JN/2\epsilon_0'$ as a function of composition can be written as

$$\left(JN/2\epsilon_0'\right)_c = \left(JN/2\epsilon_0'\right)_0\left[N(c)/N(0)\right]^{\frac{p}{p+1}} \tag{24}$$

where it is assumed that J is constant on alloying. From equation (11) we find that <u>complete spontaneous magnetization will exist</u> up to a concentration c' given by

$$\left(JN/2\epsilon_0'\right)_0\left[N(c')/N(0)\right]^{\frac{p}{p+1}} = 2^{-\frac{p}{p+1}} \tag{25}$$

and from equation (12) we find that <u>all spontaneous magnetization will disappear</u> at c" given by

$$\left(JN/2\epsilon_0'\right)_0\left[N(c'')/N(0)\right]^{\frac{p}{p+1}} = \frac{1}{p+1} \tag{26}$$

The above equations make clear an important difference between a rectangular band and a parabolic band (or any other band with $p > 0$). For the rectangular band $\frac{p}{p+1} = 0$ so that $JN/2\epsilon_0'$ is independent of composition. Hence ferromagnetism must exist as long as there are holes in a rectangular d-band. The spontaneous magnetization will decrease linearly with the number of holes. As $JN/2\epsilon_0'$ is a constant, then from equation (19) so must be $kT_c/\epsilon_0'$ or as $T_c/\epsilon_0' \sim T_c/N$ the Curie temperature will also decrease linearly with the number of holes in the d-band. For the parabolic band, however, the situation is much more complicated. For a

range of compositions up to c' the spontaneous magnetization will decrease linearly with the number of holes. From c' to c" the spontaneous magnetization must drop more rapidly than linearly and above c" there will be no ferromagnetism even though above c" there will still be holes in the d-band as N(c") is always greater than zero for anything but a rectangular band. We have from equation (22)

$$N(c'') = N(0)\left[(p+1)\frac{J\,N(0)}{2\,\epsilon_0'(0)}\right]^{-\frac{p+1}{p}} \qquad (27)$$

which for a parabolic band takes the form

$$N(c'') = N(0)\left[\frac{3}{2}\frac{J\,N(0)}{2\,\epsilon_0'(0)}\right]^{-3}$$

If, for instance, in pure nickel the value of the parameter $\frac{JN}{2\epsilon_0'}$ was just sufficient to give complete spontaneous magnetization, that is $\frac{JN}{2\epsilon_0'} = 2^{\frac{-p}{p+1}}$, we would get

$$N(c'') = 2\,N(0)\,[p+1]^{-\frac{p+1}{p}}$$

which for a parabolic band gives

$$N(c'') = .58\,N(0)$$

That is, ferromagnetism disappears before half of the holes are filled up.

The variation of the Curie temperature with the number of holes can not be obtained in a simple closed form as it is necessary to solve equation (19). It can be shown, however, that Tc will not vary linearly with the number of holes in the d-band.

The above discussion concerns the variation of the magnetic properties as a function of the number of holes in the d-band without specifying the dependence of the number of holes on fractional copper concentration. If the overlap of the s-band and d-band is ignored so that every copper atom decreases the number of holes by one, the dependence of the number of holes on c would be given by

$$N(c) = N(0) - c \qquad (28)$$

where N(0) is as above the number of holes in the d-band of pure nickel. It seems more reasonable to suppose that as copper is added to nickel a certain fraction of each electron enters the d-band and the rest goes into the s-band. Furthermore, this fraction should depend on the ratio of the density of states in the two bands. For the s-band it is a good approximation to take the density of states as constant over the range of copper concentrations giving ferromag-

netism. As the density of states is exactly constant in the rectangular d-band, it follows that for this band a practically constant fraction of each electron enters the d-band. This fraction is assumed to be given by $r/1+r$ where r is the ratio of density of states of one spin direction in the rectangular d-band to the density of states of both spin directions in the s-band. Only half of the d-band is available because, as shown above, as long as there are holes in a rectangular band there is complete spontaneous magnetization; hence only holes of one spin direction are available. We then have that

$$N(c) = N(0) - \frac{r}{1+r} c \qquad (29)$$

As the number of holes decrease linearly with concentration so must the spontaneous magnetization and the Curie temperature.

For the other band shapes the situation is more complex and the dependence of N(c) on c is no longer linear.

D. Model Compared with Previous Experimental Results

The data pertinent for the alloy problem are those of Alder[35] and of Oliver and Sucksmith[46]. Their data are discussed in some detail in part IV of this work, but for the present it is sufficient to say that up to a fractional concentration of copper equal to .4 their data indicate a linear decrease in spontaneous magnetization at $0^{\circ}K$ with composition and a linear decrease in Curie temperature with composition. Both lines extrapolate to zero at a fracticnal concentration $c \simeq .6$. The value of the spontaneous magnetization of nickel has been found to be .6 Bohr magnetons per atom.

1. The Rectangular Band - If the rectangular d-band is considered, ignoring the effects of overlap with the s-band, the agreement with these data is excellent. N(0) becomes .6 and the number of holes decreases linearly to zero at a fractional concentration $c = .6$. From the above discussion this means that the spontaneous magnetization and the Curie temperature will also decrease linearly to zero at $c = .6$. The predictions of the rectangular band shape as to the temperature dependence of the spontaneous magnetiz ation and the paramagnetic susceptibility above the Curie temperature have been compared with the experimental data on pure nickel

by Wohlfarth[30]. The agreement with the susceptibility is good but not so the agreement with the temperature dependence of the spontaneous magnetization. The situation regarding the agreement of the parabolic band shape with the susceptibility and the temperature dependence of the spontaneous magnetization is the same as for the rectangular band. Hunt[10], however, has considered the parabolic band shape with the inclusion of the $\zeta^4$ term in the exchange energy with A = .10 and has found excellent agreement with the data for pure nickel and the low copper concentration copper-nickel alloys. The use of the $\zeta^4$ term in the rectangular band model has not been compared with experiment. It is clear, however, that if it produces a correction in the right direction for the parabolic band it will do so for the rectangular band. It is interesting to note that the inclusion of the $\zeta^4$ term cannot influence the Curie temperature for any band shape, and as long as there is complete spontaneous magnetization it cannot influence the value of the spontaneous magnetization at $0^{\circ}K$. Hence the inclusion of the $\zeta^4$ term will still give agreement with those quantities.

Finally it is necessary to consider the effect of the overlapping s-band. This appears to destroy the agreement because the decrease in the number of holes will be less than one per copper atom. In order to explain the .6 Bohr magnetons per atom in nickel it is necessary to have the number of holes decreasing linearly to zero at a composition greater than c = .6; how much greater depends on r, the ratio of the density of states in the two bands. There is evidence, however, that the gyromagnetic ratio for the d-electrons in nickel is not 2 but some 10 per cent smaller. This indicates that about 10 per cent of the moment comes from orbital contributions. This would give $N(0) \cong .54$. The ratio of the density of states of the s-band and d-band can be estimated from the electronic specific heat of the copper-nickel alloys as measured by Keesom and Kurrelmeyer [42]. Their data show that the electronic specific heat of the alloys up to c = .58 is practically constant and equal to 10 times the electronic specific heat of pure copper. Not only does the constant specific heat up

to c = .6 agree with the rectangular band model, but the value it gives for r, namely r = 10 gives from (29)

$$N(c) = .54 - .9c \qquad (30)$$

or that N(c) goes linearly to zero at c = .6.

The final bit of previously available evidence for the rectangular band model is the comment of Keesom and Kurrelmeyer[42] that their c = .58 alloy was ferromagnetic at liquid helium and liquid hydrogen temperatures.

2. The Parabolic Band - As mentioned above, the number of holes in the d-band, the spontaneous magnetization at 0°K, and the Curie temperature are all nonlinear functions of the fractional concentration of copper for anything but the rectangular band model. Wohlfarth[26] has been able to explain previously existing data by assuming a value of r = 10 but, in contrast to what has been said above, J is assumed to vary with copper concentration. Though the variation is only implied it can be shown that his assumptions are equivalent to a variation of J given by

$$J = J_0\left(1 + \frac{2}{5}c - \frac{8}{15}c^2 + \frac{29}{12}c^3\right)$$

Though the combination of all these nonlinear functions to give practically linear decreases in the Curie temperature and the spontaneous magnetization at 0°K as functions of concentration which go to zero at c = .6 may not be as fortuitous as we believe, there is one necessary consequence of the parabolic band model with Wohlfarth's choice of parameters which can be checked experimentally. This is the incomplete spontaneous magnetization at 0°K. If there is incomplete spontaneous magnetization at 0°K, it will then be possible to increase the magnetization with an applied external field. Wohlfarth himself has pointed this out and has estimated the effect for c = .55. At 0°K we have from equation (15)

$$\frac{\mu H}{\epsilon_0'} + \frac{JN}{2\epsilon_0'} = \frac{1}{2}\left[(1+s)^{\frac{1}{p+1}} - (1-s)^{\frac{1}{p+1}}\right]$$

which for a parabolic band gives

$$\frac{\mu H}{\epsilon_0'} + \frac{JN}{2\epsilon_0'} = \frac{1}{2}\left[(1+s)^{2/3} - (1-s)^{2/3}\right] \qquad (31)$$

This has been solved graphically and the results are tabulated in table I using the parameters chosen by Wohlfarth to fit the parabolic band to data of Alder. It should be noted that the table gives

an increase with composition not only for the ratio of the change in magnetization between zero field and 10KG to the spontaneous magnetization in zero field, but also an increase in the actual change of magnetization between zero field and 10KG. Such effects should be easily discernible as the magnetization at 10KG for $c = .58$ is twice the spontaneous magnetization. This can be seen from table I.

Measurements of magnetization in the liquid helim temperature range on several alloys of composition near $c = .6$ have been made to check the extrapolation of the results from the lower copper concentrations and to decide whether such an effect as predicted by Wohlfarth's model is to be found. These measurements and the method of measurements are described in part III of this work and the results will be discussed in part IV. The results are found to support the arguments for the rectangular band model.

Table I

The increase of $\zeta$ with field at $0^{\circ}K$ for various compositions using parameters chosen by Wohlfarth [26] to explain the linear decrease in Curie temperature and spontaneous magnetization at $0^{\circ}K$ with fractional concentration of copper in nickel.

| c | $\zeta_0$ | N(c) | $\epsilon_0' \times 10^{14}$ | $\mu H/\epsilon_0']_{H=10KG}$ | $\zeta_{10KG}$ | $\Delta\zeta$ | $\frac{\Delta\zeta}{\zeta_0}$ |
|---|---|---|---|---|---|---|---|
| .50 | .56 | .1544 | 11.5 | .00080 | .580 | .020 | .036 |
| .55 | .35 | .1117 | 9.5 | .00095 | .405 | .065 | .186 |
| .58 | .14 | .0860 | 8.0 | .00110 | .295 | .155 | 1.00 |
| .60 | .00 | .0698 | 7.0 | .00130 | .292 | .292 | --- |

Wohlfarth's parameters, which follow from his assumed dependence of J on composition and ratio of density of states in the d-band to density of states in the s-band, are $\zeta_0$, N(c), and $\epsilon_0'$. The last three columns give the reduced magnetization in a field of 10KG, the difference between this magnetization and the spontaneous magnetization, $\Delta\zeta$, and the ratio of this difference to the spontaneous magnetization, respectively.

# III. MAGNETIZATION MEASUREMENTS AT LIQUID HELIUM TEMPERATURES

When this work was first undertaken the purpose was primarily to develop an apparatus for obtaining information about the magnetic behavior of a group of alloys which show a transition from ferromagnetism to nonferromagnetism through a composition change without an accompanying phase change. The transitions would then be characterized by the Curie temperatures of the ferromagnetic alloys going to $0^{\circ}K$ for a certain composition, as well as by a decrease in the saturation magnetization. The interesting measurements would then be those at very low temperatures. The apparatus to be described in this part of the work was designed to measure magnetizations at liquid helium temperatures on alloys whose magnetiza tions do not exceed a certain value. As this apparatus is novel both in principle and application, it is described in some detail.

The interest in the copper-nickel problem, in particular as presented in part II, led to a desire to measure magnetizations slightly larger than anticipated in the original design. For this reason a modification of the experimental procedure was necessary to obtain the data on a 58 atomic per cent copper alloy at liquid helium temperatures. This modification is discussed before presenting the results for both the 58 per cent alloy and a 63 per cent alloy which are to be found at the end of this part of the work.

## A. The Experimental Problem

It is desired to make magnetic measurements at temperatures approaching absolute zero. A practical approach to absolute zero is the range of temperatures provided by liquid helium, namely $4.2^{\circ}K$ to as low as $1.5^{\circ}K$. The materials of interest will have Curie temperatures in this region, below this region, or will not have Curie temperatures at all. An estimate of the magnetizations to be measured can be made because a material with a low Curie temperature will also have a small magnetization in direct proportion. Nickel has a Curie temperature of roughly

$6 \times 10^2$ °K and a spontaneous magnetization of $6 \times 10^3$ gauss.* Then an alloy with a Curie temperature of 4°K would be expected to have a spontaneous magnetization of 40 gauss. A lower limit on the magnetization to be measured can be seen from the data on nonferromagnetic materials. These in general show a magnetization proportional to the applied magnetic field. This leads to the definition of a quantity called the volume susceptibility which is the ratio of the magnetization to the applied field. The values of the susceptibility, $\chi = M/H$, for nonferromagnetic solids seldom run lower than $10^{-6}$.

The magnetization of ferromagnetic materials is known to be field dependent due to the existence of domains. For fields up to $6 \times 10^3$ gauss the main effect is to line up the randomly oriented domain magnetizations in the direction of the applied field; above this field the change of magnetization with field is said to arise from the influence of the field on the magnetization of the elementary domain. To obtain full understanding of the material under consideration it is then desirable to measure the dependence of the magnetization on field.

Most existing methods** of measurement measure the magnetic moment of a sample by placing it in a nonuniform magnetic field. These methods have been used at the temperatures of liquid helium. Their principle is that they give a force proportional to $M \cdot dH/dx$ where m is the magnetic dipole moment, and $dH/dx$ is the gradient of the field. The limit on the accuracy of this method is the degree to which dH/dx may be known. The standard procedure has been to take the results of the measurements on a standard sample and to use the standard sample to calibrate a given apparatus. The original determination of the standard sample involved an exceedingly precise determination of the distribution of flux in a magnetic field, an accurate placing of the sample in the field, and consideration of the effects of the

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* This is $4\pi M$ where M is the magnetic moment per unit volume.

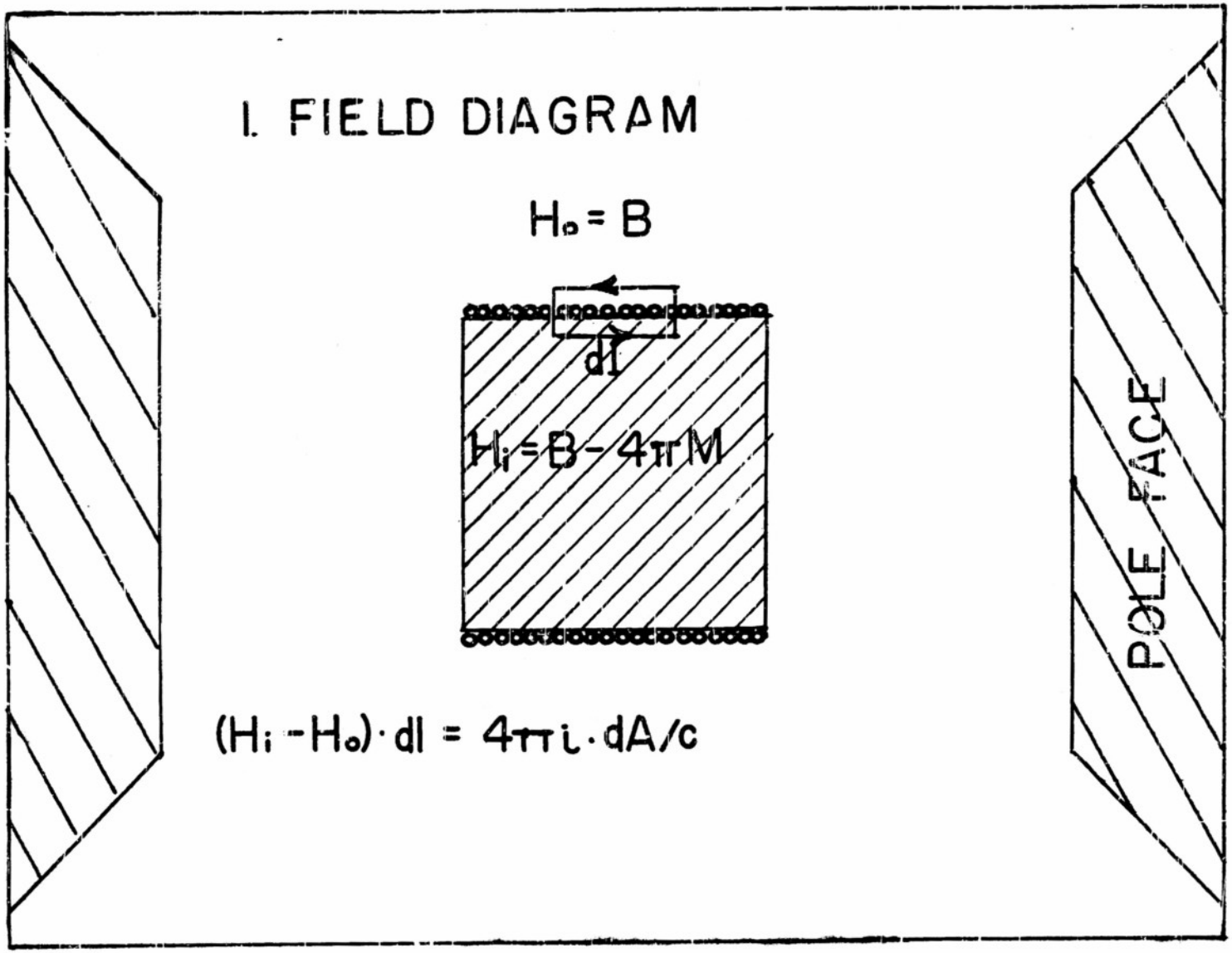
** A discussion of experimental techniques is to be found in Bates[1].

sample itself on the magnetic field. If m is field dependent, this method is in error as each part of the sample is in a different field. Also the action of a sample's own field on itself (demagnetization) and the action of the sample on the magnet producing the field (image effect) can be calculated accurately only in a uniform field. These errors will not be serious if the magnetization does not change too rapidly with field. For ferromagnetic materials the method is accurate in high fields were the magnetization changes but little with field. In nonferromagnetic materials the method is accurate where $\chi$ does not exceed $10^{-3}$. It is the in-between range in which it is more difficult to obtain meaningful results.

The force method was not used in this work primarily because of the location of the electromagnet in a room in which vibration problems are serious. The attempt to use an induction method in order to eliminate the need for sensitive force balances, led to the development of a principle of measurement which is thought not to have been properly exploited heretofore.

The principle of the measurement is that a current carrying coil on the surface of the sample to be measured can be used to cancel out the "amperian currents" on the surface of the sample. The current necessary to produce a null will be a measure of the magnetization, but at the same time, by cancelling the effects of the "amperian currents," it also eliminates the cause of nonuniform demagnetization and image effects. This principle has been adapted in an apparatus for measurements at liquid helium temperatures.

1. Principle of Measurement - The principle of measurement is made clear by considering the following problem (see figure 1): Given a uniform field $B_a$ due to the pole faces of an electromagnet; into this field a cylindrical sample of magnetic susceptibility $\chi$ is placed with its axis along the applied field $B_a$; on the cylindrical surface of the sample is wound a very fine pitched solenoid which can be taken as equivalent to a sheet with a current per unit length, I; it is to be shown that with the proper choice


I. FIELD DIAGRAM
$H_o = B$
dl
$H_i = B - 4\pi M$
POLE FACE
$(H_i - H_o) \cdot dl = 4\pi i \cdot dA/c$

of I, the B field at every point in space will be unchanged, hence the magnetization M will be uniform throughout the sample and will be given by

$$M = -I/c \qquad (32)$$

where the units are cgs gaussian units.

By way of proof it is only necessary to point out that a constant is a solution to Laplace's equation (applicable here because there are no free poles) and that the constant chosen here satisfies the boundary conditions.

The solution is:

$$B = B_a \text{ everywhere}$$

hence

$$H_o = B_a \text{ outside the sample}$$

$$H_i = B_a - 4\pi M \text{ inside the sample}$$

The boundary conditions are satisfied as follows:

1. B is a constant everywhere, therefore the normal component of B is continuous.

2. H is always in the direction of B so that the tangential component of H is zero across the ends of the cylinder; while across the cylindrical surface

$$\nabla \times H = 4\pi i/c$$

i, being the current density at the surface. Taking a path length dl inside the surface, crossing the surface and the coil, coming back a length dl outside the coil, and then closing the path gives

$$(H_i - H_o) \cdot dl = (4\pi i/c) \cdot dA$$

where dA is the area enclosed by the path (see figure 1). Hence it follows that for the boundary condition to be satisfied

$$-M = (i/c) \cdot dA/dl$$

but $i \cdot dA/dl = I$, the current per unit length. This gives then for the required current per unit length

$$I = -c \cdot M$$

Physically what this means is that in the absence of the current sheet the B field would not be uniform only because of the "amperian currents" in the sample. The "amperian currents" cause the magnetization inside the sample not to be uniform (nonuniform demagnetization) and a redistribution of flux in the pole faces (image effect) as well as produce a field in the region

just outside the sample. However, in adding the current sheet with the current flowing opposite to the direction of the "amperian currents," the source of the field disturbance is eliminated because there is now no net current on the surface. The result is that the current necessary to produce the null is a measure of the magnetization and at the same time image effect is removed and the sample is uniformly magnetized.

The argument is essentially unchanged by taking an arbitrary shape for the sample. The condition on the current in the general case is that the current per unit length along the direction of the field be uniform. Hence finite wires (as an approximation to a current sheet) would be closed packed only in the case of a cylindrical or conical surface with axis in direction of the field.

2. Measurement of Susceptibility - Susceptibility can be measured in the following way. The sample (the cylindrical shape is most convenient) is placed between the pole faces of an electromagnet. The current through a fine coil of wire wound on the surface of the sample is changed until B is found to be uniform about the region of the sample. Then B and the current per unit length, I, are measured. From the latter comes the magnetization, M, and from B and M, H inside the sample is obtained. The susceptibility then is given by

$$\chi = M/H_i = (I/c)/(B - 4\pi I/c) \qquad (33)$$

The field, B, can be measured to an accuracy of about 1 part per $10^5$ with a proton resonance meter. From the measured current and the number of turns per unit length of the coil [both these quantities can be determined to at least 1 part per $10^5$] I may be obtained. Hence the method in principle will allow absolute determination of susceptibility to 1 part per $10^5$. This is compared to a limit of the order of 1 part per 100 for the force measurement in absolute accuracy.

There are, however, practical limitations on the accuracy which have not been considered so far. These result in the apparatus described below being accurate only to 1 part per 100. A practical limitation is the finite size of the null current sheet.

If a coil of wire is used as an approximation to the current sheet, a limitation will be the size of wire. As small an insulated wire as can be used conveniently is about .05 mm copper covered with formex insulation. The correction for the finite size of the wire on a sample 20 mm in diameter is just less than 1 part per 100.

While a resonance meter would measure B to one part per $10^5$, to measure $\chi$ it may be necessary to be able to detect even smaller per cent distortions of B by the unbalance between the current sheet and the amperian currents of the sample. To measure $\chi$ to one part in $10^2$, it is necessary to detect a distortion of B to 1 part in $4\pi\chi\ 10^2$. Hence either of two things can also limit the accuracy with which one can measure a given $\chi$ :

1. The sensitivity of the detector of field distortions, or
2. The limitation on how uniform and constant a B field can be produced.

It is not necessary that the detector measure B; it is sufficient that the detector see changes in B. This suggests using a turn of wire which will pick up dB/dt as a voltage. Placing a turn of wire anywhere near the sample and displacing one from the other without rotating either in the field will induce a voltage in the turn unless the proper current is passing through the null coil on the sample. Placing enough turns of wire in the vicinity of the sample or moving the sample with respect to the turns fast enough will make the voltage sensitivity unlimited. (In practice, space and speed limitations exist and must be considered.)

The difficulty with a turn of wire as a detector is that it will not only pick up distortions due to the sample, but also distortions due to the field varying in time or space. As permanent magnets do not produce fields of sufficient strength to measure the properties of interest in this work, it is necessary to attack the problem of current control in an electromagnet.

The voltage induced by a dB/dt of the magnetic field will be proportional to the area of the turn. Hence the turns should be of the same size as the cross section of the sample to get good sensitivity to the unbalance without being overly sensitive to the field fluctuations.

In calculating the regulation necessary to measure a given $\chi$, the time factor is eliminated from discussion by considering what regulation is necessary over a time comparable to the time necessary to detect an unbalance between the sample and the null current. By considering a turn slightly larger than the sample and the sample as moving from within the turn to infinity, it is seen that the flux change in the turn will be

$$\Delta\phi_s = A_s \Delta B_s \tag{34}$$

where $A_s$ is the area of the sample and

$$\Delta B_s = B_a - B_i \tag{35}$$

where $B_i$ is the B inside the sample. $B_i$ is the same as the field which would be found inside a sample of susceptibility

$$\Delta\chi = \frac{I}{c H_i} - \chi \tag{36}$$

which has no null coil on it.

