

MEASUREMENT OF THE THERMODYNAMIC PROPERTIES OF A PARAMAGNETIC SALT BELOW ONE DEGREE KELVIN BY A NON-CALORIMETRIC METHOD

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ABSTRACT

A new method is applied to determine the complete thermodynamic properties of potassium chromium alum in the entropy range $S/R = 0.8$ to 1.1 . Most previous work has been devoted to finding $S(T^*)$ and $T(T^*)$, where the "magnetic temperature" T^* is used as an index for the entropy. These two functions are determined in the present experiment by new methods. The function $T(T^*)$ is determined by comparing adiabatic magnetization curves of the sample with those of an ideal paramagnetic gas at the same entropy. The function $S(T^*)$ is determined by comparing the asymptotic values of these curves at high fields with those of the ideal paramagnetic gas. The temperature measurements give good agreement with those of previous investigators, but the agreement of the entropy measurements is less satisfactory. The difference is attributed to our need to extrapolate our data to large magnetic fields, to the need of previous investigators to have a theoretical knowledge of the low-lying energy levels, or to an actual difference among samples.

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I INTRODUCTION

In earliest times physics dealt phenomenologically with the bulk properties of matter. With the advent of particle physics and the quantum theory, workers have been concerned primarily with systems of atomic dimensions. Increased understanding of the interactions of atoms leads us back to the investigation of the bulk properties of matter, now from a more fundamental viewpoint. These properties may be classified as those characteristic of an equilibrium state and those characteristic of transport processes involving non-equilibrium situations. Logically, the former should be investigated first as they are the most tractable theoretically. Such investigation invokes the descriptive techniques of thermodynamics and the interpretive principles of statistical mechanics.

This thesis is concerned with a new technique for the experimental study of the equilibrium properties of paramagnetic salts in the temperature range attained by adiabatic demagnetization - that is, below 1°K. This technique is intended to replace or supplement the classical experimental technique of calorimetry, which heretofore has stood alone as the generally applicable source of information of the elementary excitations of bulk matter in equilibrium.

The problem of interpretation of calorimetric data in terms of the excitations of matter has always taken for

granted the use of the temperature as the thermal independent variable. The fact that two bodies in contact have the same temperature is the basis for this choice. In addition, the ideal gas thermometer gives a reliable measurement of temperature. For use in the temperature region below 1°K , however, no reliable absolute thermometer exists; moreover, thermal equilibrium between two bodies is difficult to attain experimentally. The nature of the cooling method, however, suggests the entropy as a replacement for the temperature as the thermal independent variable. A measurement of $T(S)$ rather than $S(T)$ should not suggest a classification of this study as "thermometry." Thus, a reorientation of the problem of interpretation of the data is necessary since statistical mechanics continues to have its simplest expression in terms of the temperature, even below 1°K . The reasons for these statements are detailed in the remainder of this introduction.

The magnetic cooling method designated by the phrase "adiabatic demagnetization" consists of two processes, the latter of which gives rise to the title. A paramagnetic working substance is chosen whose atomic dipoles are nearly free near 1°K , the lowest temperature readily attainable with a liquified gas. Since the entropy of the lattice is quite small at this temperature, most of the entropy arises from the free atomic dipoles. This entropy may be decreased by aligning the dipoles with a magnetic field applied isothermally. This field is then re-

moved isentropically. The temperature must fall to such a value that the entropy of the salt without the ordering influence of the field is still as low as that of the aligned salt at the initial field and temperature. Sufficiently low temperatures must be attained to allow magnetic interactions to provide the required order. The energy is removed through the agency of magnetic work done by the thermal excitations in disaligning the dipoles when the field decreases. The demagnetization is reversible and isentropic provided the field is reduced slowly enough for this energy exchange to take place in a substantially constant field. Finally, for the present purpose, when we use the term adiabatic demagnetization we shall always impose the following restrictions: 1) The initial temperature is near 1°K , 2) the final magnetic field is zero, and 3) the working substance is one whose magnetic moment is nearly free at 1°K .

We now contrast the theoretical and experimental approaches to finding the properties of the equilibrium state achieved after adiabatic demagnetization. In the theoretical treatment of a thermodynamic system, the temperature enters as the natural thermal variable in the following way. One chooses a model for the system under consideration and computes the energy levels as a function of externally imposed parameters. The partition function, Z , which explicitly involves the temperature, is then computed and from Z the thermodynamic properties of the system may be determined. In the most elementary case the pa-

parameter which determines the energy levels is the volume, V , and the properties derived from the partition function may be expressed by the pressure and the entropy, $P(V,T)$ and $S(V,T)$. If, instead, a paramagnetic material is considered, volume changes are usually negligible, and the energy levels are determined by the imposed magnetic induction, B_e . The partition function then yields the total magnetization, \mathcal{M} , and the entropy. We then have $\mathcal{M}(B_e, T)$ and $S(B_e, T)$ from the theoretical model. One desires to check the theoretical model by experimentally determining these properties.

In the region of temperature reached by adiabatic demagnetization, the natural experimental variables are the magnetic field and the entropy, the latter of which is now the thermal variable. In order to check the theories the experimenter may determine $\mathcal{M}(B_e, S)$ and $T(B_e, S)$, and thence $\mathcal{M}(B_e, T)$ and $S(B_e, T)$. The experimental measurement of the temperature is thus not mere thermometry, but a requisite for the comparison of experiment with theory.