That is $B_i = H_i + 4\pi \Delta\chi H_i$ (37)

where $H_i = B_a - 4\pi \Delta\chi H_i D$

and D is the demagnetizing fraction for the sample shape*.

Near balance where $\Delta\chi$ is small

$$\Delta B_s = 4\pi \Delta\chi B_a (1-D) \tag{38}$$

and the flux change on moving the sample would be

$$\Delta\phi_s = A_s 4\pi \Delta\chi_s B_a (1-D) \tag{39}$$

whereas the flux change due to field fluctuations would be

$$\Delta\phi_F = A_t \Delta B_a$$

where $A_t$ is the area of the detector turn and $\Delta B_a$ is a measure of the fluctuation of the field in the time necessary to detect the unbalance. If $A_s \simeq 1/2 A_t$ and $D \simeq 1/2$, then the $\Delta\chi_s$ the limitation on the determination of $\chi$ will be

$$\Delta\chi_s = \frac{\Delta B_a}{\pi B_a}$$

so that to measure $\chi$ of the order of $10^{-6}$ to an accuracy of 1%, that is $\Delta\chi = 10^{-8}$, the field would have to have fluctuations of less than 3 parts per $10^8$.

The effect of uniformity of the field will enter in, not through the effect on the magnetization of the sample, but through the problem of moving the sample and the turns of the detector coil

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* D is 0 for a long needle, 1/3 for a sphere, and 1 for a flat plate.

with respect to each other. If the detector is moved in a non-uniform field, there will be an induced voltage. Hence it is better to move the sample and hold the detector fixed. If the detector could be held fixed in the field, there would be no difficulty from the nonuniformity of the field, but in the apparatus designed here for work at helium temperatures, vibrations of the detector in the magnetic field limit the $\Delta\chi$ which can be measured to $10^{-7}$.

A very practical limitation on measurements of high magnetization is the heating from the current necessary to null out the amperian currents of the magnetization. The power input for nulling a magnetization, M, is given by

$$P = 12 \cdot 10^4 \rho M^2 l \qquad (42)$$

where $\rho$ is the resistivity of the wire, $l$ is the length of the cylinder, and the assumption is made that the thickness of the current sheet is $\frac{1}{4}\%$ of the sample diameter. The amount of heating which can be tolerated will determine the upper limit on the M which can be measured by this method. In case of a constant temperature bath the limit depends on the heat transfer from the coil and sample to the bath. (In the actual apparatus used the limit at helim temperatures was the current at which the wires of the null coil shorted because the insulation burned off.)

In the case of the material isolated from the bath, the rate of temperature rise depends on the heat capacity per unit volume of the sample, C.

$$\frac{dT}{dt} = \frac{P}{C \cdot V} = 1.6 \times 10^5 \frac{\rho}{CD^2} M^2 ; \quad V = \frac{\pi}{4} D^2 \qquad (43)$$

Hence it is desirable to have $\rho$ small and D large. C and M depend on the sample and like $\rho$ depend also on temperature. Copper wire should be used unless at low temperatures something with a lower residual resistivity is found. Both $\rho$ and C decrease with temperature decrease. $\rho$ will drop linearly with temperature until it reaches its residual resistivity near 30°K, where the resistance is as low as it ever gets, but the heat capacity is still large. This makes the region from 30°K on up as best suited for taking susceptibility measurements on the temperature rise.

The maximum value of M anticipated in the design considerations was 10, or $4\pi M = 120$, which is three times the figure mentioned in the introduction to this section. The maximum heating for a sample 1 cm long and with a null coil of copper is from equation (42):

$$P = 12 \cdot 10^{4} \cdot 10^{-8} \cdot 10^{2} \cdot 1 = 10^{-1} \text{ (watts)}$$

which in terms of helium being boiled off is 100 cc per hour. The heating problem in a constant temperature bath can be reduced by making measurements quickly with current flowing through the null coil only for the duration of the measurement. For taking readings on the temperature rise it might be better to have continuous heating in order to know the average temperature of the sample.

a. Field Control - In detecting an unbalance between the sample and the null coil, a voltage pulse is looked for on moving the sample with respect to the detector. The duration of the pulse is less than 1 second. The pulse must be detectable over a background noise due to fluctuations of the field. It is necessary to have the noise level not much above the level of the pulse from the smallest unbalance which it is desired to detect. From the above discussion [see equations (34) to (41)], it is seen that, to detect an unbalance of 1% in a sample of susceptibility $\chi = 10^{-6}$, it is necessary to control the field so that random fluctuations of less than 1 second duration are less than 3 parts per $10^{8}$. Slow fluctuations or constant drift of the field can easily be discriminated against.

Eliminating fluctuations is done by using batteries to supply the current to the magnet*. Batteries drift slowly in time but show little in the way of short time fluctuations. The use of batteries means, however, that the field must be measured as a function of time.

It seemed reasonable when this problem was first approached that two detector coils in series opposition could be used. Then

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* A.D. Little 120 KW Magnet (32).

by moving the sample from within one coil to within the other, decreasing the flux through the one and increasing it through the other, the result would be twice the signal from the moving sample and complete discrimination against field fluctuations. Thus it was thought that using an electronic controller, that was reported to give regulation to 1 part per $5 \times 10^3$, and two coils, which were matched to 1 part per $10^4$, the noise level would be decreased to the desired parts per $10^8$. What was found, however, was that the field fluctuations, seen on an oscilloscope by using an a-c amplifier and a probe coil, had a wave form which varied from place to place in the gap between the pole faces. Thus two identical coils see different wave forms and the cancellation* is only about a factor of 10 rather than $10^4$.

The limitation with batteries is the expense involved in producing higher fields. With 16 batteries drawing 50 amps per cell, fields of 12KG in a two-inch gap are obtained. To get 18KG in the same gap, drawing the same current per cell, would take 64 batteries. High fields may be obtained by using a motor-generator set, but there is considerable increase of noise level. It is necessary to use batteries to energize the generator field. The output must be filtered with a large inductance and large capacity. For an inductance, the secondary of a welding transformer was placed in series with the output, and for a capacity, 1000 microfarads were placed directly across the magnet. The low frequency fluctuations which are left are due either to surges on the 4500 volt line from the power house to the motor or to oscillations of the drive shaft about an equilibrium speed.

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* The use of a narrow band amplifier would reduce this problem considerably. The detection would be made by oscillating the sample at the frequency of the amplifier. Such a scheme is being developed by Plotkin at M.I.T. He uses a solenoid to produce his fields. The motion of his sample is then in the vertical direction. This makes rapid oscillation of the sample possible.

b. Signal Detection - The signal from the two detector coils in series opposition is fed into a Perkin-Elmer Model 53 d.c. chopper amplifier. The amplifier proper is a high gain a.c. amplifier with a large turns ratio input transformer. When the drive belt is removed from the chopper arrangement, the amplifier can be used as an a.c. amplifier and was so used in the work on reducing the noise level of the field fluctuations.

The sensitivity of the detector depends on the number of turns of the detector coils, their resistance, the input resistance of the amplifier, the sensitivity of the amplifier and the speed of the sample movement. The limitations on the number of the turns of the detector coils and the resistance of the detector are those of the space in which the coils must fit and the resistivity of the wire used. The following design problem was solved as a guide:

Given a cylinder of diameter (Z) and length (L) choose

1) the diameter (a) of wire of resistivity ($\rho$) and

2) the diameter (D) of sample of susceptibility ($\chi$) such that when in a field (H) the removal of the sample from the coil in a time ($\Delta t$) will produce a maximum voltage (V) across the input of an amplifier with input resistance (R).

The results of this problem (and also a modification of it) are found in Appendix ii. The results show that with a Z = 3 cm and L = 1cm, using copper wire at room temperature; an amplifier input resistance of 20 ohms; taking $\Delta t = 0.2$ sec; and a $M = \chi H$ of $10^{-2}$; the maximum voltage is $10^{-6}$. With an amplifier with sensitivity of $2 \times 10^{-9}$ this is sufficient to measure a $\chi$ of $10^{-6}$ to better than 1%.

The analysis in Appendix ii shows that regardless of the value chosen for the ratio of the diameter of the sample to available diameter, the coil should have a resistance equal to the input impedance of the amplifier. The solution of the problem with the resistance set equal to the input impedance of the amplifier is

$$V = \frac{\pi^2}{4} \frac{\chi H}{\Delta t} L^{\frac{1}{2}} \left(\frac{R}{\rho}\right)^{\frac{1}{2}} D^2 \frac{(Z-D)^{\frac{1}{2}}}{(Z+D)^{1/2}} \qquad (44)$$

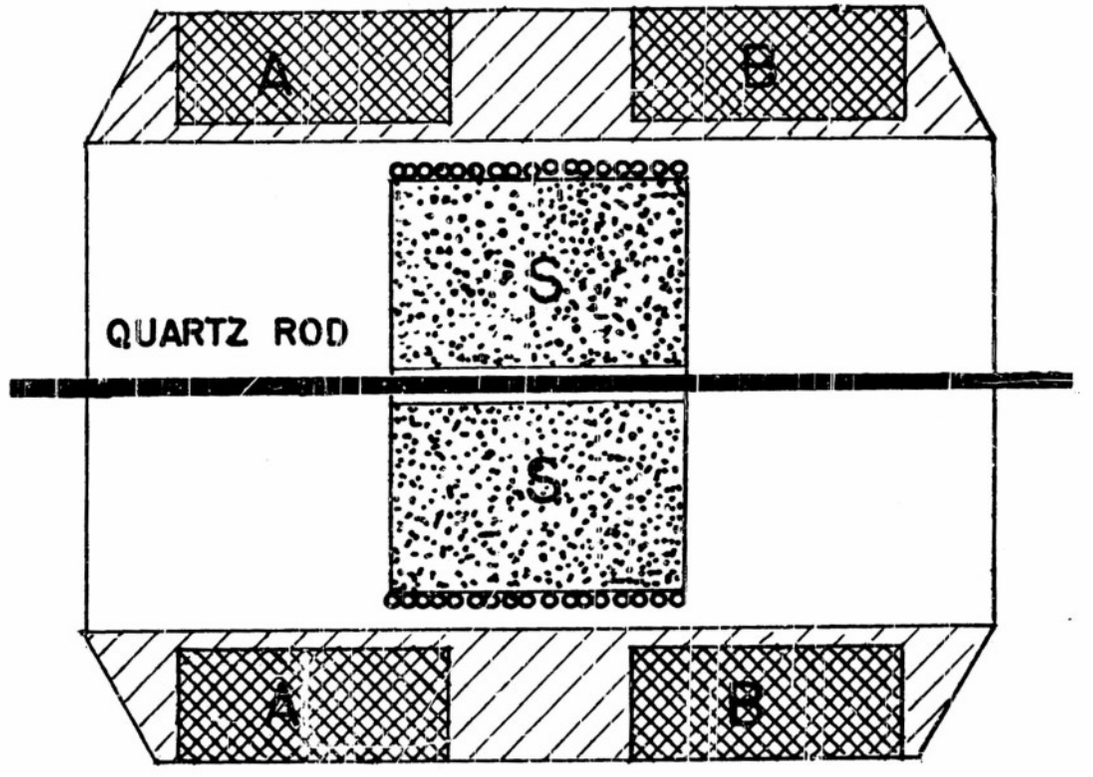
So that at lower temperatures greater sensitivity is obtained because of the decrease of $\rho$. The optimum value for D, con-

sidering Z fixed, is .78Z. That this makes the area of the largest turn only about twice that of the sample is consistent with the desire to reduce the noise level from field fluctuations. See discussion on page 31.

3. Cryogenics - a. The Apparatus - To adapt the principles outlined so far to low temperature measurements is mainly a mechanical problem: to move the sample along the direction of the field which is horizontal at the bottom of a dewar which is vertical. The sample must have its axis lined up with the direction of the field throughout its motion from within one detector coil to within the one in series opposition. In addition, the detector coils must be fixed rigidly in space.

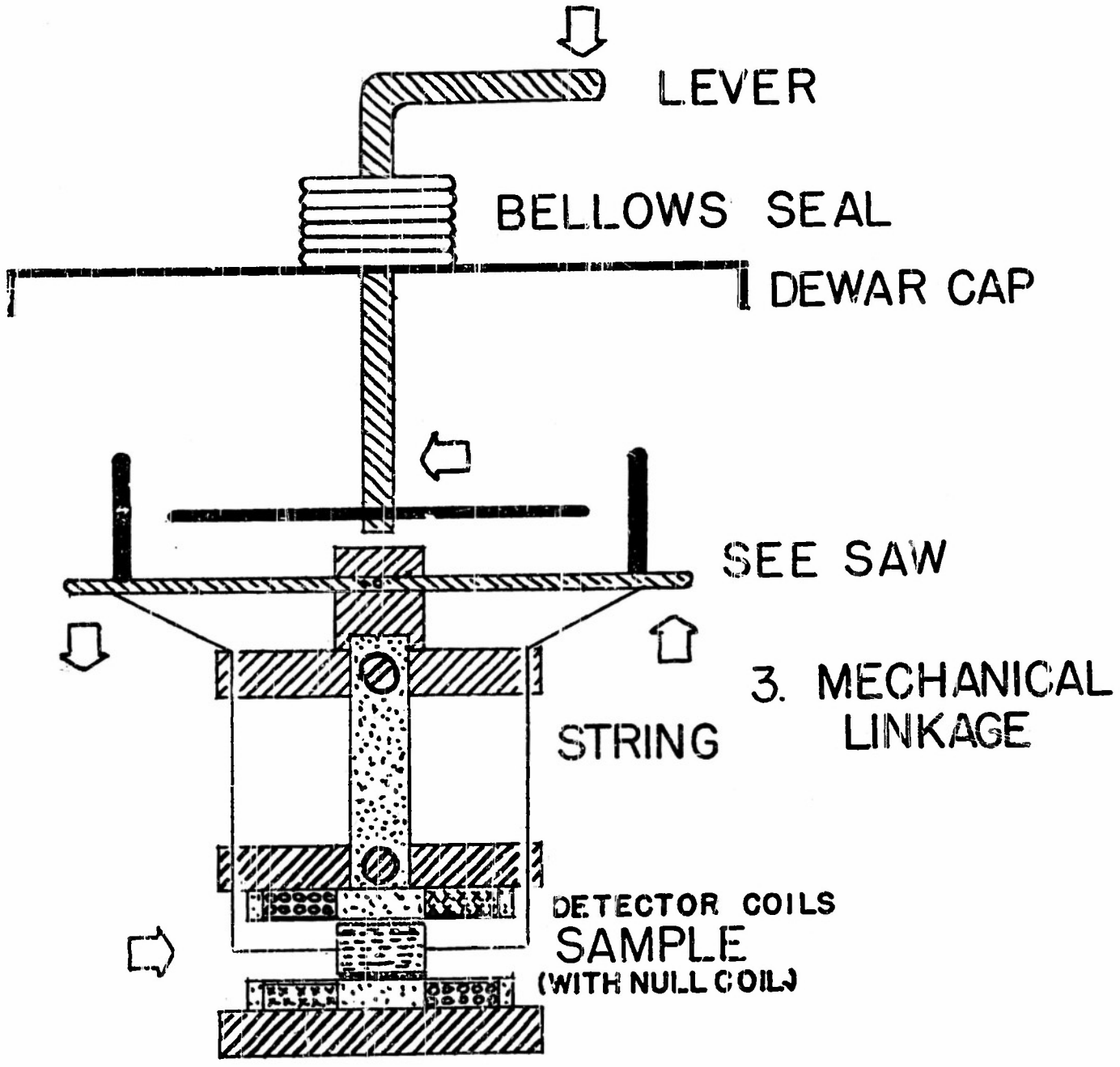
A solution to this problem is to drill a small hole along the axis of the cylindrical sample, attach strings to the sample and pull the sample along a quartz rod from within detector coil A to within detector coil B (see figure 2). The cross sectional area of the hole along the axis of the sample is less than $\frac{1}{4}\%$ of the area of the sample. The strings which move the sample are connected to a see-saw which is tripped back and forth by a lever through the cap of the dewar. (see figure 3). The apparatus fits into a dewar which is of small diameter nears its bottom, in order to fit between the pole faces of the magnet, and of larger diameter above, in order to have a sufficient reservoir (see figure 4). The short cylindrical supports (see figure 3) fit tightly in the lower portion of the dewar so that vibrations from moving the sample are not transmitted to the detector coils. The see-saw sits in the wider, upper portion of the dewar. The see-saw is hung on the 1/2" monel fill tube, which in turn is rigid to the dewar cap. No magnetic materials are used in the region between the pole faces.

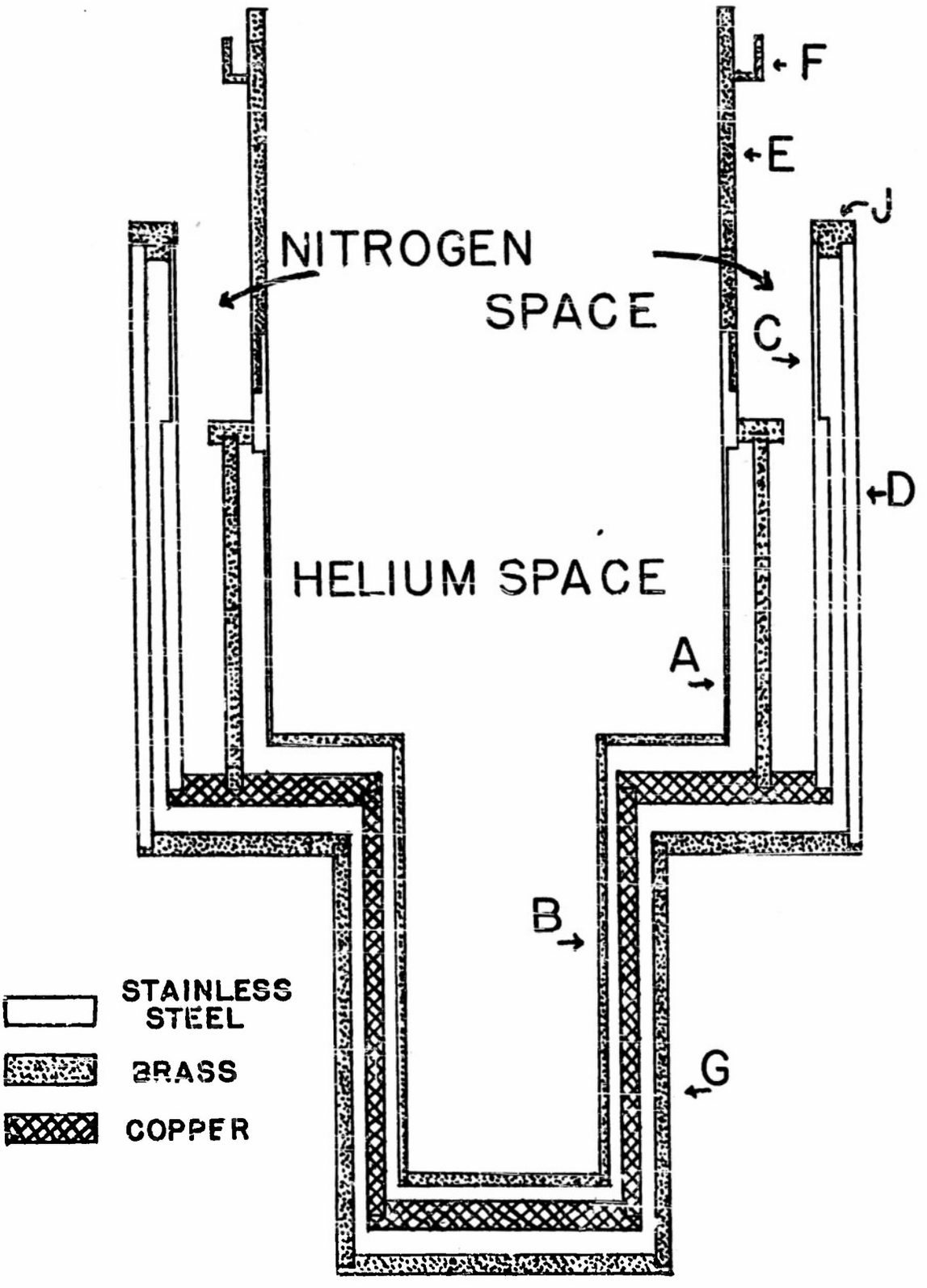
The null coil is wound on the surface of the cylinder by placing the cylinder between two discs flush with the ends of the cylinder. The wire coming from the last turn is brought straight across the sample, parallel to the cylinder axis, and then twisted with the wire coming from the first turn -- some




2. CROSS SECTION OF DETECTOR COILS

LUCITE COIL FORM  SAMPLE


LEVER
BELLOWS SEAL
DEWAR CAP
SEE SAW
3. MECHANICAL LINKAGE
STRING
DETECTOR COILS
SAMPLE
(WITH NULL COIL)




4. CROSS SECTION OF HELIUM DEWAR

20 twists to the inch. The uncompensated lead from the last turn is less than 0.1% of the length of the wire of the null coil. It has its field so as to minimize the number of lines linking the detector coils. (Coils also can be wound back on themselves to avoid uncompensated leads, but in doing so the increased thickness of the current sheet gives more serious inaccuracies than the uncompensated lead wire.) Details of the construction are found in Appendix iii.

Each time before the apparatus was placed in the dewar it was cleaned in C $Cl_4$ to free all moving parts of grease. After the apparatus was sealed into the dewar it was pumped on for 12 hours to eliminate water or any other liquids which might freeze and cause sticking of the sample. A modification of the method of moving the sample, described in Appendix iii, eliminates sticking.

b. The Dewar - The apparatus was originally designed to fit into the conventional two dewar arrangement with $N_2$ in the outer dewar providing the ambient temperature for the helium dewar. This method gave trouble due to oxygen contamination of the nitrogen bath. The susceptibility of contaminated nitrogen is proportional to the per cent oxygen, reaching a value of $250 \times 10^{-6}$ for pure oxygen. When the liquid boils, the gas bubbles which are formed have negligible susceptibility compared to the liquid. The resultant field fluctuations are picked up by the detector coils and cause a noise level many times the signal to be measured. One solution to this problem is to get pure nitrogen and try to keep it pure. Another is to pump on the nitrogen until it is around $65^{\circ}K$, then increase the pressure, and take measurements while the nitrogen is warming up but has not yet reached its boiling temperature for the increase pressure. This was done with success in the early part of the work.

A better solution is to use a dewar designed by Henry and Dolecek[33]. The purpose of this design was to reduce the space needed for dewar walls and nitrogen bath. In so doing one eliminated nitrogen from the part of the dewar which goes into the magnetic field. The model of the Henry and Dolecek type dewar

used in this work is shown in figure 4. The details of the construction are given in Appendix iv. The upper parts are of stainless steel and the parts which go into the magnetic field are of brass and copper.

The novel feature of the Henry & Dolecek design is the use of a nitrogen-cooled copper radiation shield to provide the ambient for the inner helium chamber in the lower part of the dewar. The copper takes the place of the inner wall of the outer dewar, the nitrogen space, and the outer wall of the helium dewar, all of which would be present in the conventional two dewar arrangement. The result is the ability to use smaller pole face gaps and the absence of nitrogen in the magnetic field.

4. Instrumentation - a. Temperature Measurement - Temperatures are measured in several ways in this work. From 30°K up to room temperature, the resistance of the copper null coil, wound directly on the sample, is used as a thermometer. From helium temperatures to nitrogen temperatures, carbon resistors are used as thermometers. The vapor pressures of $O_2$, $H_2$, and He are used for calibrating the carbon thermometers. The null coil thermometer is calibrated from room temperature and a comparison with the carbon thermometers at nitrogen temperatures and below. The vapor pressures of the liquids are controlled with a bellows-actuated manostat and are measured on a mercury manometer.

The Clements and Quinell[34] empirical formula for carbon resistors is used, namely

$$\log R + \frac{K}{\log R} = A + \frac{B}{T} \qquad (45)$$

The resistance values from room temperature, nitrogen temperatures and helium temperatures are used to solve three equations for K, A, and B. The results for two carbon thermometers are given as

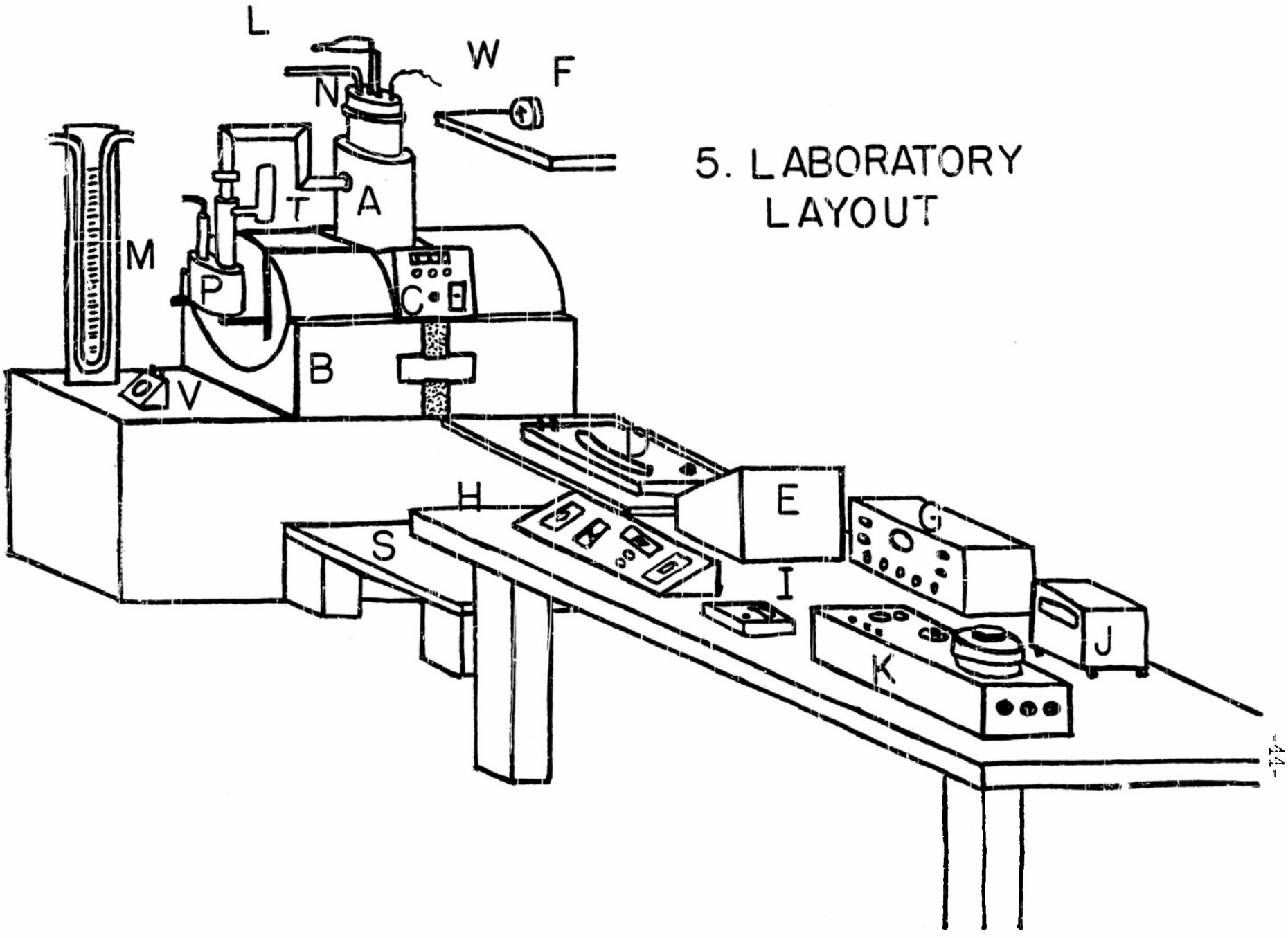
| # | $R_{300}$ | $R_{74.3}$ | $R_{74.1}$ | $R_{4.19}$ | A | B | K |
|---|---|---|---|---|---|---|---|
| 3 | 66.5 | 89.95 | — | 1385 | 3.32876 | 2.9000 | 2.7627 |
| 4 | 66.0 | — | 87.19 | 1311 | 3.27384 | 2.9256 | 2.6639 |

The results are checked by comparing the calculated values for $H_2$ boiling point with the observed values. The agreement is within .1°K for both thermometers.

b. Field Measurements - The field is measured by a rotating coil flux meter made by the Rawson Company. The meter has been calibrated and found to read about 3% low. After this correction has been applied to the readings, they are probably within 1%. The calibration has been made with a coil and a mutual inductance. The NA of the coil was found using a proton resonance meter. The inductance is known to much better than 1% (stated accuracy .1%).

c. Measuring Techniques - The "layout" used during the measurements is shown in figure 5. The dewar (A) sits in the A.D.L. magnet (B). Attached to the dewar is the diffusion pump (P), which is backed up by a Welch pump some 8 feet of 7/16" I.D. tubing away. The pressure is indicated by a thermocouple vacuum gauge (T) and read on panel meter (V). The sample down in the dewar is moved by the lever (L) through the bellows seals on the cap of the dewar. The cap of the dewar is sealed on with Woods metal and the pressure inside the dewar is controlled by a manostat which is connected to the pump tube (N) through a four-way junction. The other two arms of the junction are used for pressure measurement by the manometer (M) and for letting dry gases from cylinders into the dewar.

The induced voltage in the null coil is led out of the dewar on number 33 formex covered copper wires (W), twisted with 10 or more twists to the inch. The signal is fed into chopper amplifier (E), and the output is seen on panel meter (F) which is at eye level to the operator, standing on platform (S), working the lever. The current through the null coil is varied by control panel (C), attached to the side of the magnet. The operator works the lever with the left hand and varies the null current with the right hand while watching the meter (F). The current through the null coil can be easily read on a large Sensitive Research Instruments milliammeter (D). Being able to make readings

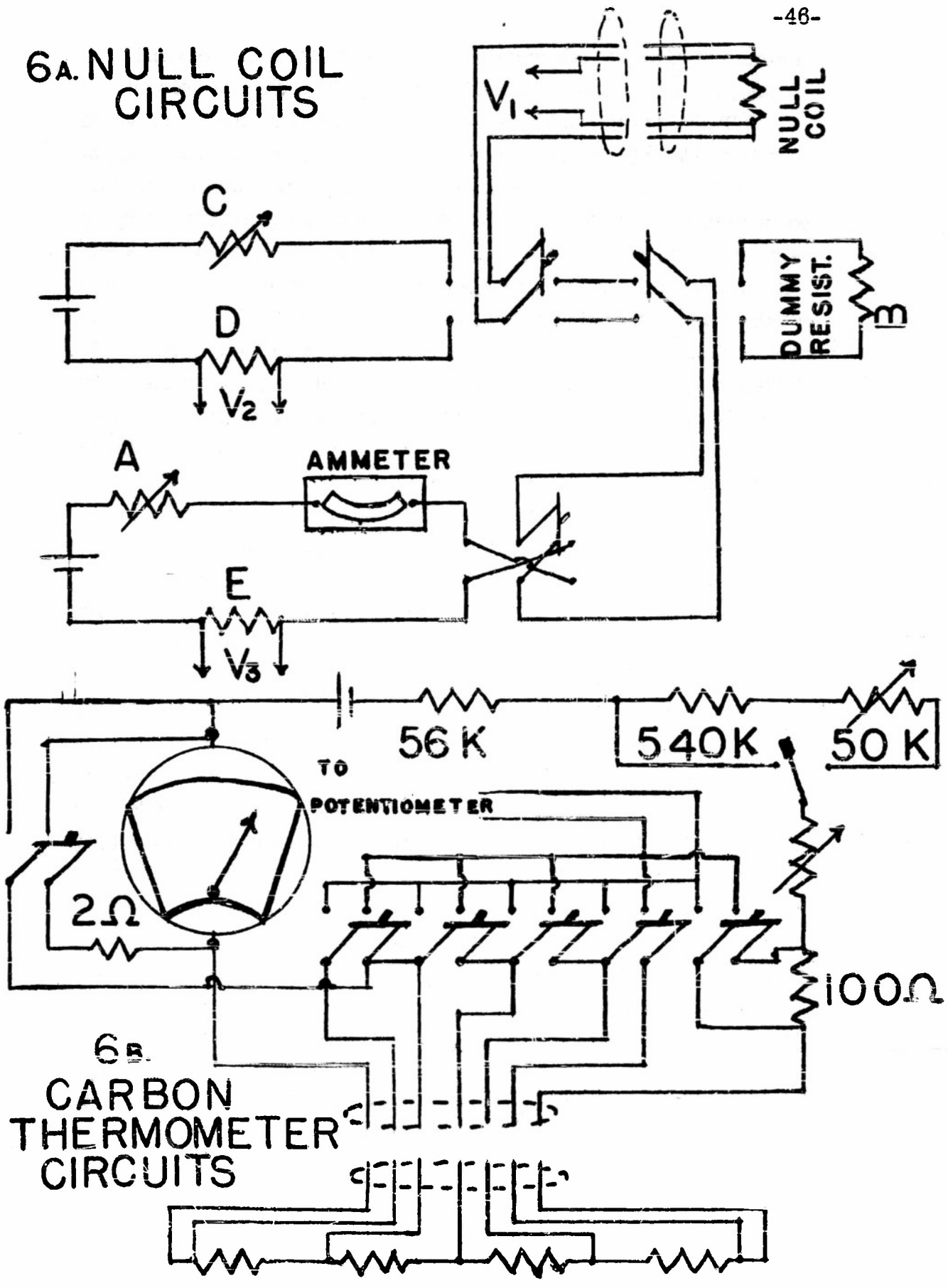



# 5. LABORATORY LAYOUT

quickly is a great convenience where heating of the sample due to the current in the null coil is a problem. Temperatures are read by using a Type K potentiometer, with galvonometer (J), to standardize the measuring currents and to read the voltages across the resistance thermometers. There are four carbon thermometers which may be selected by using switches on box (G). A switch on the control panel (C) will connect the null coil to a standardized current produced by control panel (H). Control panel (H) also selects a number of variables which are to be read on the Type K potentiometer. The fields are read on meter (I) and the rotating coil can be turned on and off near to (I).

d. Circuits - The circuits connected to the null coil are shown in figure 6a. The variable resistance (A) is a series parallel arrangement of wire wound pots allowing resistance to change from 15 to 75,000 ohms in steps of .02 ohms. When used with 18 volts from storage batteries the range is from 1 amp to less than 1 milliamp. Smaller currents can be had by using lower voltages. The variable dummy resistor (B) is used to cut down heating due to the null current. The null current is made to pass through the dummy resistor except at the instant when the detection of the unbalance between the null coil and the sample is to be made. The dummy is such that the current is the same whether it flows through the null coil or the dummy. Hence a current is set going through the dummy, the current is then thrown through the null coil for an instant while the lever is pushed to detect the off balance. The current is then switched back to the dummy, reset in the direction indicated by the detector coils and the process repeated until a null is obtained.

A measuring current is standardized by the variable resistor (C) for measuring the resistance of the null coil. The drain is low enough that standardizing does not have to be repeated often. The variable resistance (C) gives sufficient range to standardize all the null coils used to a voltage reading of 25 mv at 295$^{o}$K. This is done to allow rapid calculation of the temperature by adding 45 to the reading in units of $10^{-4}$ volts.

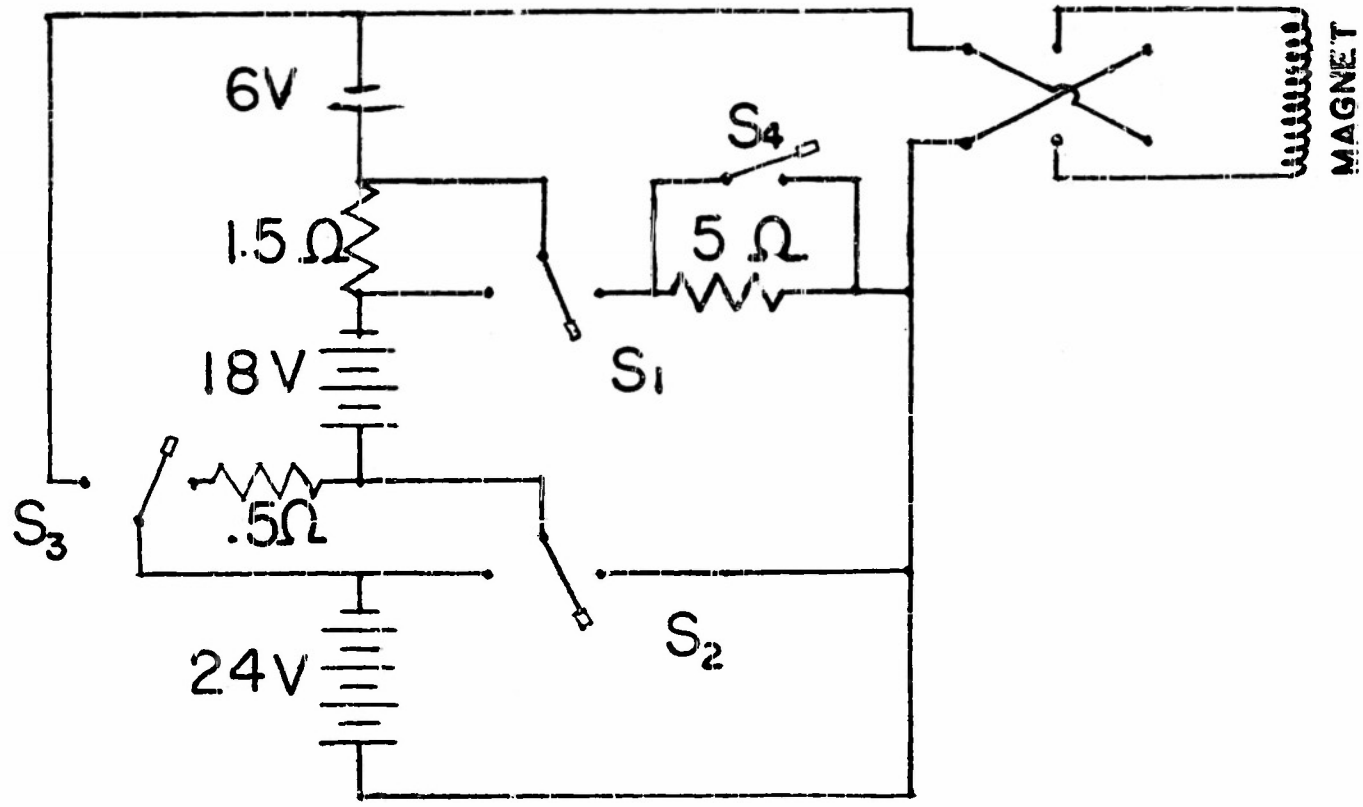

6A. NULL COIL CIRCUITS
V1
NULL COIL
C
D
V2
DUMMY RESIST.
B
A
AMMETER
E
V3
56 K
540K
50 K
TO POTENTIOMETER
2Ω
100Ω
6B.
CARBON THERMOMETER CIRCUITS

The carbon thermometers (see figure 6b) are four in number and located so that C/T #1 is near the see-saw, C/T #2 is just below the upper end of the lower portion of the dewar, C/T #3 is just above the holder of the detector coil, and C/T #4 is at the bottom of the dewar. All the thermometers are used as level gauges. Thermometers #3 and #4 are calibrated for temperature measurements. C/T #4 is also used as a heater which will indicate its own temperature on a panel meter. This last feature is used in precooling the dewar with nitrogen. It is desired to drive off the last bit of nitrogen with a heater but not to heat up the dewar after the nitrogen is gone. C/T #4 can be heated from a constant voltage source and the current read on a microammeter which is shunted when the heater is turned on. When the last nitrogen is gone the resistance of the heater drops rapidly due to heating and the meter gives a sharp indication by changing some 20%.

There are two choices of measuring currents -- 100 microamps for the nitrogen range and the 10 microamps for the helium range. These currents flow through a microammeter only because the indication is valuable when trouble-shooting. The currents are set by the 50K and 5K variable resistors. There are five DPST switches which allow the voltage drop across any of the four thermometers of a standard resistor to be read on the potentiometer.

Fields are changed by the switching arrangement shown in figure 7, a circuit which permits switching without opening the magnet circuit. The circuit also includes a reversing switch which shorts the magnet at the same time it breaks the magnet connection to the batteries, this being done to prevent possible arcing in the magnet itself.

In all this work the problem of measuring a number of quantities one after another with the possibility of the readings changing with time necessitates all readings being made versus time and then extrapolated to get all readings at the same time. Hence a clock, easily seen from all stations of measurement, is added to the experimental equipment.




7. SWITCHING ARRANGEMENT MAGNET CURRENT SUPPLY

B. Measurements of Larger Magnetizations

To make measurements with higher magnetizations than originally anticipated, the principle of the measurement has to be modified. The detector coils are connected directly to a galvanometer with a long time constant and a CDR much larger than the resistance of the coil. The galvanometer is calibrated by using fields which give magnetizations less than 10 emu. The deflection of the galvanometer without current through the null coil is noted for several magnetizations up to 10 emu and in the same fields as the magnetization is measured using the null coil. This information is used to deduce larger moments from the galvanometer deflections. The error introduced in this way is due to demagnetizing effect. These measurements are made in the range of the residual resistivity of the detector, so that there is no difficulty from change of the resistance of the circuit with temperature. The problem of moving the sample between the same two points is not so serious as might be guessed. The detector coils are separated sufficiently so that the deflection is not very sensitive to the final positions of the samples. In addition, the final positions are quite reproducible as the sample moves between fixed stops.

The demagnetizing effect complicates the calibration of the galvanometer when $\chi$ is a function of field. Consider the change in B seen by a single coil for an ellipsoid moving from within the coil to infinity,

$$\Delta B = (H_i + 4\pi M) - B_a$$

where $H_i = B_a - 4\pi M D$

hence $$\Delta B = 4\pi M(1-D) \qquad (46)$$

$H_a$ does not change between measuring M with the null coil and noting the deflection of the galvanometer without the null coil, but M does. This is because $H_i$ is increased

$(H_i)_s = H_a - 4\pi M_s D$ without null coil (s) (47)

$(H_i)_c = H_a - 4\pi M_c$ with null coil (c) (48)

Thus if a moment, M, is measured with the null coil and then the deflection of the galvanometer is noted for the same applied

field but no current through the null coil, the reading will not be proportional to M, but to

$$M_S = M_C \frac{1+4\pi\left(\frac{\partial M}{\partial H}\right)_C}{1+4\pi D\left(\frac{\partial M}{\partial H}\right)_C} \qquad (49)$$

This follows from

$$M_S = M_C + \left(\frac{\partial M}{\partial H}\right)_C \left[(H_i)_S - (H_i)_C\right]$$

and equations (47) and (48).

The demagnetizing factor can be calculated exactly for an ellipsoid. For a cylinder the best one can do is to get an effective demagnetizing factor by measuring the ratio of the deflection to the magnetization measured by the null coil at several fields.

C. Results of Measurements

The following procedure is used in considering the results of the experiments. The data are in the form of a null current reading, field readings, and readings of various thermometers. The field readings are increased by 3% to correct for the fluxmeter. The current is converted into magnetization per unit volume by knowing the number of turns on the null coil and the thickness of the sample. The magnetization is approximately 10 times the current in amperes.

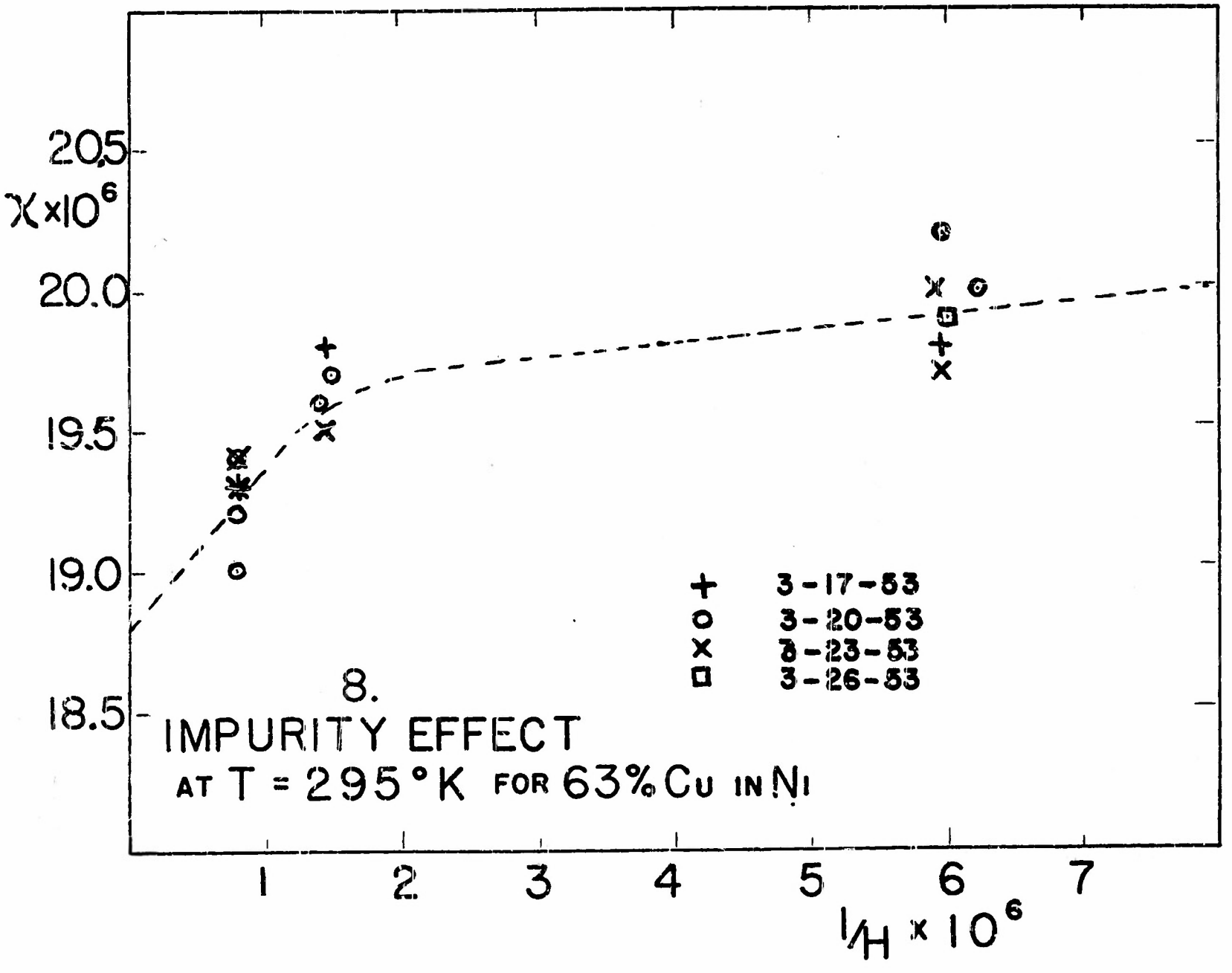
The battery circuits supply 6, 24, or 48 volts which produced fields of 1.5KG, 6.8KG, and 12.5KG. Later the circuits were modified to give also 12 and 36 volts, producing fields of 3.2KG and 9.8KG. Values of the order of 20G were obtained from the residual field, and fields of .16KG were produced using a dropping resistor in the magnet circuit.

The measurements on the 63-37 copper-nickel alloy show the presence of ferromagnetic impurities[37]. Corrections can be made for this at room temperature, and, assuming the impurity effects are temperature-independent, at all lower temperatures, too. The magnetization curves show slight hysterisis; generally noticed by a remanence in fields of less than 30G. The correction is made for these impurities by assuming that they are well saturated in fields of 6.8KG. A plot of $\chi$ versus 1/H is extrapolated to infinite field to get the $\chi$ of the material if there

were no impurities present. A comparison of the curve of the magnetization to be expected from this $\chi$ with the observed curve gives the magnetization curve of the impurities.

Figure 8 gives $\chi$ versus 1/H for $T = 295^{\circ}K$; it also shows the spread for readings taken on several different days. The variation is about 1% about a mean. The extrapolated value of $\chi$ shows that the impurities affect the susceptibility as measured in the field of 1.5KG by $\Delta\chi = 1.2 \times 10^{-6}$ and in the field of 6.5KG by $\Delta\chi = 0.8 \times 10^{-6}$. These fields are more convenient for measuring $\chi$ as a function of temperature than sould be 12.5KG. The latter causes too great a drain on the batteries for the continued operation which is desired when taking readings on the temperature rise. Hence measurements are taken on the rise for the lower fields and must be corrected for impurities.

Measurements of $\chi$ as a function of temperature, corrected for impurities, are tabulated in table II. The values of $1/\chi$ versus T were plotted and showed a curvature concave toward the T axis at higher temperatures, similar to that shown by Kaufman and Starr[40]. These data have been fitted to the expression $\chi = a + \frac{C}{T-\Theta}$. Extrapolating $\chi$ versus 1/T to 1/T = 0 gives the value of a. The a is subtracted from all readings and the resultant $1/\chi$ is plotted versus T to get C and $\Theta$. In table II are listed $\chi - a$, for $a = 8.0 \times 10^{-6}$, and the expression $C/(T-\Theta)$ for $C = 3.06 \times 10^{-3}$ and $\Theta = 6^{\circ}K$. The per cent deviation of the measurements are shown in figure 9. The points are for four slightly different experimental arrangements. As the calibration of the thermometers was not completed until several months later, there is room for error due to drift of thermometer characteristics. Hence the deviation to be expected from an error of $1^{\circ}K$ in T is also shown in figure 9. The magnetization of the sample as a function of field was measured at liquid helium temperatures. The reproducibility of the results was found to be within $\pm$ 1% for several runs at $4.19^{\circ}K$. Measurements at liquid helium temperatures have also been made on a 58-42 copper-nickel alloy, two alloys of chromium-nickel, and a sample




8.

IMPURITY EFFECT

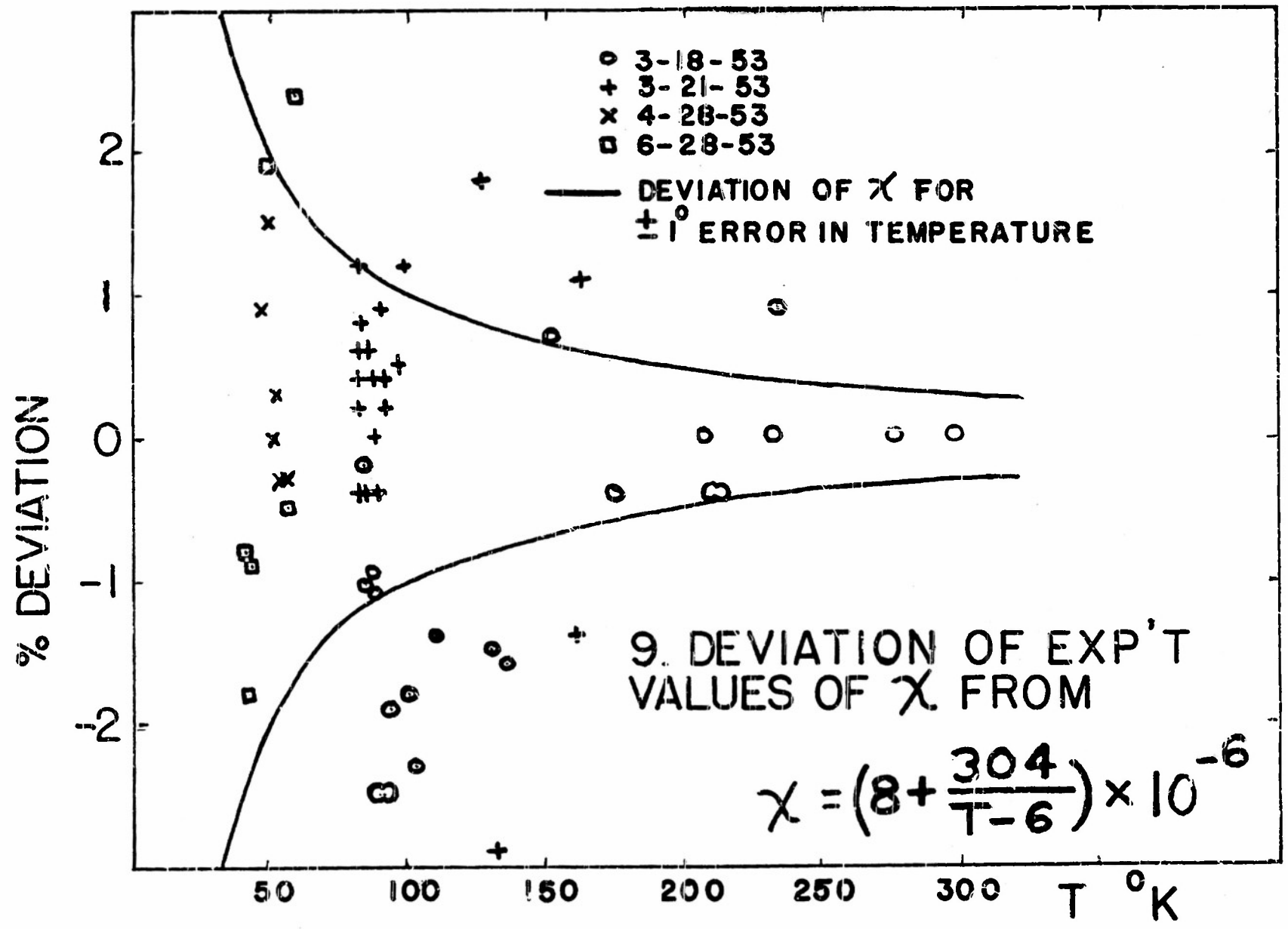
AT T = 295°K FOR 63% Cu IN Ni

Table II

Susceptibility of 63-37 Copper-Nickel as a Function of Temperature

| T | $\chi \times 10^6$ | $(\chi-8)\times 10^6$ | $\frac{306}{T-6}$ | T | $\chi \times 10^6$ | $(\chi-8)\times 10^6$ | $\frac{306}{T-6}$ |
|---|---|---|---|---|---|---|---|
| 83.5 | 47.4 | 39.4 | 39.5 | 82.3 | 48.3 | 40.3 | 40.1 |
| 84.7 | 46.4 | 38.4 | 38.9 | 81.8 | 48.5 | 40.5 | 40.4 |
| 86.0 | 45.8 | 37.8 | 38.2 | 81.3 | 48.4 | 40.4 | 40.6 |
| 87.7 | 45.0 | 37.0 | 37.5 | 81.8 | 48.7 | 40.7 | 40.4 |
| 89.0 | 43.8 | 35.8 | 36.9 | 82.3 | 48.7 | 40.7 | 40.1 |
| 91.0 | 43.1 | 35.1 | 36.0 | 83.3 | 48.0 | 40.0 | 39.6 |
| 93.5 | 42.2 | 34.2 | 35.0 | 84.5 | 46.8 | 38.8 | 39.0 |
| 100.0 | 39.9 | 31.9 | 32.6 | 85.7 | 46.7 | 38.7 | 38.4 |
| 102.8 | 38.7 | 30.7 | 31.6 | 87.4 | 45.8 | 37.8 | 37.6 |
| 110.4 | 36.8 | 28.8 | 29.3 | 87.8 | 45.4 | 37.4 | 37.4 |
| 130.4 | 31.9 | 23.9 | 24.4 | 89.0 | 44.7 | 36.7 | 36.9 |
| 135.2 | 31.2 | 23.2 | 23.7 | 89.9 | 44.9 | 36.9 | 36.5 |
| 152.5 | 29.1 | 21.1 | 20.9 | 92.0 | 43.8 | 35.8 | 35.6 |
| 174.6 | 26.0 | 18.0 | 18.1 | 92.2 | 43.6 | 35.6 | 35.5 |
| 207.2 | 23.2 | 15.2 | 15.2 | 97.1 | 41.8 | 33.8 | 33.6 |
| 209.0 | 23.0 | 15.0 | 15.1 | 97.9 | 41.8 | 33.8 | 33.3 |
| 212.0 | 23.0 | 15.0 | 14.9 | 127.7 | 33.7 | 25.7 | 25.1 |
| 231.8 | 21.6 | 13.6 | 13.6 | 130.2 | 33.6 | 25.6 | 24.1 |
| 232.6 | 21.7 | 13.7 | 13.5 | 160.5 | 28.2 | 20.2 | 19.8 |
| 275.6 | 19.4 | 11.4 | 11.4 | 163.1 | 27.8 | 19.8 | 19.5 |
| 295 | 18.6 | 10.6 | 10.6 | | | | |
| 41.5 | 93.5 | 85.5 | 86.2 | 47.5 | 82.4 | 74.4 | 73.7 |
| 42.1 | 91.4 | 83.4 | 84.8 | 49.5 | 79.5 | 71.5 | 70.3 |
| 43.0 | 89.9 | 81.9 | 82.7 | 51.8 | 74.8 | 66.8 | 66.8 |
| 49.0 | 80.7 | 72.7 | 71.2 | 53.8 | 71.8 | 63.8 | 64.0 |
| 56.0 | 68.8 | 60.8 | 61.2 | 55.0 | 70.6 | 62.6 | 62.4 |
| 58.4 | 67.5 | 59.5 | 57.9 | 55.6 | 69.5 | 61.5 | 61.7 |

The data are grouped as taken from four different runs. The room temperature figure is an average of a number of results. The temperatures below 60°K are somewhat uncertain, perhaps off by one or two °K.




9. DEVIATION OF EXP'T VALUES OF $\chi$ FROM

$$\chi = \left(8 + \frac{304}{T-6}\right) \times 10^{-6}$$

of vanadium. The 58-42 copper-nickel alloy has been measured at hydrogen temperatures, also.

From the work on these samples the following observations are made:

1) The measuring apparatus is capable of operation from 300°K to 2°K. This is not a trivial observation inasmuch as considerable difficulty was encountered due to the sample sticking at low temperatures. Another modification of the apparatus was used for some of the later measurements in order to reduce further the difficulty from this source. It is described in Appendix iii.

2) The precision and reproducibility of the measurement of magnetization is better than ± 2%.

3) The limit on the precision of the measurement is the vibration of the detector coils on moving the sample. If a comparison of experiences with the 63-37 sample to those with a 74-26 is made, it is noted that the absolute uncertainty in the measurements is the same even though the susceptibility has decreased. The mass of the two samples is the same, hence the vibrational disturbances should be the same and the uncertainty in the measurement from vibration should be the same. This uncertainty was found to be $\pm\ 0.2 \times 10^{-7}$.

4) The agreement with a previous measurement of vanadium is within 1%.

The data for 63-37 copper-nickel at liquid helium temperatures are given in table III. The original observations were those of the current necessary to give a null indication and the reading of the fluxmeter. The magnetization is obtained from the current using

$$M = nI/10\ L$$

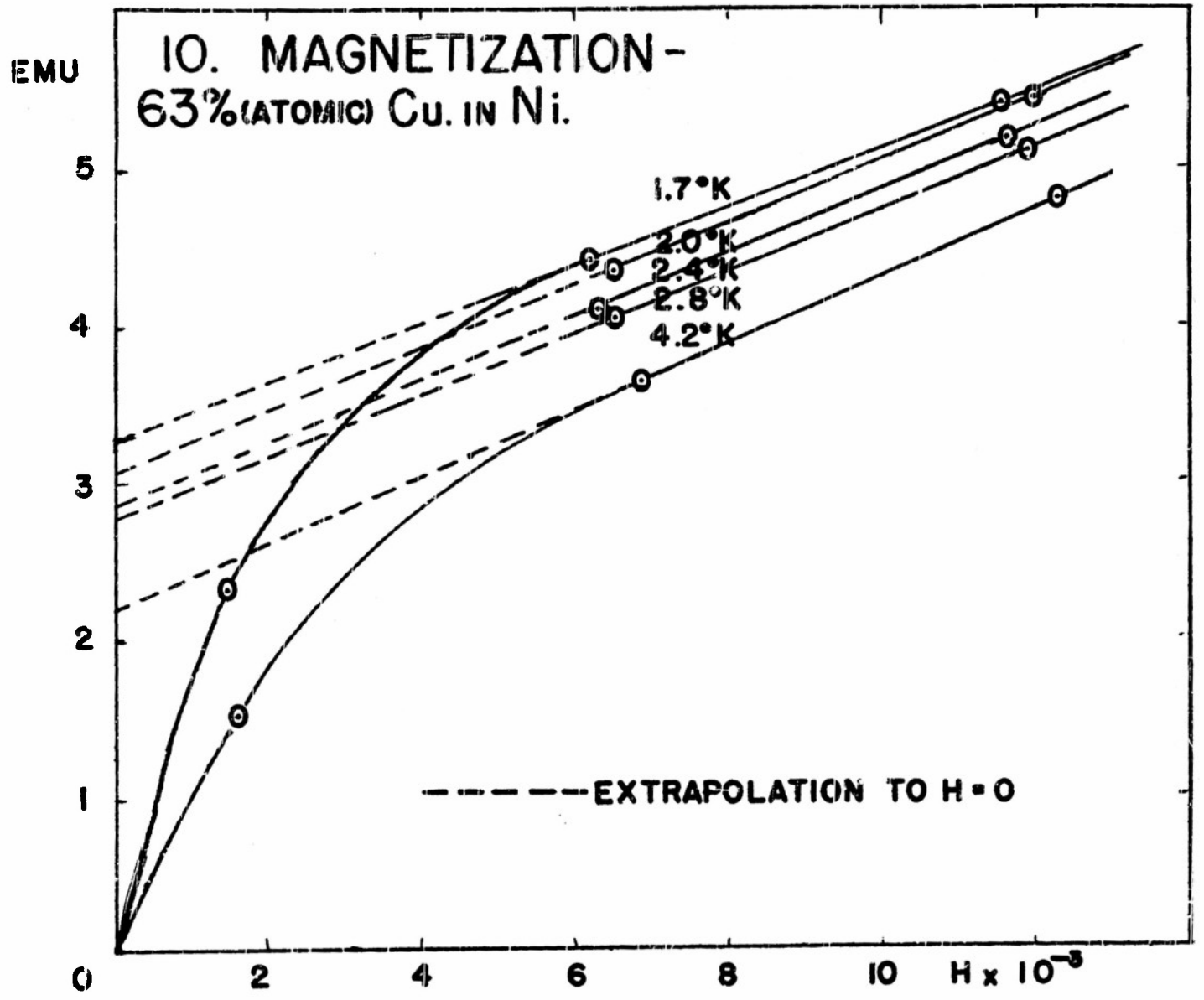
where I is in amps, n is the number of turns of the coil and L is the length of the coil (the thickness of the sample). The fluxmeter reading is corrected by 3% to give the applied field. The field inside the sample, $H_i$ is given by subtracting $4\pi M$. The values of M vs $H_i$ are plotted in figure 10.

The data for 58-42 copper-nickel were taken using the pro-

Table III

Magnetization of 63-37 Copper-Nickel at Liquid Helium Temperatures

| $T = 4.2^{\circ}K$ | | | $T = 1.7^{\circ}K$ | | |
|---|---|---|---|---|---|
| M | $H_a \times 10^3$ | $H_i \times 10^3$ | M | $H_a \times 10^3$ | $H_i \times 10^3$ |
| 1.50 | 1.64 | 1.62 | 2.32 | 1.50 | 1.47 |
| 3.64 | 6.90 | 6.85 | 4.40 | 6.24 | 6.18 |
| 4.78 | 12.36 | 12.35 | 5.41 | 11.64 | 11.57 |
| | $T = 2.78^{\circ}K$ | | | $T = 2.38^{\circ}K$ | |
| 4.05 | 6.58 | 6.53 | 4.10 | 6.28 | 6.23 |
| 5.10 | 11.95 | 11.89 | 5.19 | 11.75 | 11.68 |
| | $T = 2.00^{\circ}K$ | | | | |
| 4.34 | 6.53 | 6.47 | | | |
| 5.44 | 12.05 | 11.98 | | | |


10. MAGNETIZATION -
63% (ATOMIC) Cu. IN Ni.
EMU
5
4
3
2
1
0
1.7°K
2.0°K
2.4°K
2.8°K
4.2°K
EXTRAPOLATION TO H = 0
2
4
6
8
10
H x 10⁻³

cedure given in section B. The conversion of galvanometer deflections into magnetization and the applied field values into the internal field values are obtained from the values of the two constants K and D, where K is the proportionality constant between the galvanometer deflection and the magnetization and D is the demagnetizing fraction. The latter is obviously independent of temperature. The value of K should not depend on temperature below 30°K as the resistance of the circuit remains constant and dimensional chan ges should be negligible.

Equation (49) gives

$$M_s = M_c \frac{1 + 4\pi \left(\frac{\partial M}{\partial H}\right)_c}{1 + 4\pi D \left(\frac{\partial M}{\partial H}\right)_c}$$

where $M_s$ is the magnetization observed in a given applied field $H_a$ with the deflection method and $M_c$ is the magnetization observed in the same applied field $H_a$ with the null coil. Now if

$$4\pi \left(\frac{\partial M}{\partial H}\right)_c \ll 1$$

then

$$M_s = M_c \left[1 + (1-D) 4\pi \left(\frac{\partial M}{\partial H}\right)_c\right] \qquad (50)$$

and the galvanometer constant becomes

$$K = \frac{G}{M_c}\left[1 - (1-D) 4\pi \left(\frac{\partial M}{\partial H}\right)_c\right] \qquad (51)$$

where G is the galvanometer reading.

The values of $M_c$ as a function of $H_i$ are obtained as for the 63-37 sample up to magnetizations of 10 emu; these are given in table IVa. From a plot of these data the values of $(\partial M/\partial H)_c$ are obtained. The values for 20°K and 14°K at 1.5 KG and 3.2KG are found to be approximately $10^{-3}$. It is then seen that complete uncertainty in D gives an uncertainty in K of only 1%. D is taken as .55 from geometrical considerations and the resulting value of K, determined from the readings at 14°K and 20°K is found to be K = .32.

The comparison of the magnetizations deduced from the galvanometer deflections with the magnetization measured with the null coil is much more sensitive to D when $(\partial M/\partial H)_c$ is large. Values of the order of $10^{-1}$ are found for $(\partial M/\partial H)_c$ in the low applied fields (20g and 150G) at liquid helium temperatures. Here it is found that the best agreement is obtained with D = .55 ± .02.

Table IV

Magnetization vs Field for 58-42 Copper-Nickel Alloy.

a. Using null coil method

| $T = 20.2^{\circ}K$ | | | $T = 14.5^{\circ}K$ | | |
|---|---|---|---|---|---|
| $M_c$ | $H_a$ | $H_i$ | $M_c$ | $H_a$ | $H_i$ |
| 1.59 | .174 | .154 | 2.08 | .139 | .113 |
| 4.84 | 1.67 | 1.61 | 9.23 | 3.54 | 3.42 |
| 6.82 | 3.29 | 3.20 | 6.72 | 1.64 | 1.56 |

b. Using deflection method, K = .92, D = .55

| $T = 20.2^{\circ}K$ | | | | $T = 14.5^{\circ}K$ | | | |
|---|---|---|---|---|---|---|---|
| $KM_s$ | $H_a$ | $M_s$ | $H_i$ | $KM_s$ | $H_a$ | $M_s$ | $H_i$ |
| 1.51 | .174 | 1.64 | .163 | 2.00 | .139 | 2.18 | .124 |
| 4.49 | 1.67 | 4.89 | 1.64 | 6.19 | 1.64 | 6.73 | 1.595 |
| 6.30 | 3.29 | 6.85 | 3.25 | 8.60 | 3.549 | 9.36 | 3.47 |
| 9.08 | 6.94 | 9.88 | 6.87 | 11.07 | 6.73 | 12.04 | 6.65 |
| 11.80 | 12.44 | 12.84 | 12.35 | 13.05 | 10.70 | 14.20 | 10.60 |
| $T = 4.2^{\circ}K$ | | | | $T = 1.8^{\circ}K$ | | | |
| 1.8 | .024 | 1.96 | .011 | 2.65 | .025 | 2.88 | .006 |
| 6.4 | .173 | 6.96 | .125 | 6.45 | .129 | 7.02 | .081 |
| 12.6 | 1.66 | 13.7 | 1.57 | 13.9 | 1.63 | 15.1 | 1.53 |
| 14.6 | 3.47 | 15.9 | 3.36 | 15.8 | 3.38 | 17.2 | 3.26 |
| 16.7 | 7.13 | 18.2 | 7.00 | 17.6 | 6.88 | 19.1 | 6.75 |
| 17.6 | 10.05 | 19.1 | 9.92 | 18.4 | 9.84 | 20.0 | 9.70 |
| 18.4 | 12.75 | 20.0 | 12.6 | 19.1 | 12.44 | 20.8 | 12.3 |

Table IVb gives the data for 58-42 copper-nickel where the magnetizations have been obtained from the deflection using k = .92 and the internal fields $H_i$ by using D = .55. The data of tables IVa and IVb are plotted together in figure 11. These data are discussed in part IV of this work.

The data for the chromium-nickel alloys and vanadium are treated as indicated above for the 63-37 alloy. The results are given in tables V and VI and are discussed in parts V and VI respectively.

## IV. DISCUSSION OF THE ALLOYS OF COPPER WITH NICKEL

### A. Introduction

The interest in the transition from ferromagnetism to the diamagnetism as copper is added to nickel is based on the facts that:

1) Copper and nickel form a solid solution at all compositions,

2) The internuclear distance varies only slightly with composition,

3) The spontaneous magnetization at $0^{\circ}K$ appears to decrease (at least for small percentages of copper from 0.6N Bohr magnetons per atom in pure nickel at a rate of one Bohr magneton for each copper atom which replaces a nickel atom.

The suggestion of Mott that the alloying process is one of adding electrons to an otherwise unaffected band leads to the conclusion that ferromagnetism should not persist above a fractional concentration of copper in nickel of $c = 0.6$. As discussed in part II, the band picture does not necessarily lead to the conclusion that the ferromagnetism should persist all the way to $c = 0.6$. Mott's conclusions were only a necessary condition for ferromagnetism, namely that there are holes in the d-band. The sufficient condition, as pointed out by Stoner, is that the exchange energy per particle is a certain fraction of the energy of a hole at the top of the inverted band, the fraction depending on band shape. It was shown in part II that for a rectangular band relatively simple assumptions lead to a linear decrease in the spontaneous magnetization at $0^{\circ}K$ at a rate of 1 Bohr magneton per copper atom.

Above a certain fractional concentration it is to be expected that the d-band is full. Consequently only the s-band should contribute to the magnetic properties at low temperatures. As for pure copper, these alloys

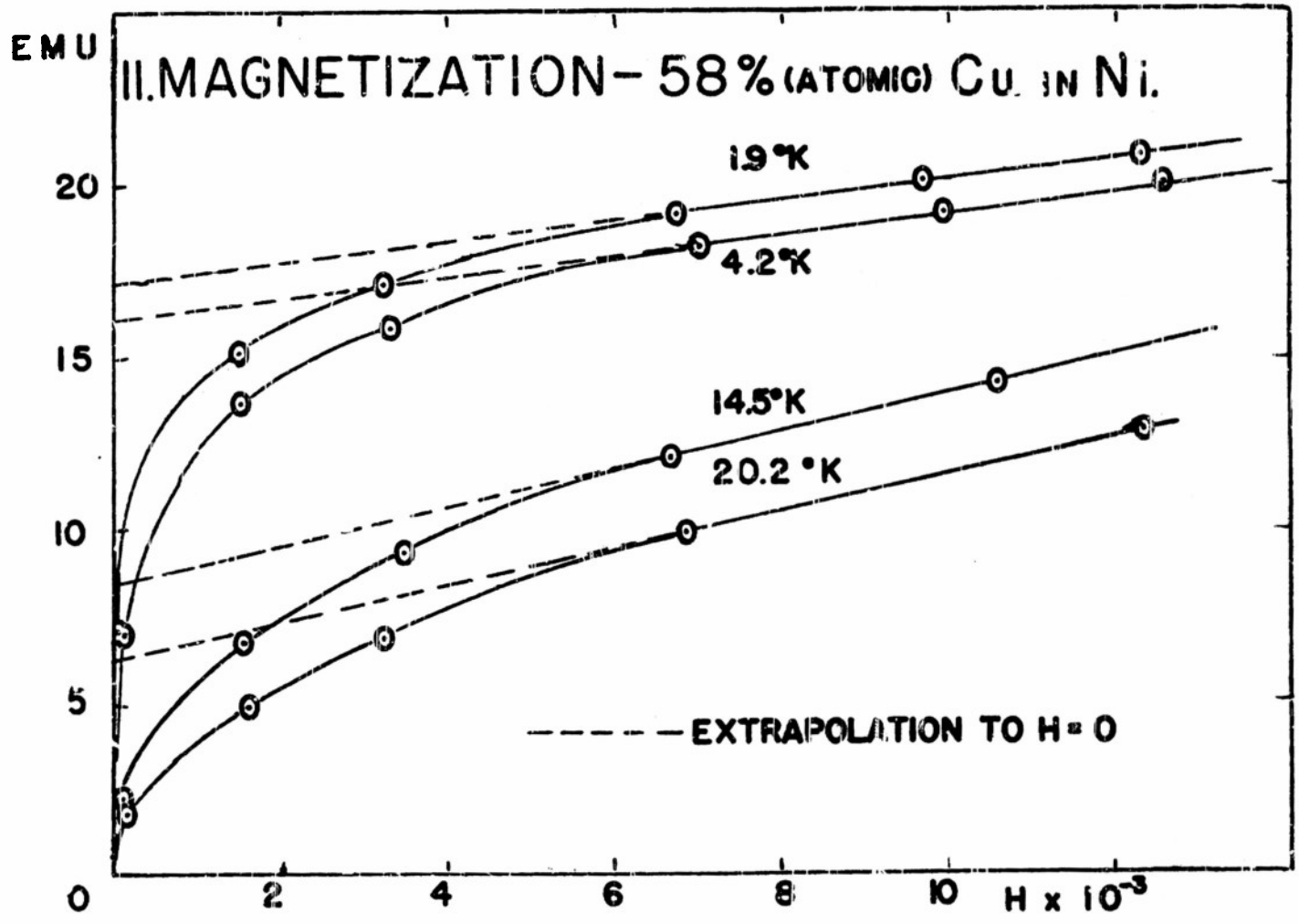

EMU
II. MAGNETIZATION – 58% (ATOMIC) Cu IN Ni.
1.9°K
4.2°K
14.5°K
20.2°K
EXTRAPOLATION TO H = 0
20
15
10
5
0
2
4
6
8
10
H x 10⁻³

Table V

Magnetizations of Chromium-Nickel Alloys below Room Temperature

| 15.5 atomic per cent chromium, Density = 8.83 | | | | 19.9 atomic per cent chromium, Density = 8.49 | | | |
|---|---|---|---|---|---|---|---|
| $M \times 10^2$ | $H \times 10^{-3}$ | $\chi \times 10^6$ | $T^oK$ | $M \times 10^2$ | $H \times 10^{-3}$ | $\chi \times 10^6$ | $T^oK$ |
| 35.2 | 6.94 | 49.2 | 298.0 | 27.2 | 7.18 | 37.9 | 297 |
| 63.0 | 12.9 | 48.8 | | 48.0 | 12.67 | 37.9 | |
| 40.6 | 7.14 | 56.9 | 88.6 | 30.5 | 7.25 | 42.1 | 63.6 |
| 41.4 | 7.15 | 57.9 | 73.4 | 54.0 | 12.82 | 42.1 | |
| 74.7 | 13.0 | 57.5 | 72.9 | | | | |
| 41.6 | 7.15 | 58.2 | 69.4 | 8.7 | 1.72 | 50.6 | |
| | | | | 35.1 | 7.05 | 49.7 | 4.2 |
| 1.48 | .147 | 100.7 | | 62.6 | 12.7 | 49.2 | |
| 15.9 | 1.62 | 98.3 | 4.2 | | | | |
| 65.4 | 7.00 | 93.4 | | 10.1 | 1.64 | 61.6 | |
| 111 | 12.8 | 86.7 | | 20.5 | 3.38 | 60.6 | |
| | | | | 41.0 | 6.96 | 58.9 | 1.8 |
| 73.7 | 6.90 | 106.8 | 2.55 | 56.2 | 9.78 | 57.4 | |
| | | | | 70.3 | 12.57 | 55.9 | |
| 75.1 | 6.86 | 110.5 | 2.26 | | | | |
| 2.70 | .179 | 151 | | | | | |
| 22.6 | 1.60 | 138 | | | | | |
| 81.0 | 6.90 | 119 | 1.68 | | | | |
| 129. | 12.36 | 104 | | | | | |

Table VI

Susceptibility of Vanadium at Liquid Helium Temperatures

| Magnetizations EMU x $10^2$ | Field KG | $\chi \times 10^6$ | Temperature | Average value $\chi$ per gram |
|---|---|---|---|---|
| 21.1 | 7.0 | 30.2 | | |
| 20.8 | 7.02 | 29.7 | 304°K | $5.04 \times 10^{-6}$ |
| 37.8 | 12.7 | 29.8 | | |
| 21.65 | 7.08 | 30.7 | | |
| 39.6 | 12.78 | 31.0 | 4.2°K | |
| 21.65 | 6.99 | 31.1 | | |
| 39.6 | 12.78 | 31.0 | 2.3°K | $5.23 \times 10^{-6}$ |
| 29.9 | 9.70 | 30.9 | | |
| 38.8 | 12.68 | 30.6 | 1.95°K | |

Density measurement = 5.91 grams/cc

would be expected to be diamagnetic, the temperature in dependent paramagnetism being less than the diamagnetism of the copper electron core.

1. Paramagnetism of Copper-rich Alloys - This is not what is found experimentally. The results of Wheeler[52] and of Kaufman and Starr[40] for the copper-rich alloys show a more complicated behavior than would be expected on any simple theory. The alloys with low fractional concentrations of copper show a behavior above the Curie point which can be explained reasonably well by the collective electron theory. The consideration of the transfer effect by Wohlfarth[26] has given even better agreement. The transfer effect is the spilling out of electrons from the d-band into the s-band at high temperatures, giving rise to a term in the expression for the susceptibility which increases with temperature. But for compositions with fractional copper concentrations greater than .6 the experimental results are hopeless from the collective electron approach. Instead of diamagnetism, one finds paramagnetism with an unusual temperature dependence. The results* can be summarized by giving the parameters in the expression

$$\chi = \frac{a}{T} + b + cT \qquad (52)$$

The strong temperature dependence at low temperatures given by the first term looks like a Curie-Weiss type paramagnetism, but it would be stretching the analysis to attach meaning to the values of effective number of carriers of the moment without a mechanism to explain the existence of such carriers and why they should obey classical statistics. The transfer effect can to some degree account for the last term, but without some mechanism for the other terms little can be learned by elaborate calculations of the transfer effect and comparison with the parameters found by forcing the above formula on the data.

The strong increase at low temperatures of the paramagnetism of alloys with fractional copper concentrations greater than 0.6 has given rise to speculation that these alloys may become ferromagnetic at low enough temperatures. The magnitude of ferromagnetism to be expected from the observed paramagnetism can not be predicted.

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* See also discussion by Stoner[5].

By the application of classical statistics to uncoupled particles of spin 1/2, the susceptibility above the Curie temperature is found to be

$$\chi = \frac{C}{T-\Theta} \qquad (53)$$

where $C = n' \frac{\beta^2}{k} N$, n' being the effective number of carriers of spin 1/2 per atom of the solid. If all these carriers are lined up at $0^\circ K$, the spontaneous specific magnetization would be

$$\sigma_0 = \frac{\sigma_0 A}{A} = n' \beta N/A \qquad (54)$$

However, one of the difficulties of the Brillouin-Weiss theory of ferromagnetism is that the values of n' calculated above the Curie temperature do not agree with the values found from below the Curie temperature. For nickel the difference is between the values 0.86 and 0.60 respectively.

This was one of the difficulties overcome by the use of Fermi-Dirac statistics in the collective electron theory. With a given number of carriers a comparison of the predictions of the classical statistics and the Fermi-Dirac statistics shows that the slope of the $1/\chi$ vs T curve is always less on the basis of the Fermi-Dirac statistics except in the limit of high temperatures. Hence, if the classical picture is fitted to data which actually are results of Fermi-Dirac statistics, the use of classical statistics will give a number of carriers that is greater than the actual number. The constant in the above equation therefore gives only an upper limit on the magnetization to be found if the alloys go ferromagnetic at low temperatures.

2. Electronic Specific Heat - It is of interest to note that not only is there a sharp contrast between the apparent simplicity of the ferromagnetic properties and the complexity of the paramagnetic properties of the copper-nickel alloys, but also there is a sharp contrast between the high temperature measurements and the low temperature measurements of the electronic specific heats of the alloys as a function of concentration. The high temperature data of Grew[38] indicate that the electronic contribution to the specific heat decreases directly as the spontaneous magnetization at $0^\circ K$ does with increasing copper concentration; that is, it appears to be going linearly to zero at $c = 0.6$. The measurements of Keesom and Kurrelmeyer[42] on the electronic specific heat at helium temperatures show a constant electronic specific heat for all compositi-

tions up to $c \leq 0.6$ and gradual decrease with higher copper concentrations. In terms of density of states this implies, in the first case, a triangular band shape and, in the latter, a rectangular band shape.

Measurements at liquid helium temperatures of alloys in the region of $c = 0.6$ should shed some light on all the above-mentioned problems as well as on the problem detailed in part II. The interesting quantities, as far as the discussion of the collective electron theory and the electronic specific heat is concerned, are the spontaneous magnetization of the individual domains and their temperature dependence. For the problem of the paramagnetism of the high copper concentrations, it is of interest just to give a yes or no answer to whether these alloys are ferromagnetic at low temperatures.

The measurements of alloys of $c = 0.58$ and $c = 0.63$ are given in part III of this work and are to be discussed in this part of the work in connection with the problems outlined above. The handling of the data needs, first of all, a criterion for determining whether a sample is ferromagnetic and, secondly, a means of extracting the spontaneous magnetization of an individual domain from the data on an aggregate of ferromagnetic domains. This will be discussed before turning to the data of part III.

3. A Criterion for the Presence of Ferromagnetism - If it were possible to make measurements on single domains, the necessary and sufficient condition for a sample to be ferromagnetic would be the presence of a magnetization in zero field. For an aggregation of domains this is still a sufficient condition and any material which exhibits a "remanence," that is, a magnetization in zero field, is ferromagnetic. As the remanence of a polydomain structure can be a very small fraction of the magnetization of the elementary domains, the remanence is not a useful necessary condition for ferromagnetism. We consider magnetic isotherms and their temperature dependence in order to find a useful necessary and sufficient condition for a material to be termed ferromagnetic. The necessary condition is that the isotherms show some sort of "knee." The sufficient condition is that the family of isotherms approaches higher and higher values of magnetizations at all fields beyond the "knees" as the temperature decreases. This is to distinguish between ferromagnetism and the saturation of a paramagnetic material. While the

paramagnetic isotherms may show "knees," the family of isotherms all approach a given saturation magnetization. The usefulness and reasonableness of this criterion should become clearer after the following discussion of the data on materials which do show a marked remanence well below their Curie points.

4. Extraction of the Spontaneous Magnetization - The magnetic isotherms for ferromagnetic materials may be characterized by a twofold effect of the applied field on the materials. The first effect is to give a preferred direction for the spontaneously magnetized domains. The second effect is to increase the magnetization of the individual domains. As a first approximation the second effect is negligible compared to the first for the ferromagnetic elements. This is, of course, intimately connected with Weiss's hypothesis that there is a strong effective field within a domain, hence the additional field which can be supplied in the laboratory can have little effect on the domains themselves. The main effect of the applied field is to line up domains; thus the magnetization as a function of field is given by

$$M = M_0 [1 - f(H)] \tag{55}$$

where $M_0$ is the spontaneous magnetization of a domain and f(H) is an expression going to zero for large values of H. The mechanisms entering into f(H) form the study of the technical magnetization curve and have, for practical reasons, received a great deal of attention throughout the years. For values of the field of the order of KG's, the main effects have been isolated in two terms:

$$f(H) = \frac{a}{H} + \frac{b}{H^2} \tag{56}$$

where the "b" is an anisotropy effect and "a" has been partly explained by Neel[59] as an effect due to inclusions and dislocations. From all this follows a very simple way of extracting $M_0$ from the magnetic isotherms. One merely plots M vs 1/H and extrapolates M linearly to 1/H = 0.

Unfortunately, such a method does not always work. For the pure elements at temperatures approaching the Curie temperature and for the alloys in general it is found that the magnetization does not approach a limit in high fields but continues to increase with a small slope. Such an effect is what would be expected from an increase in the spontaneous magnetization with field; thus the equation for the magnetic isotherms

is more properly given by

$$M = M_0 [1 - f(H)] + \chi_p H \qquad (57)$$

where $\chi_p$ is a term expressing a superimposed paramagnetism, given the name of "parasitic" paramagnetism by Neel[60].

The data of Weiss and Forrer[50] on pure nickel show that, except in the region of the Curie temperature, the above expression fits the data well. The isotherms all become linear in fields greater than 6KG. The spontaneous magnetization found by a linear extrapolation of the high field magnetization back to zero field agrees with that found by measurements of the magneto-caloric effect, giving further evidence of the validity of the expression for the isotherms.

The behavior of materials in the neighborhood of their Curie temperatures is more complicated than this. The analysis of Weiss and Forrer of the data on nickel and of Oliver and Sucksmith[46] for a copper-nickel alloy of fraction copper concentration $c = 0.239$ includes not only a determination of a large number of closely spaced magnetic isotherms but also measurements of the magneto-caloric effect. Their measurements can be analyzed to give the spontaneous magnetization from both the magnetic isotherms and the magneto-caloric effect and also from the lines of constant magnetization on a plot of H vs T. The agreement is excellent until the temperatures approach the Curie temperature.

As will be discussed below, the Curie temperature is extremely sensitive to concentration gradients in the alloys. Even in pure nickel the Curie temperature is found to be structure-sensitive. However, in this work it is the spontaneous magnetizations at temperatures well below the Curie temperature that are of importance as the interest is centered on determining the spontaneous magnetization at $0^{\circ}K$ of the alloys.

For the isotherms below the Curie temperature region the extrapolation using equation (57) can be justified for all the metals and alloys previously measured.* For pure nickel well below the Curie temperature the term linear in H becomes completely negligible as far as determining the spontaneous magnetization, but in the alloys of nickel measured by Sadron[48] and Marian[45] the linear term becomes a larger fraction

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* See, for instance, Rado and Kaufman[47].

of the observed magnetization as the concentration of nickel is reduced. In the measurements of Kaufman, Pan, and Clark[41] on iron-gold alloys of low iron concentration the linear term gives a magnetization in fields of 10KG of the same order of magnitude as the spontaneous magnetization.

All this is mentioned in connection with the previous discussion of the criterion for a material to be ferromagnetic. Put more precisely, the necessary and sufficient condition for ferromagnetism is that as the temperature is increased from $0^{\circ}K$ the magnetic isotherms must be of the form given by equation (57) with the value of $M_0$ decreasing with increasing temperature. The analysis of the isotherms in this manner is permitted to fail in the region of temperature where $M_0$ tends toward zero. Above this region the behavior is characterized by the values of $\chi_p$.

## B. Analysis of the Data for the 58 and 63 Atomic Per Cent Copper Alloys

In this section an analysis is made of the data of part III of this work concerning the copper-nickel alloys with $c = 0.58$ and $c = 0.63$. In order to give some indication of where the analysis is headed, an outline is given here at the beginning.

1) The magnetic isotherms are shown to fit the criterion for ferromagnetism.

2) The spontaneous magnetization and the value of the superimposed "parasitic" susceptibility are found for each temperature.

3) The spontaneous magnetization versus temperature curves are compared with the results for lower concentrations of copper.

4) The nature of these curves is shown to be indicative of inhomogeneities over either macro or micro regions.

5) The problem of inhomogeneities is considered and it is shown that the data for the 58 per cent alloy should yield the same value for the spontaneous magnetization at $0^{\circ}K$ whether the observed form of the magnetization vs temperature curve is due to inhomogeneities or not. This does not appear to be true for the 63 per cent alloy.

6) The data are then discussed in relation to the collective electron theory, the problem of the paramagnetic behavior of the high copper concentration alloys, and the appearance of the parasitic paramagnetism.

1. The Magnetic Isotherms - The magnetic isotherms for the two copper-nickel alloys are tabulated in tables III, IVa, and IVb and are graphed in figures 10 and 11. The curves can be fitted to the form of equation (57). It is to be noticed that though the linear term makes a considerable contribution to the magnetization, the first term increases with decreasing temperature in such a way as to rule out the possibility of explaining the isotherms as arising from the saturation of a paramagnetic material.

The data for $c = 0.58$ show three points for fields greater than 6KG. These points lie on a straight line to within the experimental error. Hence f(H) vanishes in these alloys in fields of the same order as the field for which it is found to vanish in pure nickel. It is interesting to note that the order of magnitude of the values of $\chi_p$ found for these alloys is the same order of magnitude as found for pure nickel. This point will be returned to later in the discussion of the origin of the linear term.

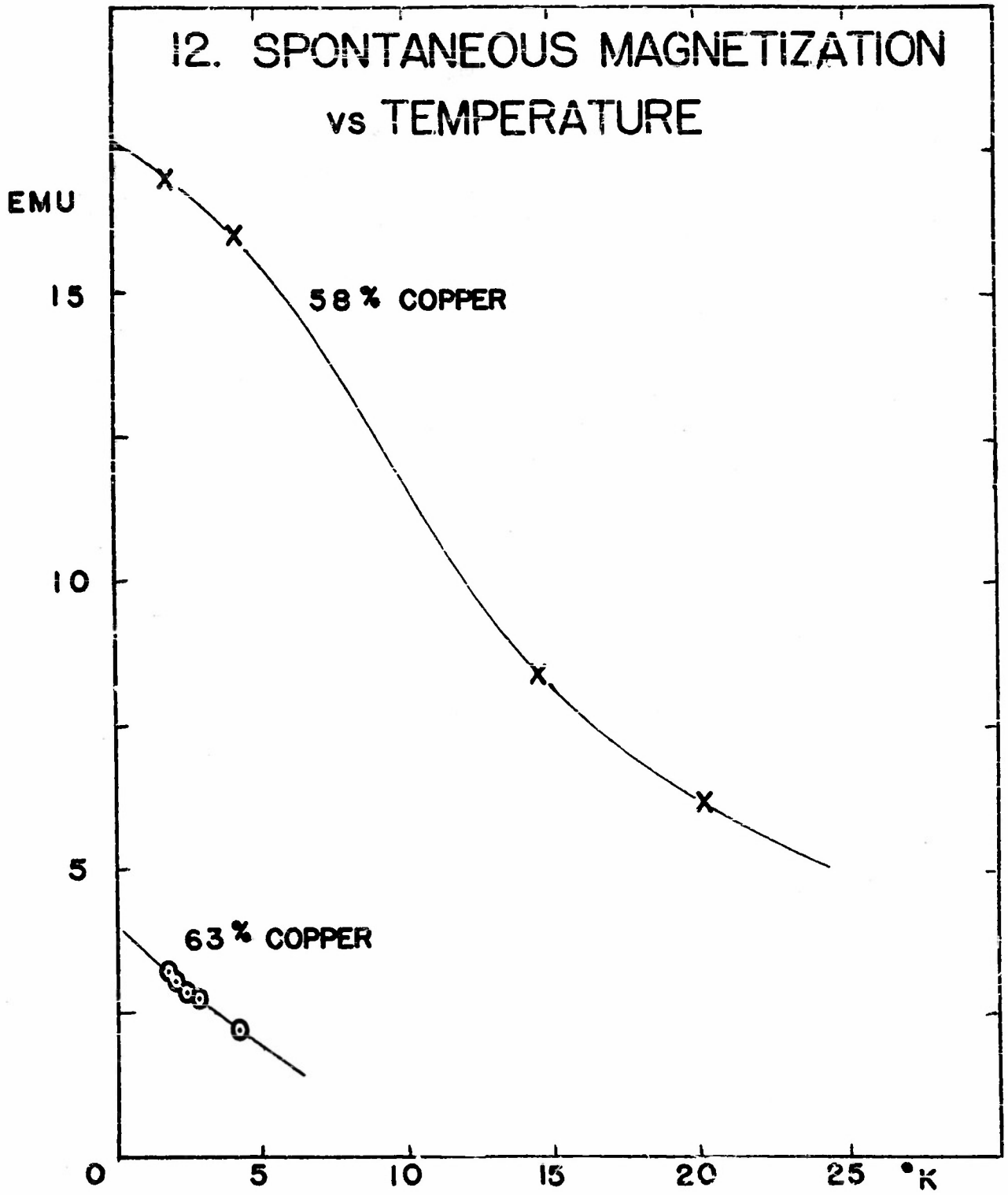
The ferromagnetism of these alloys differs from the ferromagnetism of pure nickel principally in the large reduction in the values of $M_o$. It is clear from the above discussion that both alloys demonstrate ferromagnetism and that this ferromagnetism can be characterized by giving the values of $M_o$ as a function of temperature. The values of $M_o$, in view of what has been said above, are found by extrapolating the linear high field portion of the magnetic isotherms to zero field. The slope of the linear high field portion of the magnetic isotherms is the parasitic susceptibility. It, as well as the values of $M_o$, is tabulated in table VII.

2. Spontaneous Magnetization as a Function of Temperature - The values of $M_o$ as a function of temperature are plotted in figure 12. These can be compared to the data for lower concentrations of copper taken from the work of Alder and the work of Oliver and Sucksmith. The gradual distortion of the magnetization curves on decreasing nickel content seen for copper-nickel is also a property of all sixteen alloys investigated by Marian[45]. The effect has since been discussed by Went[51]. Both Went and Marian put the blame on inhomogeneities and give arguments in support of this. Marian's argument is not clear-cut, but as it is of interest and has been generally overlooked, it is given here. Marian classifies the magnetization versus temperature curves by

Table VII

Spontaneous Magnetization and Parasitic Paramagnetic Susceptibility as a Function of Temperature.

| 58-42 Copper-Nickel | | | 63-37 Copper-Nickel | | |
|---|---|---|---|---|---|
| $T^{o}K$ | $M_o$ | $(\partial M/\partial H)_T \times 10^4$ | $T^{o}K$ | $M_o$ | $(\partial M/\partial H)_T \times 10^4$ |
| 20.2 | 6.2 | 5.4 | 4.2 | 2.21 | 2.1 |
| 14.5 | 8.4 | 5.4 | 2.8 | 2.77 | 2.0 |
| 4.2 | 16.0 | 3.2 | 2.4 | 2.85 | 2.0 |
| 1.8 | 17.0 | 3.1 | 2.0 | 3.04 | 2.0 |
| | | | 1.7 | 3.25 | 1.9 |


12. SPONTANEOUS MAGNETIZATION
vs TEMPERATURE
EMU
15
10
5
0
58 % COPPER
63 % COPPER
5
10
15
20
25
°K

letters A, B, C, D. Curve type A shows a sharp decrease in magnetization on approaching the Curie temperature; curve type D is a smooth gradual washing out of the magnetization with temperature increase; types B and C are in between these two extremes of a sharply-defined Curie temperature and no definite Curie temperature. Marian finds that increasing the element alloyed with nickel always produces a change from A to B to C to D, with the notable exceptions that on approaching a solubility limit and entering a two-phase region the curves go back again from D to A through C and B. The implication given by Marian is that there is some mechanism which tends to sharpen the composition distribution of the ferromagnetic phase as the two-phase region is entered. We have investigated this, using the thermodynamics of two-phase systems (see, for instance, Cotrell[3]), and have found no justification on the basis of free energy arguments.

Went shows that the effect of inhomogeneities is to give a smeared out Curie temperature as observed by Marian. Went further cites the case of $Ni_3Fe$ which in the disordered case gives a smeared out Curie temperature, but in the ordered case the indications are that if the ordered phase were maintained through the Curie temperature region, the Curie temperature would be sharper.

The possibility that the data are the results of inhomogeneities must be considered in drawing any conclusions on the quantity in which this work is primarily interested, namely the spontaneous magnetization of a domain of a given composition. Hence something must be said about the role of concentration fluctuations.

3. Fluctuations in Concentration - It is noted as a preliminary remark that if a property of an alloy is a linear function of composition, then the effect of macroscopic or microscopic inhomogeneities is that for every region which decreases the property there is one which increases it and the net effect is that the property of the inhomogeneous alloys is that of the average composition.

Hence if copper-nickel alloys have a spontaneous magnetization at $0^{\circ}K$ such that the magnetization in terms of Bohr magnetons per atom is given by

$$\sigma_0 = c' - c \quad \text{for} \quad c < c'$$

$$\sigma_0 = 0 \quad \text{for} \quad c > c'$$

where c is the fractional copper concentration of the alloy and c' is the

fractional copper concentration for which the spontaneous magnetization goes to zero, then as long as there are no regions of the sample with $c > c'$ the inhomogeneous sample should give a saturation magnetization at $0^{\circ}K$ corresponding to that of a homogeneous sample with a fractional concentration equal to the average fractional concentration $\bar{c}$ of the inhomogeneous sample. If there are regions of the sample with $c > c'$, then the saturation magnetization will be greater than that of a homogeneous sample of concentration $\bar{c}$.

For finite temperatures the magnetization depends on the degree of inhomogeneity even if there are no regions with fractional concentration $c > c'$. This is because the magnetization as a function of composition for finite temperatures is linear only for those compositions for which the given finite temperature is well below the Curie temperature of that composition. The curves of magnetization vs composition will for finite temperatures curve toward the composition axis at lower and lower compositions as the value of T is increased. The composition for which the Curie temperature is less than the finite temperature will contribute nothing to the magnetization. Thus the magnetization vs temperature curves of inhomogeneous samples show Curie temperatures corresponding to the Curie temperature of the region of lowest fractional concentration of copper. The comparison of a magnetization curve for a homogeneous specimen with an inhomogeneous specimen would give for the case of no regions with compositions $c > c'$ a correspondence at $0^{\circ}K$ but for finite temperature the inhomogeneous sample would give lower values at low temperatures and higher values at high temperatures than would the homogeneous sample.

For the sake of argument it can be assumed that homogeneous samples would have the properties obtained by extrapolation of the low concentration data, namely

1) The magnetization at $0^{\circ}K$ is given by

$$\sigma_0 = c' - c$$

2) The Curie point is given by

$$\Theta = K(c' - c)$$

3) The magnetization as a function of temperature for each composition is given by

$$\sigma = \sigma_0 \left[1 - \left(\frac{T}{\Theta}\right)^3\right]$$

where this is an approximation to the actual curve for pure nickel made for ease of calculation. The values of the constants from the low concentration data give $c' = .606$ and $K = 1.04 \times 10^3$.

The magnetization vs temperature curves for inhomogeneous alloys can be calculated on the basis of assumption as to the percentage of the sample at each composition. The choices of this assumption are not particularly restricted. For instance, it could be Gaussian from simple temperature induced fluctuations which are frozen in from high temperatures. It could be rectangular or even two-peaked depending on how it was cooled through the liquid-solidus region and the degree to which annealing allowed diffusion to take place. It is also possible that the interaction of copper and nickel atoms is such that there is some tendency to form regions of certain compositions such as NiCu or $Ni_2Cu_3$ etc., or that the equilibrium state is one of "antiordering," i.e. clustering. The following general features should be observed independent of the type of distribution.

For $\bar{c} < c'$

1) The value of $\bar{\sigma}_o$, the measured saturation magnetization at $0^\circ K$ should be greater than or equal to $\sigma_o$ for the composition $c = \bar{c}'$. The greater than is for the case when there is a region for which $c > c'$.

2) The value of the Curie point is determined by

$$\Theta = K(c' - c_{min})$$

where $c_{min}$ is the lowest fractional concentration present in the inhomogeneous sample.

For $\bar{c} > c'$

1) The value of $\bar{\sigma}_o$ is zero unless there is some region of the sample with $c < c'$.

2) The value of $\bar{\sigma}_o$ can only be found by measurements all the way to absolute zero as there will be contributions to the magnetization from regions whose Curie temperatures approach absolute zero.

3) The Curie temperature as before will be determined by $c_{min}$.

Calculation of the shape of the Curie curves for various assumptions for the distribution of the compositions of the sample shows that the magnetization curves shown in figure 12 are consistent with what would be expected on the basis of inhomogeneities. On the other hand, the dependence on temperature of the magnetization is inconsistent with any exist-

ing theory for the behavior of a homogeneous substance.

If the samples are said to be inhomogeneous, the only measurements of direct significance would be those for $\bar{c} < c'$ and at temperatures far below the Curie temperature corresponding to the composition $\bar{c}$. In terms of the measurements under consideration here, the useful data are those on the 58 per cent alloy at liquid helium temperatures. The measurements should give the same $\sigma_0$ as a homogeneous sample provided the inhomogeneities are within definite boundaries. If the lowest concentration present is $c_{min}$, given by $c_{min} \geq c' - \theta/k$, it may not be too unreasonable to assume that the highest concentration present $c_{max}$ would be given by

$$\bar{c} - c_{min} = c_{max} - \bar{c}$$

If $c_{max}$ is less than $c'$ then it would follow that $\bar{\sigma}_0$ for the inhomogeneous alloy would be the same as $\sigma_0$ for a homogeneous alloy of the composition $\bar{c}$. This condition is that

$$c' - \bar{c} > \theta/2k \qquad (58)$$

Using the values $c' = .606$, $\bar{c} = .58$, and $k = 10^3$ this gives, as the criterion for an inhomogeneous alloy to be sufficiently homogeneous for the extraction of the saturation magnetization at $0^\circ K$, the value of $70^\circ K$ as the upper limit for ferromagnetism. The data in figure 12 certainly seem to justify placing the Curie temperature of the alloy considerably below $50^\circ K$, so that the value found by extrapolation to $0^\circ K$ can be considered as representing the spontaneous magnetization of a single domain of composition $c = 0.53$.

4. Spontaneous Magnetization at $0^\circ K$ as a Function of Composition -

The value for the spontaneous magnetization at $0^\circ K$ depends on the extrapolation procedure. Assuming the value to be somewhere between a linear extrapolation and a $T^2$ extrapolation leads to a value of $M_0$ for the $c = .58$ sample of between 17.5 emu and 17.2 emu. This is an uncertainty of only $\pm$ 1% which is smaller than the errors to be expected by considering that this is a deflection measurement.

With the density, $\rho$, and per cent nickel by weight this can be converted into $\sigma$, the specific magnetization per gram, $\sigma_A$, the specific magnetization per atom, and into n', the number of effective carriers of one Bohr magneton per atom. These quantities are:

| $M_o$ | $\rho$ | $\sigma$ | A | $(\sigma_o)_A$ | n' |
|---|---|---|---|---|---|
| 17.2 - 17.5 | 8.84 | 1.95 | 61.5 | 120 | .0216 - .0220 |

Copper-nickel alloys were investigated by Alder [35] in 1916. This investigation consisted of susceptibility measurements for the entire series and magnetization measurements for the alloys up to 55 per cent copper by weight. The susceptibility results have since been repeated by several observers[52] who demonstrated that certain effects shown by Alder do not exist. The magnetization measurements have not been repeated. Sadron[48], though he measured sixteen series of alloys with nickel, accepted Alder's results. Alder's results have been accepted by all the theoreticians who have formulated theories showing that the moment in nickel should decrease by one Bohr magneton per copper atom added.

Alder used two separate methods for his measurements of the magnetization. For room temperature and above, he used the maximum torque on an ellipsoid in a uniform applied field. For below room temperature he used the induction in a pair of coils on removal of the ellipsoid from the uniform field. It is the results below room temperature which are of importance in determining the spontaneous magnetization at $0^{\circ}K$. The calibration was by comparison with pure nickel. Demagnetizing fields were corrected for, but no attention was given to image effect. The measurements were made at 2, 3, 4, and 5KG. and were arbitrarily extrapolated to 10KG to obtain the spontaneous magnetization. Though no justification exists for such a procedure, the magnetization data for 3, 4, and 5KG were flat enough so that it made little difference whether the extrapolation was done in this way or by extrapolating back to zero field. These extrapolated values for the spontaneous magnetization below room temperature are given in table VIII. The data are plotted in figure 13.

Nowhere in his thesis does Alder say how he extrapolated back to get the spontaneous magnetization at $0^{\circ}K$. The nominal composition of the samples, the analysis by weight, the analysis by atomic per cent, Alder's values for the magnetization at $0^{\circ}K$, the values found by using a linear extrapolation to $0^{\circ}K$, and the values found by using a $T^2$ extrapolation are all recorded in table IX. It is to be noticed that Alder's extrapolations vary considerably from sample to sample within the limits

Table VIII

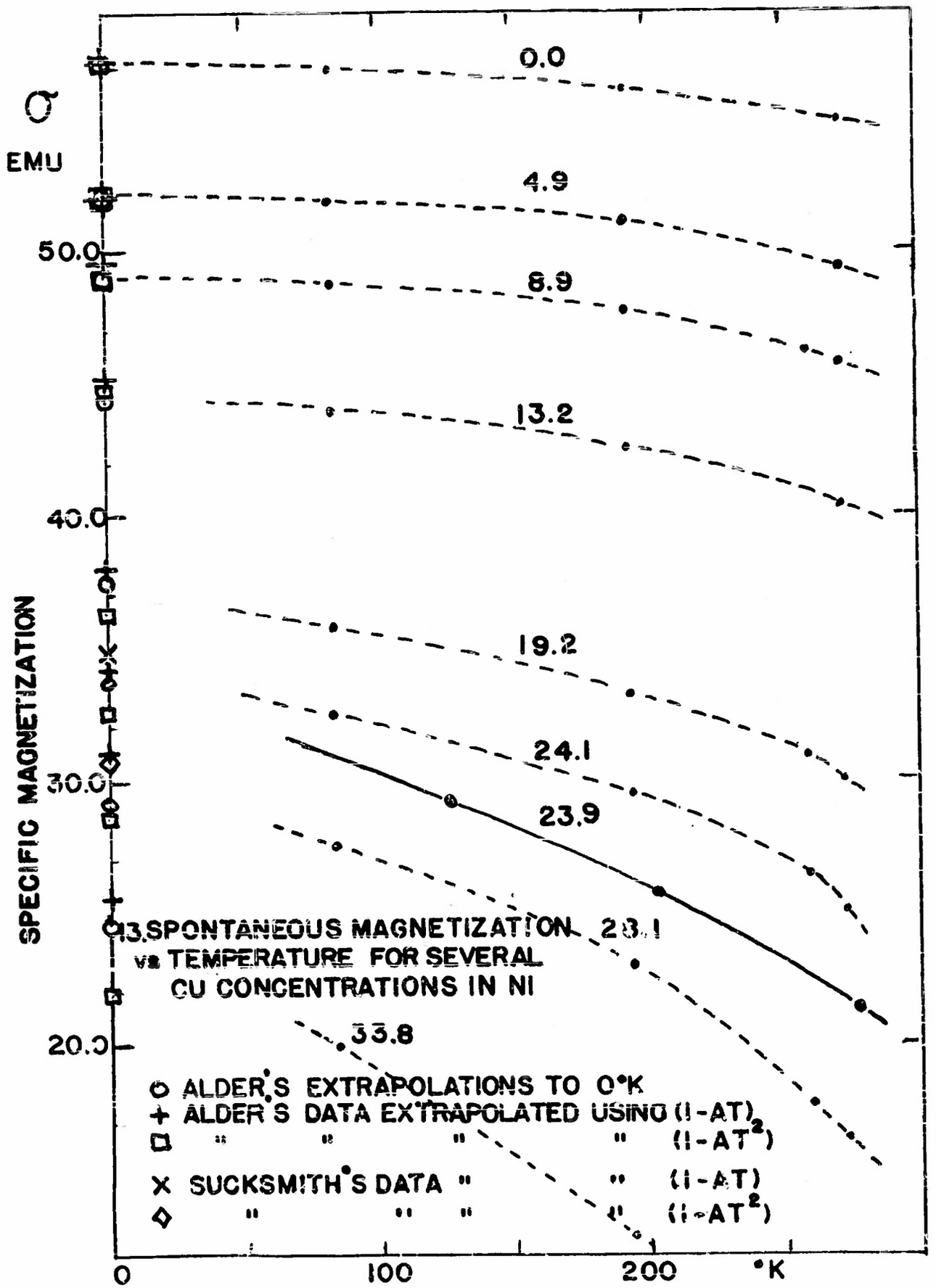
Alder's Data for Copper-Nickel Alloys below Room Temperature.
Data obtained by induction method, values at 3, 4, and 5KG extrapolated to H = 10KG.

| Approx. % Ni | 273°K | 260°K | 255°K | 252°K | 194°K | 85°K |
|---|---|---|---|---|---|---|
| 100 | 54.94 | - | - | - | 56.18 | 56.95 |
| 95 | 49.42 | - | - | - | 51.28 | 51.97 |
| 90 | 45.77 | 46.26 | - | - | 47.77 | 48.79 |
| 85 | 40.40 | 40.98 | - | - | 42.60 | 44.10 |
| 80 | 30.00 | 31.02 | - | - | 33.38 | 35.97 |
| 75 | 25.15 | 26.46 | - | - | 29.52 | 32.16 |
| 70 | 16.44 | 17.85 | - | - | 23.11 | 27.67 |
| 65 | 7.05 | - | - | 8.55 | 12.72 | 20.05 |
| 60 | 4.25 | - | 4.70 | - | 8.40 | 15.72 |
| 55 | - | - | - | - | 3.4 | 11.25 |

Table IX

Analysis of Alder's Data

| Approx. %Ni | Wt. %Ni | Atomic %Ni | Atomic Wt. | ($\sigma_o$ by different extrapolations) Alder | Linear | Quadratic | Bohr Magnetons |
|---|---|---|---|---|---|---|---|
| 100 | 100. | 100. | 58.69 | 57.23 | 57.2 | 57.2 | .601 |
| 95 | 94.71 | 95.1 | 58.93 | 52.20 | 52.2 | 52.2 | .550 |
| 90 | 90.92 | 91.6 | 59.10 | 49.04 | 49.7 | 49.1 | .519 |
| 85 | 85.87 | 86.8 | 59.30 | 44.44 | 45.3 | 44.8 | .472 |
| 80 | 79.54 | 80.8 | 59.63 | 37.70 | 38.0 | 36.4 | .403 |
| 75 | 74.38 | 75.9 | 59.87 | 33.88 | 34.2 | 32.7 | .363 |
| 70 | 70.30 | 71.9 | 60.06 | 29.24 | 31.2 | 28.7 | .314 |
| 65 | 64.52 | 66.2 | 60.34 | 24.55 | 25.6 | 22.0 | .265 |


σ
EMU
50.0
40.0
30.0
20.0
SPECIFIC MAGNETIZATION
0.0
4.9
6.9
13.2
19.2
24.1
23.9
23.1
33.8
0
100
200
°K
SPONTANEOUS MAGNETIZATION vs TEMPERATURE FOR SEVERAL CU CONCENTRATIONS IN NI
ALDER'S EXTRAPOLATIONS TO 0°K
ALDER'S DATA EXTRAPOLATED USING (1-AT)
" " " " (1-AT²)
SUCKSMITH'S DATA " " (1-AT)
" " " " (1-AT²)

of the linear and the $T^2$ extrapolation.

There is also some uncertainty as to the composition of Alder's sample. The analysis shows about 1/2% as the upper limit of the impurities. If these impurities were iron, the impurity expected to have the greatest effect, the presence of the impurities would shift the effective concentration of magnetic atoms about 1%.

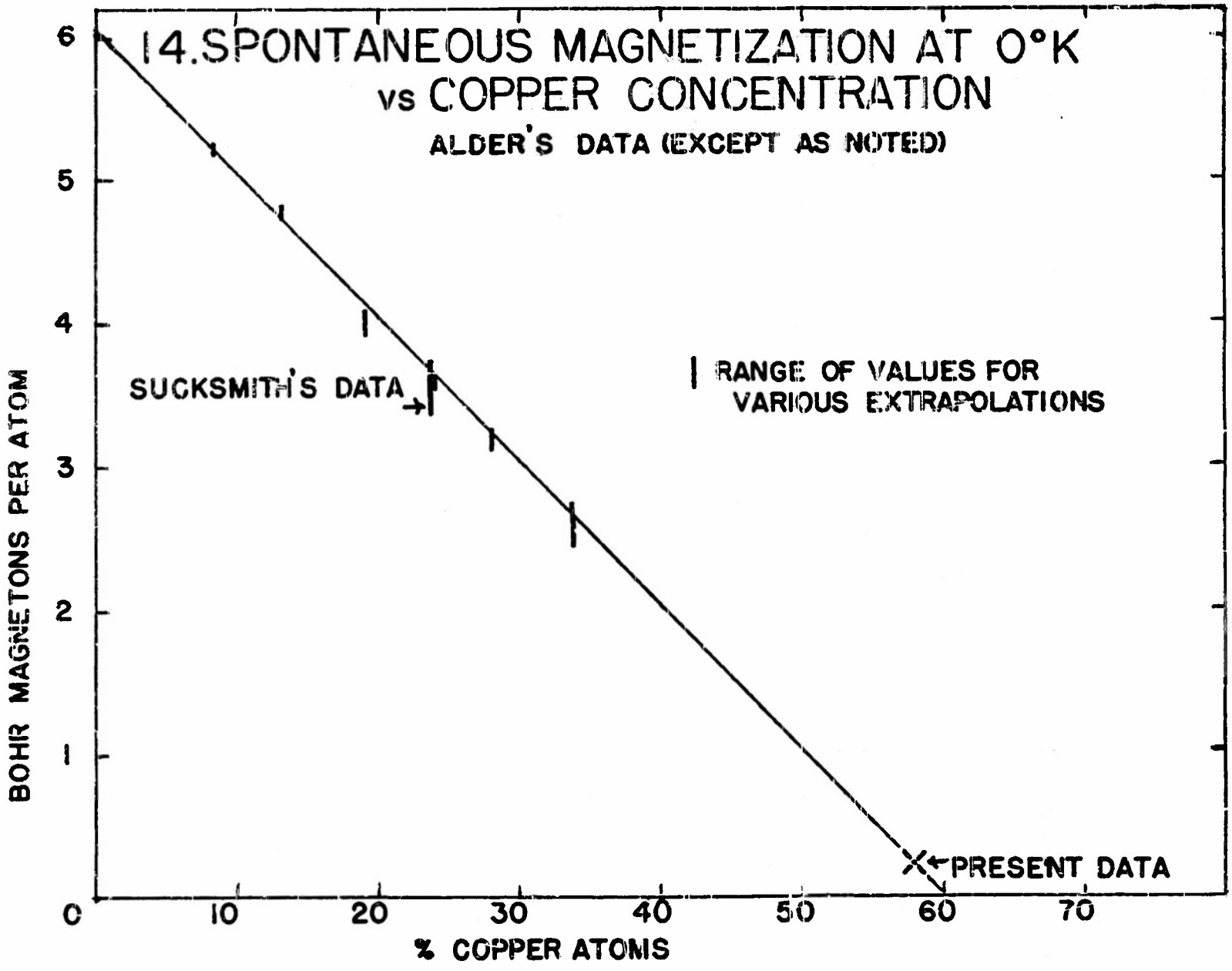
These uncertainties are considered in plotting the spontaneous magnetization versus composition in figure 14. This plot also includes the value recently published by Oliver and Sucksmith[46] for 23.9 atomic per cent copper. This value was obtained by a $T^2$ extrapolation from values of the spontaneous magnetization between the oxygen boiling point and room temperature.

The spontaneous magnetization at $0^{\circ}K$ for the sample with 58 atomic per cent copper is also shown in figure 14.

From figure 14 it is observed that a straight line through the pure nickel point and the point for 58 per cent copper is consistent with Alder's data, but that the point of Oliver and Sucksmith lies 10% below this line. The difference between applying the $T^2$ extrapolation as Oliver and Sucksmith do and using a linear extrapolation of their data will just make up this 10% difference. It is noted in this connection that Oliver and Sucksmith's lowest temperature is $140^{\circ}K$. From the shape of Alder's magnetization vs temperature curves and those observed here for $c = .58$ and $c = .63$ it appears that a linear extrapolation from so far away from $0^{\circ}K$ may be closer to what would be found by measurements at lower temperatures.

The conclusion reached here from the measurements on the 58 atomic per cent copper alloy and the measurements of Alder and of Oliver and Sucksmith is that the spontaneous magnetization at $0^{\circ}K$ decreases at a rate of 1.0 Bohr magneton per copper atom to within the limit of the uncertainty imposed by the experimental data and the extrapolations used in the analysis.

5. Comments on the Observations of 63 Atomic Per Cent Copper Specimen - The curve deduced for the spontaneous magnetization vs temperature for the 63 atomic per cent alloy has much the appearance to be expected from an inhomogeneous alloy. If, however, one wishes to


14. SPONTANEOUS MAGNETIZATION AT 0°K
vs COPPER CONCENTRATION
ALDER'S DATA (EXCEPT AS NOTED)
SUCKSMITH'S DATA
RANGE OF VALUES FOR VARIOUS EXTRAPOLATIONS
PRESENT DATA
BOHR MAGNETONS PER ATOM
% COPPER ATOMS
0
1
2
3
4
5
6
10
20
30
40
50
60
70

conclude that none of this ferromagnetism is a property of a homogeneous alloy of this composition, it is necessary to consider the spread of composition about the mean needed to fit the inhomogeneity hypothesis. If it is supposed that the magnetization of a homogeneous alloy goes to zero at a lower composition, say, at 61 per cent copper, and that the Curie temperature of homogeneous alloys varies linearly with composition going to $0^{\circ}K$ at 61 per cent copper also, then it is necessary to have a spread of at least $\pm 3\%$ to explain the observations which indicated a Curie temperature for at least some region of the sample near $10^{\circ}K$.

The magnetization corresponding to an alloy with a Curie temperature of $10^{\circ}K$ would be, on the same linear extrapolation used above, about 10 emu. Then in order to explain the magnetization observed, 4 emu, about half of the sample would have to have its composition in the range from 2% to 3% to one side of the mean composition. This does not seem too likely as this can be compared with the results for the 58% alloy for which it was shown that the variation in composition was at most 2%. The evidence points to the conclusion that the observed ferromagnetism must be at least partly associated with the magnetization of a single domain of composition $c = .63$. However, the measurements can give only an upper limit on this magnetization.

## C. Conclusions

1. Rectangular versus Parabolic Bands - The relative merits of the parabolic and rectangular density of states curves for explaining a linear decrease of both the spontaneous magnetization and the Curie temperature were discussed in part II of this work. It was pointed out that whereas the linear decreases were to be expected for the rectangular band, for the parabolic band they could be explained only by invoking a particular variation of the exchange parameter J as a function of composition. In addition it was shown that a necessary consequence of the values of J chosen to explain a linear decrease for the parabolic band model is an incomplete spontaneous magnetization at $0^{\circ}K$ for alloys near 60 per cent copper. In particular, it was shown that for a 58 per cent copper alloy the increase in magnetization at $0^{\circ}K$ with field should be such that a field of 10KG would increase the magnetization to twice the value of the

spontaneous magnetization. It has been shown above that the linear decrease is supported by the measurements on the 58 per cent alloy. In addition, the 58 per cent alloy shows less than a 15% increase in the spontaneous magnetization in a field of 10KG. On the basis of these two experimental observations it is concluded that the ferromagnetic alloys can not be explained on the basis of the parabolic density of states curve.

2. The Success of the Rectangular Band Model - If the overlap of the s- and d-bands is not neglected, the rectangular density of states curve predicts a linear decrease in spontaneous magnetization at $0^{\circ}K$ of less than one Bohr magneton per copper atom added as the process of alloying will add electrons to both the s- and d-bands. The ratio of the density of the states in the d-band to that in the s-band is certainly not much different from that indicated by the ratio of the low temperature electronic specific heat of nickel to that of copper, that is 10 to 1. On this basis the rate of decrease should be .9 Bohr magnetons per copper atom. This is not consistent with the magnetic data. The magnetic data and the electronic specific heat data are consistent with the arguments concerning the rectangular density of states curve versus the parabolic, but they are not in agreement on the magnitude of the density of states. One possible explanation is that there is an orbital contribution to the magnetic moment. The measurements of the "g factor" of nickel indicate that as much as 10% of the moment may be due to orbital contributions. In this case there would be only .54 holes in the d-band. If the ratio of the density of states in the d-band to the density of states in the s-band is 10 to 1, the alloys then would show a linear decrease of just one Bohr magneton per atom. Hence the consideration of orbital contributions to the moment could bring the specific heat and magnetic data into agreement, and the rectangular band shape is found capable of explaining the results up to 60 per cent copper in nickel.

3. The Copper-Rich Alloys - The rectangular band description fails to account for the paramagnetism and specific heat of the alloys with more than 60 per cent copper. In order to deal with the copper-rich region we could choose a density of states curve for the electrons which

is constant up to a certain energy and then drops off rapidly, but not so sharply as the rectangular density of states curve. If the interaction parameter is just large enough to give ferromagnetism for the rectangular band, it will not be large enough to fill up all the holes of one spin direction for the band with the "tail," hence holes of both spin direction will be present in the tail. The magnetic moment will still decrease linearly as the holes are filled up, but after the ferromagnetism disappears the model will give paramagnetism. This model will also give a parasitic paramagnetism at $0^{\circ}K$ which will be the same for all the ferromagnetic copper-nickel alloys and equal to the paramagnetism of the alloy which is just at the composition for which ferromagnetism disappears. (An alternative explanation for the parasitic paramagnetism is given in Appendix V.) It is possible that the change of the shape of the magnetization versus temperature curves as copper is added to nickel is associated with the existence of such a tail rather than with possible concentration fluctuations as discussed above.

The electronic specific heat for the rectangular band with a tail will be constant for the ferromagnetic alloys and decrease for the paramagnetic alloys as the holes in the tail are filled. But as the electronic specific heat would in this model be coming from the holes of both spin directions, it must be concluded that the density of states for one spin must then be only five times the density of states in the s-band. This of course leads to the inconsistent conclusion that the holes are filled on alloying at a rate of only .8 per copper atom. Coles[55] has given additional arguments for the presence of holes in copper-nickel alloys even at concentrations as high as 99% copper, which on this model would imply an extremely long tail on the density of states curve. It is clear, therefore, that while this model affords a satisfactory explanation of the properties of the nickel-rich copper-nickel alloys, a complete description of the whole alloy series on the collective electron theory is not without difficulty.

## V. DISCUSSION OF THE ALLOYS OF CHROMIUM WITH NICKEL

Measurements are reported in part III for two alloys of chromium with nickel. These alloys have a higher concentration of chromium than that which extrapolation of low concentration data indicates is necessary to destroy ferromagnetism. Before these measurements were made, it was not known whether alloys in this range of composition were paramagnetic, diamagnetic, or even antiferromagnetic. The present measurements on alloys with 15 and 20 atomic per cent chromium show paramagnetism down to 1.7°K. The paramagnetism as a function of temperature can be separated into two terms, one an almost temperature independent paramagnetism, the other of the Curie-Weiss type (see table VI and figure 15). There is a small field dependence of the susceptibility at liquid helium temperatures which could be either a slight tendence toward ferromagnetism or simply a low-temperature high-field effect.

These results for the susceptibility and those of Marian and Sadron for the magnetization as a function of composition indicate a strong similarity between the copper-nickel and the chromium-nickel alloy series. The theoretical model for copper-nickel can be adapted directly to the chromium-nickel system if it is assumed that chromium decreases the number of holes in the rectangular d-band at a rate of approximately five holes per chromium atom added to the nickel lattice. A qualitative argument based on the band model as to why this may be the case has been given by Goldman[56,57]. *

Neel[61], Zener[62], and others[54] have considered antiferromagnetic interactions in metals and have indicated that the rapid decrease in the moment of the alloys of nickel with concentration of chromium, vanadium, titanium, etc., is the result of antiferromagnetic coupling of solvent and solute atoms, giving ferrimagnetism. A major difficulty of this approach is to explain the accompanying rapid decrease in the Curie temperature, let alone to explain the linearity of the Curie temperature as a function of concentration. Using this approach, it may also be difficult to account for the paramagnetism of the alloys of higher

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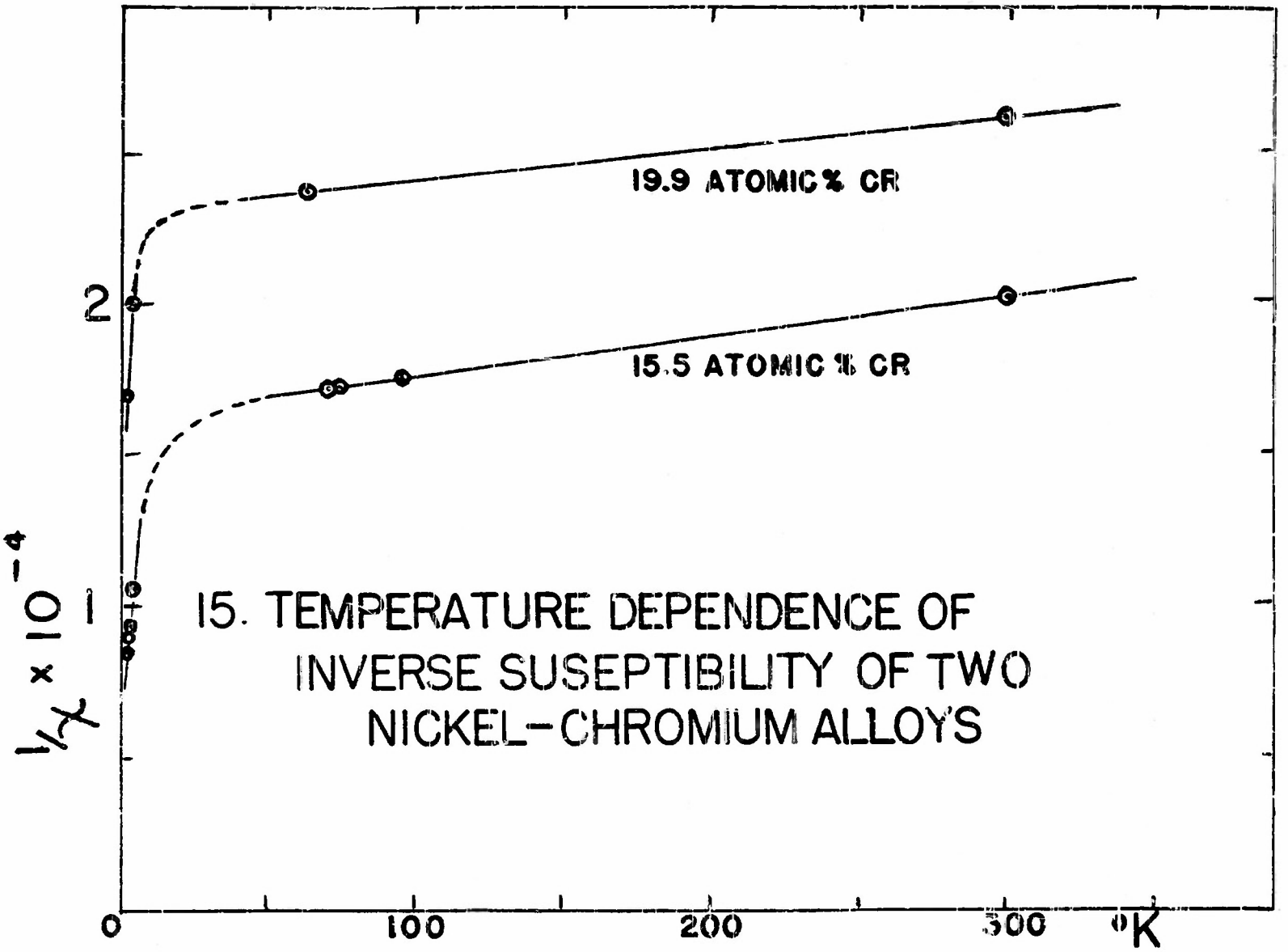
* Note added in proof: A quantitative treatment of this problem has recently been given by Slater ( J.C. Slater, Technical Report No. 6, Solid State and Molecular Theory Group, M.I.T.-April 15,1954).




15. TEMPERATURE DEPENDENCE OF INVERSE SUSEPTIBILITY OF TWO NICKEL–CHROMIUM ALLOYS

concentrations than necessary to destroy the supposed ferrimagnetism. In the collective electron theory, however, the number of effective carriers of the moment enters directly into the value of the exchange interaction parameter which determines the Curie temperature. For the collective electron approach a decrease in the number of effective carriers of the moment is always accompanied by a decrease in the Curie temperature (J, the interaction energy between any pair of electrons of parallel spin directions, assumed constant); for the rectangular band shape the decrease is linear with composition for both the moment and the Curie temperature. The decrease in the number of holes appears to require that chromium atoms enter the lattice as Argon cores; that the density of states curve remain rectangular, but with only 10 eigenstates per nickel atom; and that the six electrons per chromium atom outside the Argon core fill up the 10 eigenstates per nickel atom while maintaining electrical neutrality about the ion core through the s-band.

## VI. THE SUSCEPTIBILITY OF VANADIUM AT LIQUID HELIUM TEMPERATURES

Zemansky* found an anomaly in the specific heat of vanadium at liquid helium temperatures. The measurements were made in "high" fields to suppress the superconductivity. It was felt desirable to make magnetic measurements in this same region to see if this anomaly was correlated with any magnetic anomaly.

The results show that the critical field to suppress the superconductivity increased to 7KG at $2^{\circ}K$, but otherwise the magnetic susceptibility in fields greater than the critical field was only slightly greater than at room temperature (see tableVI). A subsequent discussion of these results by J. E. Goldman with Zemansky's co-workers made clear the origin of the observed specific heat anomaly. The specific heat measurements were made in fields of 3KG which on the basis of the magnetic measurements are shown here to be insufficient to suppress the superconductivity at $2^{\circ}K$.

While the moment of the superconducting state can not be measured with the null coil (without infinite currents which would destroy the superconducting state, anyway), the direction of the moment can be detected by the pick up coils. The vanadium sample showed all the effects to be expected from trapped flux.

The sample used was not pure vanadium, but as it came from the same source** as a sample measured by Kriessman[43], the following comparison is significant:

| | $\chi \cdot 10^6$ |
|---|---|
| present data | 5.04 |
| Kriessman's data | 5.00 |

Such agreement of two completely different methods of measurement is, needless to say, always agreeable, and particularly agre able to the originator of the newer of the methods.

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* Private communication

** Electro-Metallurgical Corporation. Our sample is with the kindness of A. Wexler, Westinghouse Research Laboratory.

APPENDIX I

Magnetization as a Function of Exchange Parameter, External Field, and Temperature

In order to find the magnetization as a function of the three independent variables -- the exchange interaction energy between pairs of electrons with parallel spin direction, the external applied magnet field, and the temperature -- it is necessary to minimize the free energy with respect of transfer of electrons from the gas of ↑ spin direction to the gas of ↓ spin direction. The free energy is obtained from the partition function which we evaluate by the method of steepest descent. The discussion is restricted to bands with density of states curves of the form

$$\nu_p(\epsilon) = C\epsilon^p \qquad (1)$$

The partition function for any system is given by

$$Z(N,V,\beta) = \sum_j e^{-\beta E_j} \qquad \beta \equiv \frac{1}{kT} \qquad (59)$$

For the system under consideration here all possible values of the energy are given by

$$E_j = \sum N_i^{\uparrow}\epsilon_i^{\uparrow} + \sum N_i^{\downarrow}\epsilon_i^{\downarrow} - \mu H(N^{\uparrow}-N^{\downarrow}) - \frac{I}{2}(N^{\uparrow 2}+N^{\downarrow 2}) \qquad (60)$$

where the $N_i$'s are the occupation numbers of the various states ($N_i$ =0 or 1) and the restriction is made that

$$N = N^{\uparrow} + N^{\downarrow} = \sum N_i^{\uparrow} + \sum N_i^{\downarrow}$$

The third term is the energy from the external field and the fourth term is the exchange interaction energy per pair of electrons with parallel spin directions multiplied by the total number of such pairs (we have neglected one against N). The partition function becomes

$$Z(N,V,\beta) = e^{\beta\frac{I}{2}(N^{\uparrow 2}+N^{\downarrow 2})+\beta\mu H(N^{\uparrow}-N^{\downarrow})} \sum_{\substack{N_1N_2N_3\cdots \\ \sum N_i^{\uparrow}=N^{\uparrow}}} e^{-\beta\sum N_i^{\uparrow}\epsilon_i^{\uparrow}} \cdot \sum_{\substack{N_1'N_2'N_3'\cdots \\ \sum N_i^{\downarrow}=N^{\downarrow}}} e^{-\beta\sum N_i^{\downarrow}\epsilon_i^{\downarrow}} \qquad (61)$$

Each of the sums is the usual partition function in the absence of all interaction. This sum is evaluated as usual by the method of steepest

descent from which it follows

$$\sum_{\substack{N,N_2N_3\ldots \\ \Sigma N_i = N}} e^{-\beta \Sigma n_i \epsilon_i} = \phi(\alpha) e^{\alpha N} \qquad (62)$$

where

$$\frac{d \ln \phi}{d\alpha} = -N \qquad (63)$$

and, for Fermi-Dirac statistics,

$$\ln \phi(\alpha) = \prod_i (1 + e^{-\beta\epsilon_i - \alpha}) \qquad (64)$$

The number of electrons of each spin direction is then

$$N^{\uparrow} = -\frac{d \ln \phi(\alpha^{\uparrow})}{d\alpha^{\uparrow}} = \sum \frac{1}{e^{\beta\epsilon_i^{\uparrow} + \alpha^{\uparrow}} + 1}$$

$$N^{\downarrow} = -\frac{d \ln \phi(\alpha^{\downarrow})}{d\alpha^{\downarrow}} = \sum \frac{1}{e^{\beta\epsilon_i^{\downarrow} + \alpha^{\downarrow}} + 1}$$

hence the reduced magnetization, defined as $\zeta = (N^{\uparrow} - N^{\downarrow})/N$ is given by

$$\zeta = \frac{1}{N}\left[\sum \frac{1}{e^{\beta\epsilon_i^{\uparrow} + \alpha^{\uparrow}} + 1} - \sum \frac{1}{e^{\beta\epsilon_i^{\downarrow} + \alpha^{\downarrow}} + 1}\right]$$

We may replace the sums by integrals by introducing the density of states, here restricted to

$$\nu_p(\epsilon) = \frac{N}{2}(p+1)\left(\frac{1}{\epsilon_0'}\right)^{p+1} \epsilon^p \qquad (65)$$

where, as in the text, $\epsilon_0'$ is the energy of the highest occupied state in the absence of any field (applied or exchange). Thus the sums become

$$N^{\uparrow} = \frac{N}{2}(p+1)\left(\frac{1}{\beta\epsilon_0'}\right)^{p+1} F_p(\alpha^{\uparrow}); \quad N^{\downarrow} = \frac{N}{2}(p+1)\left(\frac{1}{\beta\epsilon_0'}\right)^{p+1} F_p(\alpha^{\downarrow})$$

and

$$\zeta = \frac{(p+1)}{2}\left(\frac{1}{\beta\epsilon_0'}\right)^{p+1}\left[F_p(\alpha^{\uparrow}) - F_p(\alpha^{\downarrow})\right] \qquad (66)$$

where

$$F_p(\alpha) \equiv \int_0^\infty \frac{x^p\,dx}{e^{x+\alpha}+1}$$

As $N = N^\uparrow + N^\downarrow$ we have the condition

$$1 = \frac{p+1}{2}\left(\frac{1}{\beta\epsilon_0'}\right)\left[F_p(\alpha^\uparrow) + F_p(\alpha^\downarrow)\right] \qquad (67)$$

Equations (66) and (67) can then be solved explicitly (in principle) for $\alpha^\uparrow$ and $\alpha^\downarrow$ as functions of $\zeta, \beta\epsilon_0'$, and $p$. The difference of $\alpha^\uparrow$ and $\alpha^\downarrow$ will also be a function of the same variables; let this function be

$$\alpha^\downarrow - \alpha^\uparrow = 2\,g_p\left(\frac{1}{\beta\epsilon_0'}, \zeta\right) \qquad (68)$$

From the minimization of the free energy, $F = kT \ln Z$ we can determine $\alpha^\downarrow - \alpha^\uparrow$. The free energy is given by

$$F = \frac{J}{2}(N^{\uparrow 2} + N^{\downarrow 2}) + \mu H(N^\uparrow - N^\downarrow) + kT \ln \phi(\alpha^\uparrow) + kT \ln \phi(\alpha^\downarrow) + kT\alpha^\uparrow N^\uparrow + kT\alpha^\downarrow N^\downarrow$$

The change in the free energy on transferring one electron from the gas of $\uparrow$ spin direction to the gas of $\downarrow$ spin direction must be zero, that is

$$\frac{\partial F}{\partial N^\uparrow} - \frac{\partial F}{\partial N^\downarrow} = 0$$

it follows then that

$$J(N^\uparrow - N^\downarrow) + 2\mu H + kT\alpha^\uparrow - kT\alpha^\downarrow = 0$$

or

$$\alpha^\downarrow - \alpha^\uparrow = \beta J N \zeta + 2\beta\mu H \qquad (69)$$

hence we have

$$\frac{JN}{2\epsilon_0'}\zeta + \frac{\mu H}{\epsilon_0'} = \frac{kT}{\epsilon_0'}\,g_p\left(\frac{kT}{\epsilon_0'}, \zeta\right) \qquad (70)$$

Only in the case of the rectangular band ($p = 0$) can we evaluate $g_p(kT/\epsilon_0', \zeta)$ explicitly. For $p > 0$ the function must be given in the form of a numerical table in all but the limiting cases of low and high temperatures. We have given the function in closed form for $0^\circ K$ in

the text; see equation (15). For high temperatures we must approach classical statistics so that

$$g_p\left(\frac{kT}{\epsilon_0'}, \zeta\right) \longrightarrow \tanh^{-1}\zeta \qquad (71)$$

This is true for all p. The quantum statistics merge with the classical for $kT/\epsilon_0'$ of the order of unity.

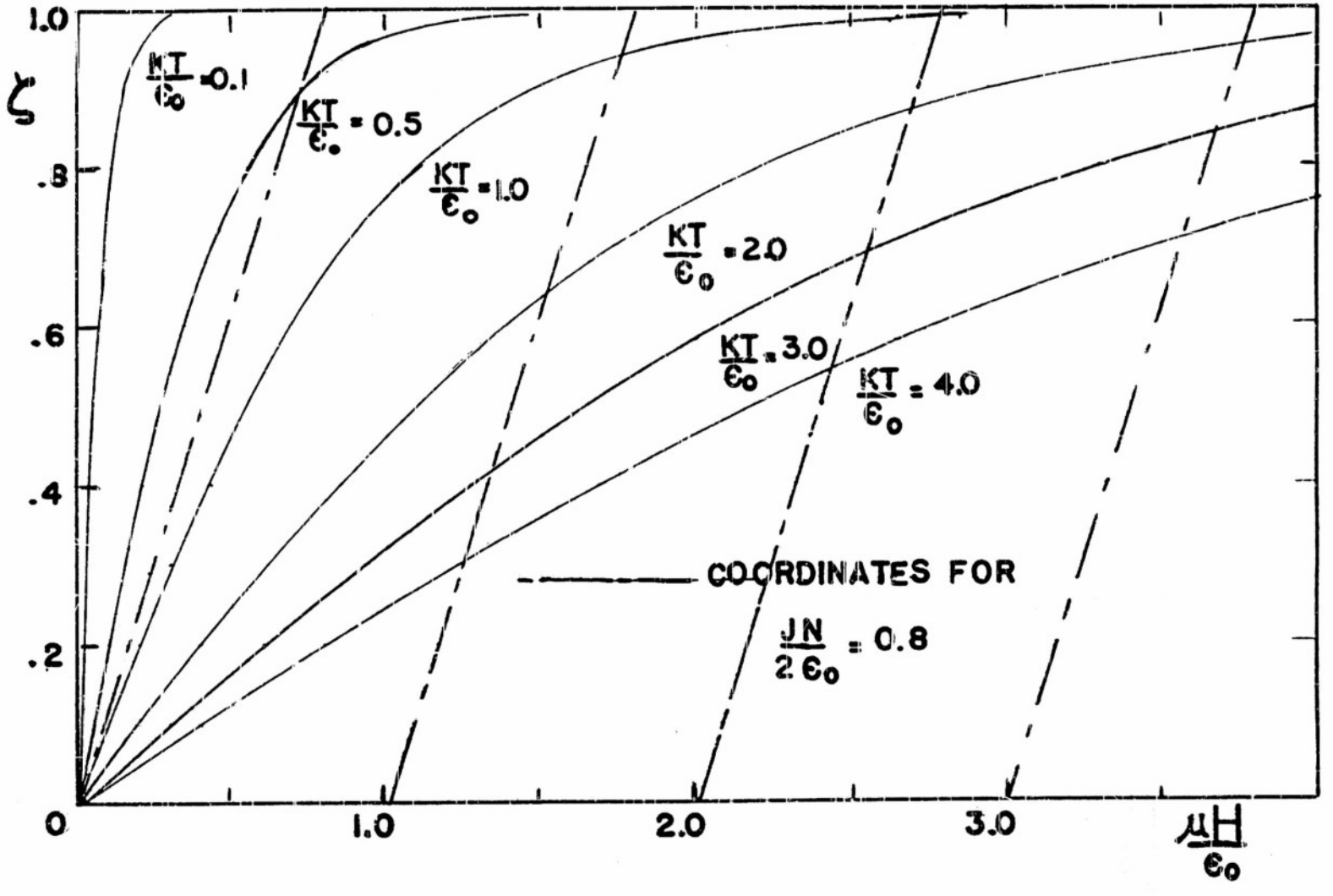
Wohlfarth[30] has given the expression for the rectangular band, namely

$$g_0\left(\frac{kT}{\epsilon_0'}, \zeta\right) = \frac{1}{2}\ln\left[e^{(1+\zeta)\epsilon_0'/kT} - 1\right] - \frac{1}{2}\ln\left[e^{(1-\zeta)\epsilon_0'/kT} - 1\right] \qquad (72)$$

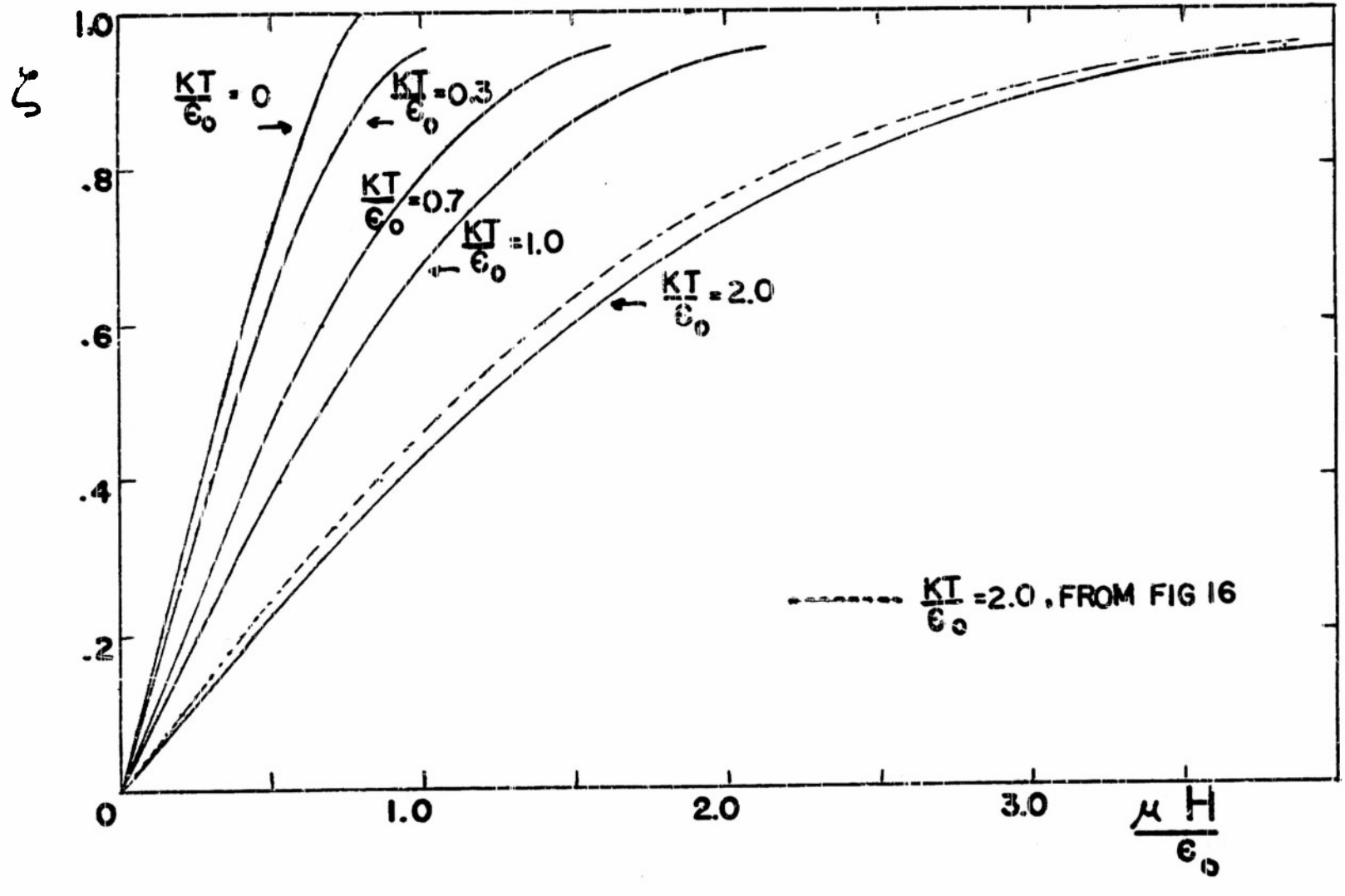
Stoner[23] has tabulated a closely related function for the parabolic band. We have plotted in figures 16, 17, and 18 $\zeta$ against $\mu H/\epsilon_0'$ in the absence of exchange for the limit of classical statistics, for the parabolic band shape, and for the rectangular band shape, respectively. In the presence of exchange the curves are modified as follows: a series of parallel straight lines are drawn which make angles with the $\mu H/\epsilon_0'$ axis equal to $\tan^{-1}\frac{2\epsilon_0'}{JN}$ ; these lines become the new lines of constant field for the field given by their intercept with the field axis. The Curie temperature is given by the line of constant $kT/\epsilon_0'$ which is tangent to the straight line of slope $2\epsilon_0'/JN$ through the origin. The spontaneous magnetization at a given temperature is given by the intercept of the straight line of slope $2\epsilon_0'/JN$ through the origin with the line of constant temperature in question.

# 16. MAGNETIC ISOTHERMS FOR BRILLOUIN FUNCTION

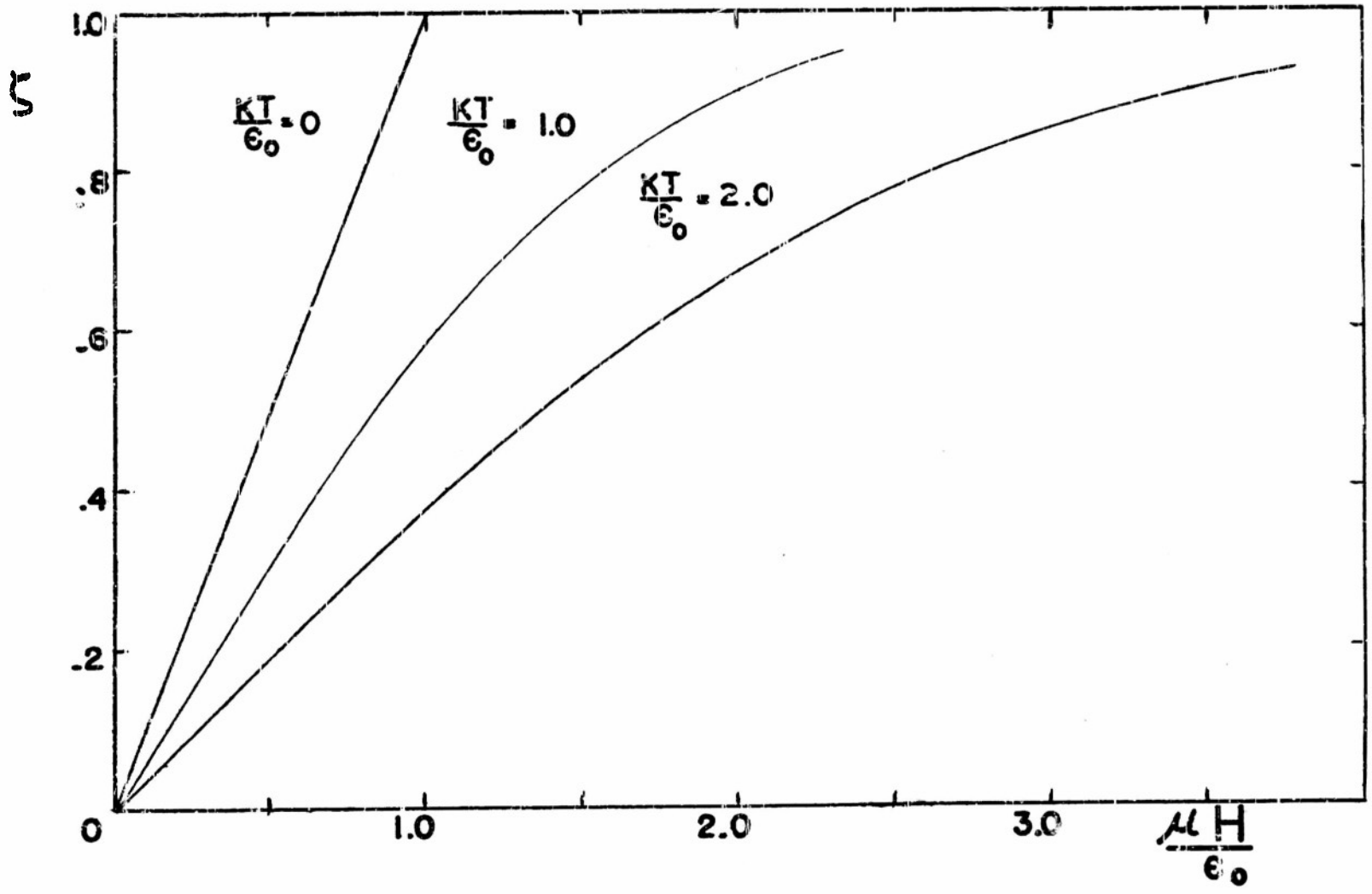
(SPIN 1/2)



# 17. MAGNETIC ISOTHERMS FOR PARABOLIC BAND



# 18. MAGNETIC ISOTHERMS FOR RECTANGULAR BAND



APPENDIX ii

Design for Maximum Sensitivity

Given a cylinder of diameter (Z) and length (L) choose

1) The diameter (a) of wire of resistivity ($\rho$) and

2) The diameter (D) of core of susceptibility ($\chi$) such that when in a field (H) the removal of the core from the coil in a time ($\Delta t$) will produce a maximum voltage (V) across the input of an amplifier of input resistance (R).

Solution:

The removal of the core from the coil will cause a change in B, the magnetic flux density vector, giving rise to a voltage V'; this is shown as follows:

From Maxwell's equations

$$\nabla \times E = -\frac{\partial B}{\partial t} \quad \text{in emu}$$

integrating over the surface bounded by the coil

$$\int \nabla \times E \cdot d\vec{S} = -\frac{\partial}{\partial t} \int B \cdot d\vec{S}$$

$$\int E \cdot dl = -\frac{\partial}{\partial t} B \cdot A; \quad A = \text{area of core}$$

$$V' = N \int E \cdot dl = -NA \frac{\Delta B}{\Delta t} \quad N = \text{no. of turns in coil}$$

but $B = H + 4\pi M$, so that the change in B being only a change in M, where $M = \chi H$, this gives for the voltage developed in the coil on removing the core:

$$V' = -4\pi \frac{\Delta \chi}{\Delta t} NAH$$

The voltage across the amplifier is given by

$$V = V' \frac{R}{R+r}$$

where r is the resistance of the coil and R, as defined above, is the input resistance of the amplifier.

The problem is then to maximize V after putting the resistance and number of turns in terms of the parameters Z, L, and $\rho$ and the variables a and D.

N = number of turns per layer x the number of layers $= (L/a) \cdot (Z-D)/2a$

$r = \rho l \cdot 4/\pi a^2$, where $l$ is the length of the wire.

$\ell = \sum_{k=1}^{m} \ell_k$ where m is the number of layers and $\ell_k$ is the length of the kth layer.

$\ell_k = (L/a) \cdot \pi ( D - a + 2ka)$

so that $\ell = \pi L/4a^2 \cdot (Z - D)(Z + D)$ and

$$V = \frac{L(z-D)/2a^2}{1+(9L/Ra^4)(z-D)(z+D)} \cdot \frac{\pi D^2}{4} \cdot \left(-4\pi \frac{\Delta\chi}{\Delta t} H\right)$$

The maximum value of V is then found to be given by

$D = Z(\sqrt{17} - 1)/4 = .7808\ Z$

and $a^4 = (1 + .7808)(1 - .7808) \cdot LZ^2/R$

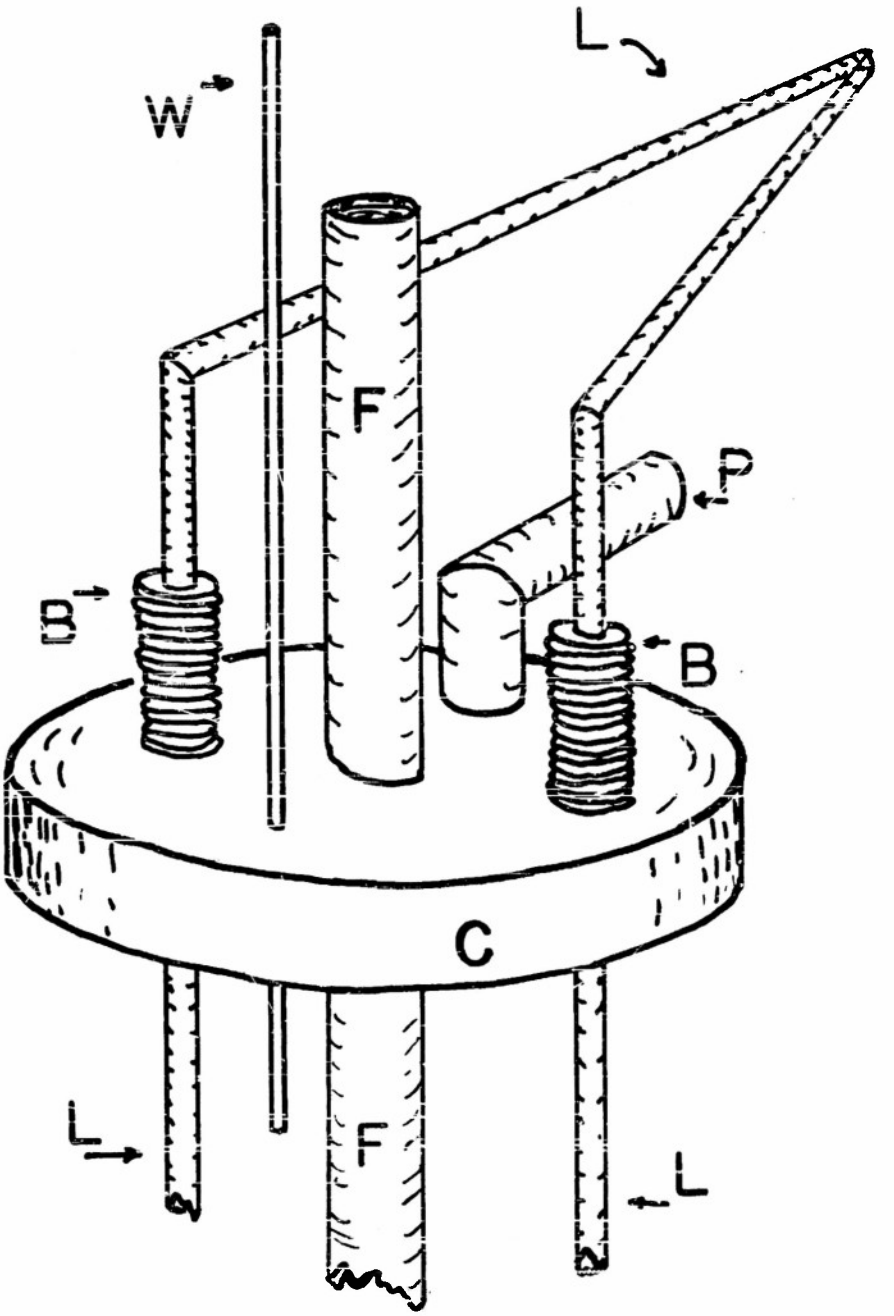
This says that the resistance of the coil should be equal to the resistance of the input of the amplifier, which should astound no one. It also says that a little less than half the available volume should be taken up by the coil.

APPENDIX iii

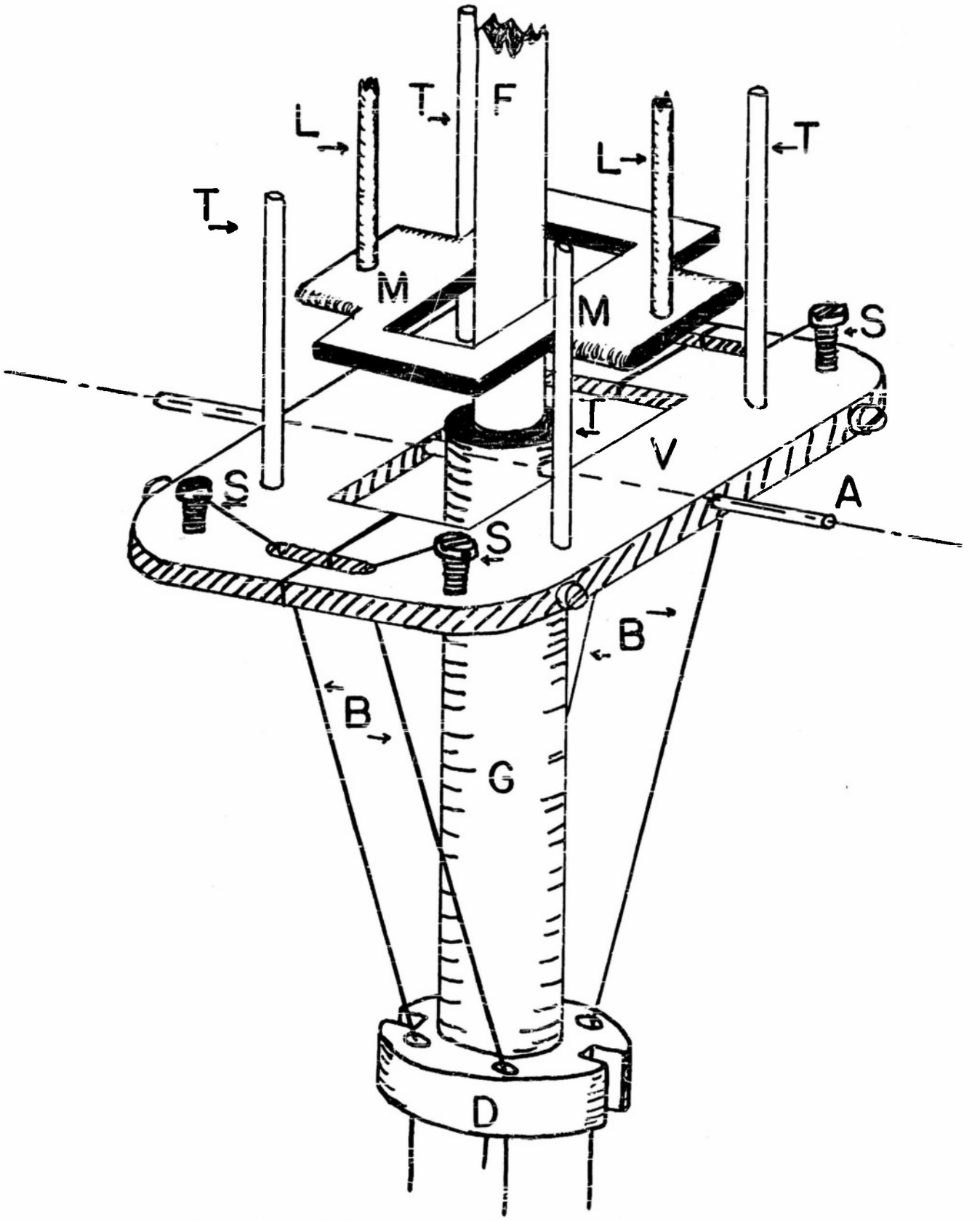
Details of the Apparatus

The details of the apparatus are shown in figures 19, 20, 21, and 22. Figure 19 shows the dewar cap (C). The cap is made of 1/32" walled brass tubing silver-soldered to a 1/16" brass disc 3" in diameter. The phosphor bronze bellows (B) are soft soldered to the cap and, by using spacers, to the lever (L). The fill tube (F) is made of 1/2" monel tubing as is the pumping tube (P). The leads to the apparatus are waxed into the 1/8" monel tube (W). The seal between the dewar and the cap is made with Woods metal.

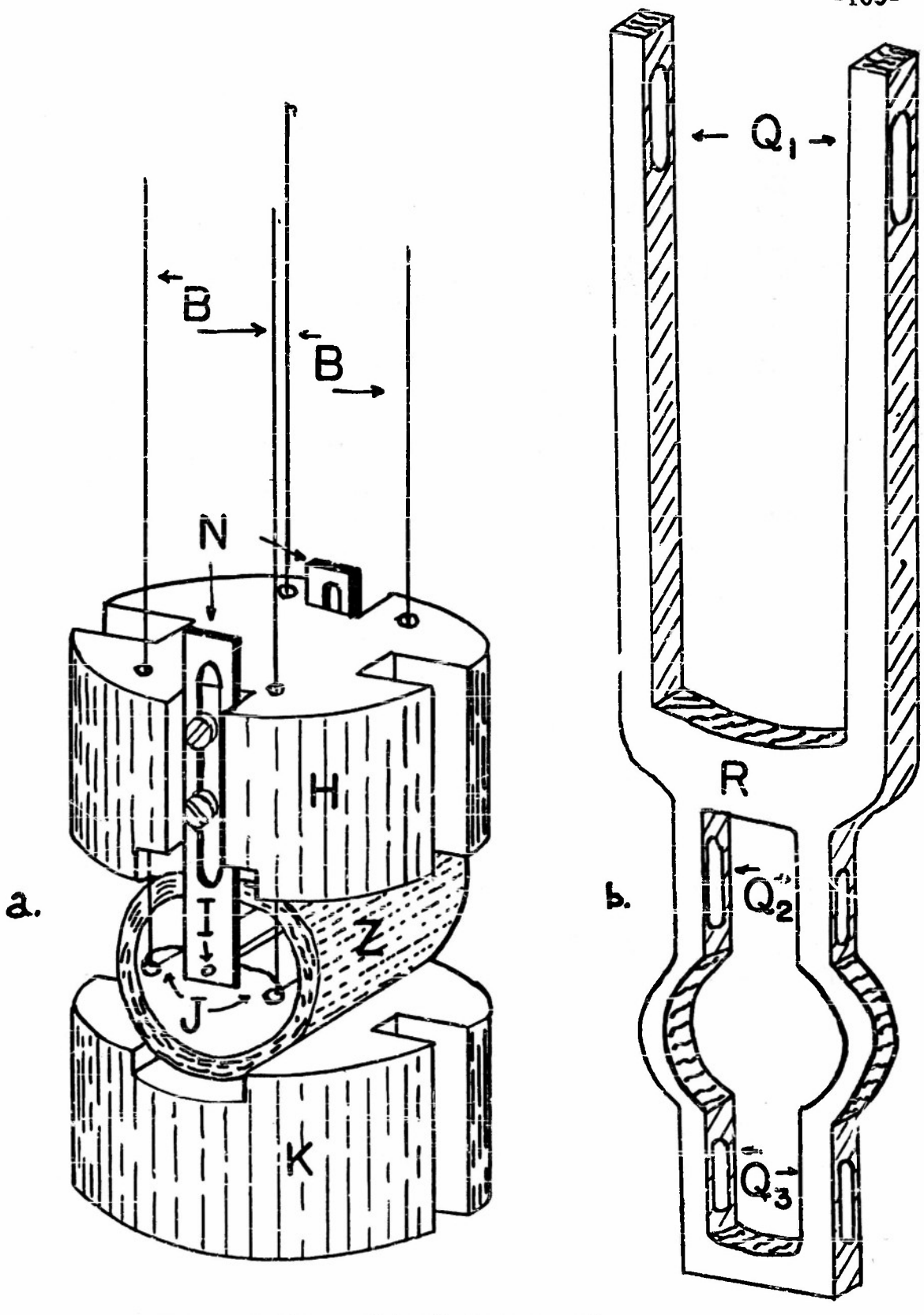
Figure 20 is a continuation of figure 19. The fill tube (F) is hung from the dewar cap. It is the support for the see-saw and the rest of the apparatus. A short cylinder (D) of linen micarta is attached to a flange (not shown) which was silver soldered on the fill tube (F) after the cylinder (D) and the cylinder (G) were slid on to and up the fill tube. The cylinder (G) is of bakelite. The axis (A) of the see-saw (V) is in two pieces. The two pieces are brass screws with all but a few threads removed. The few threads are to screw into the bakelite cylinder (G), thus giving an axis which does not block the fill tube. The see-saw (V) is in two pieces of linen micarta held together by bolts (U). The see-saw is tripped by the levers (L), moving a linen micarta frame (M)



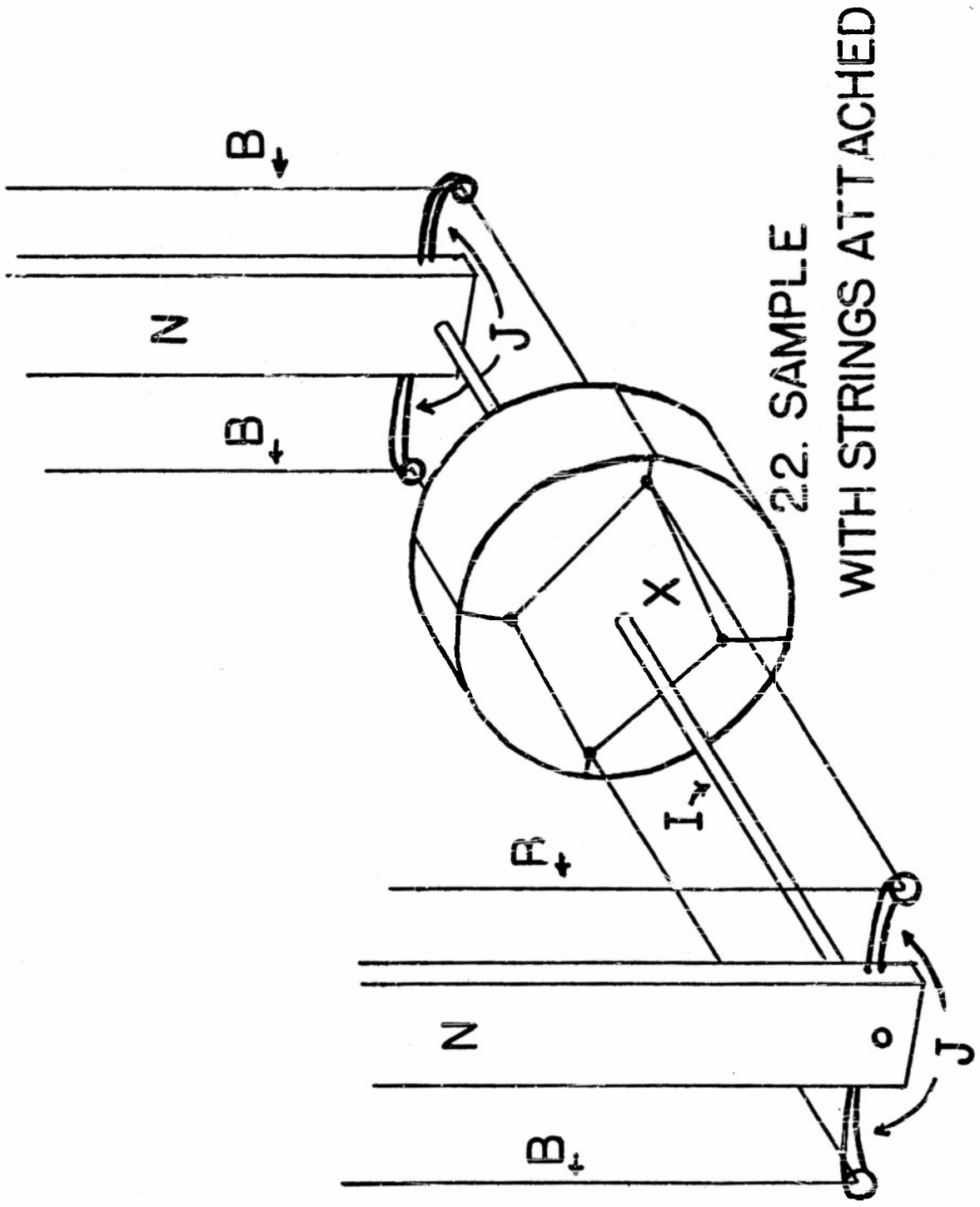

19. THE DEWAR CAP




20. SEE SAW DETAILS




21. COIL SUPPORTS


B↓
N
B↓
J
2.2. SAMPLE
WITH STRINGS ATTACHED
X
I↑
B↓
N
o
J
B↓

against the four brass posts (T), two at a time. The posts are attached to the see-saw which, in turn, pulls on two of the strings (B) which are attached to the four screws (S). The screws allow adjustment of the tension in the strings (B). The strings are silk from the see-saw down almost to the sample. There they are spliced to braided nylon fishing tackle. The braided nylon has been found to work best around sharp corners at low temperatures. It is not used all the way up to the see-saw because it appears to have a large negative coefficient of thermal expansion. The screws (S) are locked in position by nuts (not shown) on the underside of the see-saw.

The support (R) running from the short cylinder (D) in figure 20 to the detector coil (Z) and short cylinders (H) and (K) in figure 21a is left out of figure 20 and figure 21a. It is shown by itself in figure 21b. The slots ($Q_1$) are for screws to join (R) to (D) of figure 20. The parts of 21a fit in the cut-out of support (R). They are held by screws through slots ($Q_2$) to short cylinder (H) and through slots ($Q_3$) to short cylinder (K). Assembling the parts of 21a inside of (R) is a bit of a Chinese puzzle.

Figure 21 shows the detector coil (Z) held between two slotted cylinders (H) and (K). (H) and (K) and also (D) of figure 20 are machined to fit snugly inside the lower portion of the dewar. At low temperatures the fit is a pressure fit due to differential contraction. The cylinders (H) and (K) are only in outline as shown in figure 21a. They were originally as shown, but, to reduce mass and increase the ratio of surface area to volume, saw cuts and drill holes have been used. The mass is probably $\frac{1}{4}$ the original mass. Figures 21a and 22 show the quartz rod (I), its supports (N) and the eyelets (J) used to guide the braided nylon around the bend. The quartz rod is aligned by moving the supports (N). The eyelets (J) are positioned by bending. The eyelets on each end are made with one continuous molydenum wire. The knots between the silk and the nylon are made just above cylinder (H).

Linen micarta is used for (H), (K), (R), (D), and (N). The only solid parts not made from linen micarta are the lucite coil form of the detector coil (Z) and the bakelite cylinder (G). The bakelite stands up well at low temperatures; the lucite, however, does not. An early model using lucite fell apart from strains after being subjected to liquid nitrogen

temperatures. The present detector coil shows crazing.

Figure 22 shows the sample (X) as it would look if the detector coil (Z) were invisible. The strings (B) are tied on the sample in the form of a net.

We have also used a modification of this design which eliminates the quartz rod. The strings are tied on much the same as shown in figure 22, but the pull strings come from adjacent corners of the square rather than opposite. The effect is that the strings act as sled runners on the inside of the coil form. The force of the pulling strings is such as to give no torque about the point of friction. This arrangement doesn't stick even on removing the apparatus from liquid nitrogen and allowing ice to form. There is, of course, no problem of breaking the quartz rod. The surface on which the sled slides is a piece of lucite inserted into the detector coil form. It is a cylinder with O.D. equal to the I.D. of the coil form and an I.D. just bigger than the sample plus twice the diameter of the strings. So that there can be no friction at the top of the sample and hence no torque, the cylinder is cut in half along its axis and the top half removed. The disadvantage of this method is that the degree to which the sample can wobble is not limited as it is with the quartz rod.

## APPENDIX iv

### The Dewar

A cross section of the helium dewar is shown in figure 4. The most difficult operation in its construction was the machining of the wall of the helium chamber. It is made in two pieces marked (E) and (A). (A) is turned out of a heavy-walled 3" I.D. stainless steel tube by boring the inside, shrinking on a mandrel, and turning the outside. The wall is between .009" and .012". The tube is made in two sections so as to have a shorter piece on which to do the precision work. Henry and Dolecek used a fabricated wall for the helium chamber. This was avoided here in order to reduce the problem of hunting and repairing leaks. Walls (C) and (D) were likewise machined out of heavy-walled stainless steel tubes.

All joints are along at least two surfaces except for the ring connecting tube (A) to the outer wall of the inner dewar. This joint was made first and is of high-melting-point silver solder (1400°F). The rest of the joints are "Easy Flo" (1175°F) except for joint (J) which is soft

soldered. The soft solder was used so that the outer shell may be removed with ease for repairing leaks.

The upper wall of the helium chamber is fitted with a grooved ring (F) to hold the Woods metal used to seal the cap shown in figure 19 on to the dewar.

The inner vacuum chamber is connected to the outer vacuum chamber through a $\frac{1}{4}$" copper tube which can be used to test the inner vacuum when the outside shell is removed. The outer vacuum chamber is connected through the side of tube (D) to a diffusion pump by means of a one-inch diameter brass tube about one foot long. The diffusion pump can be connected and disconnected from the pump line by means of an O-ring seal. This is to allow the dewar to be turned upside down to drain water which may condense in the nitrogen space after a run.

The dewar and the diffusion pump are held in a rigid frame which fits over the movable pole piece of the ADL magnet. The framework has adjustments for positioning the dewar.

## APPENDIX v

## Parasitic Paramagnetism

The increase of magnetization with field may not be an increase in the spontaneous magnetization of a single domain as implied above. Stoner[25] pointed out some time ago that the magnitude of the parasitic paramagnetism in nickel is structure sensitive. Sucksmith[49] has recently compared the magnetic properties of polycrystalline nickel with a single crystal of nickel. He found that the value of the parasitic paramagnetism for the polycrystalline material was $.14 \times 10^{-4}$ emu/gram. His apparatus was not sensitive enough to measure this quantity for the single crystal, but he was able to place an upper limit of $.04 \times 10^{-4}$ emu/gram. This compares with the value found in this work for the 58 per cent alloy, namely $.3 \times 10^{-4}$ emu/gram. It is here mentioned that the difference in the results of the many observers[35,36,39,40,52,53] of the paramagnetism of the copper-rich alloys might also be due to the paramagnetism being structure sensitive.

The realm of speculation is entered at this point to give a possible explanation of not only the parasitic paramagnetism of the ferromagnetic alloys but also of the paramagnetism of the copper rich alloys. The

nickel atoms in the grain boundaries could contribute electrons to a Fermi-Dirac gas which shows as usual a temperature-independent susceptibility at temperatures such that $kT < \epsilon_0'$ and classical behavior as kT increases above $\epsilon_0'$. Then if $\epsilon_0'$ decreases with increasing copper content it is necessary to go to lower and lower temperatures to show the leveling off of the susceptibility which increases with temperature decrease. This hypothesis could be checked experimentally in two ways; either by looking for a change of susceptibility in the alloys with grain size, or by looking for a leveling off of the susceptibility of, say, a 75 per cent copper alloy at helium temperatures.

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