The function $\mathcal{M}(B_e, S)$ may be determined by simple magnetic measurements. The experimental determination of $T(B_e, S)$ is more difficult and we consider first the determination of $T(S) = T(0, S)$, from which we can find $T(B_e, S)$ using (2) below.

Heretofore, the most reliable determination of temperature, in the region reached by adiabatic demagnetization, has

been to make use of the definition, $T = \frac{\partial U}{\partial S}$. Internal energy changes are induced by heating the sample. Determining the rate of heating is, however, a difficult experimental task. Entropy changes are determined by computation of the isothermal entropy reduction arising from the application of the magnetic field before demagnetization. We call this computation of entropy change the isothermal method. In Chapter III we discuss in detail the method of temperature determination $T = \frac{\partial U}{\partial S}$, together with other methods which have been previously applied, and a new method which we now outline.

To determine $T(S)$, we compare isentropic magnetization curves of an actual paramagnetic salt with those of an ideal paramagnetic gas. If \mathcal{M}_I is the magnetization of an ideal paramagnetic gas and \mathcal{M} is the magnetization of the actual salt at the same entropy we find in Section III that the final temperature reached in an adiabatic demagnetization is

$$T_f(S) = \left(\frac{\partial}{\partial S} \right)_{B_e} \int_0^{\infty} (\mathcal{M} - \mathcal{M}_I) (dB_e)_S. \quad (1)$$

To evaluate $T_f(S)$ from (1), measurements of $\mathcal{M}(B_e)$ along several isentropes are required. It is possible to identify an isentrope without actually knowing the value of the entropy. However, at large fields, asymptotically \mathcal{M} approaches \mathcal{M}_I and the entropy may be computed using formulas for the ideal paramagnetic gas. We call this determination the asymptotic method.

The data mentioned in the last paragraph then give us the following:

1. $\mathcal{M}(B_e, S)$
2. A new method of measuring entropy
3. $T_f(S) = T(0, S)$
4. $T(B_e, S) = T(0, S) - \int_0^{B_e} \left(\frac{\partial \mathcal{M}}{\partial S} \right)_{B_e} (dB_e), \quad (2)$

We could in theory use (2) to determine the final temperature in an adiabatic demagnetization but the demands on experimental accuracy would be much greater than when (1) is used.

The present experiment was undertaken primarily to test the applicability of (1) for the determination of temperature and of the asymptotic method for the entropy as a preliminary to comparing the behavior of actual salts with that of theoretical models. Therefore, a salt, potassium chromium alum, with known properties was chosen for the experimental substance. Equation (1) was found to give good results for the temperature, but the asymptotic method did not agree with the isothermal method as applied by other workers. The latter discrepancy is attributed to our need to extrapolate $\mathcal{M}(B_e)$ at large fields, or to a failing of the isothermal method, which requires a knowledge of the low-lying energy levels of the salt. These levels are not well understood.

In Section II, after presenting preliminary material, the isothermal method of entropy determination is discussed. We are then in a position to present in Section III a discussion

of various methods of temperature determination. The remainder of the thesis is a presentation and evaluation of the present experiment.

II THE ENTROPY OF DILUTE PARAMAGNETIC SALTS

In order to compute thermodynamic properties from the partition function it is necessary to know what external parameter determines the energy levels of the system under consideration. This information can be obtained by examining the expression for the differential of the internal energy. The independent variables in this expression will be the entropy and, in addition, those variables which determine the energy levels of the system. We proceed to establish the fact that the energy levels of a paramagnetic salt are determined by the external magnetic induction, B_e , as a preliminary to a discussion of the computation of the entropy.

We confine our attention to substances which contain paramagnetic ions and which are magnetically so dilute that no cooperative phenomena occur above 1°K. In the limited region of temperature which we wish to consider the volume changes of paramagnetic salts are negligible. In particular, our work is carried out under very low pressure. Mechanical work is therefore completely negligible. We consider then the change in magnetic field energy associated with the insertion of a sample in the field. If we exclude remanent and irreversible magnetization, the energy contained in the field is

$$E = \int dV \int_0^B H \cdot dB, \text{ where the integral is extended over all space.}$$

The quantity B is the actual induction. Rationalized MKS units are used. We restrict ourselves to the case where the induction, B_e , before the insertion of the sample,

is uniform and in a medium of permeability μ_0 , and where the magnetization in the sample is uniform after its insertion in the field. In this case, Guggenheim² computes the change in field energy, ΔE , which occurs upon insertion of the sample as $\Delta E = -V \int M \cdot dB_e$, where M is the magnetization of the system, and V its volume. We then have for the differential of the internal energy of the sample

$$dU = TdS - VMdB_e = TdS - m dB_e$$

where $m = MV$ is the total magnetization.

If $Z = \sum e^{-\frac{E_i}{kT}}$ is the partition function of the system, with the E_i being the system energy levels, then the entropy is given by

$$S = k \left(\frac{\partial (\ln Z)}{\partial T} \right)_{B_e}.$$

We consider the various terms which contribute to the energy levels which appear in the partition function and evaluate their contribution to the entropy in the region of 1°K for our paramagnetic salt. At these temperatures the entropy derived from vibrations is given by the Debye theory as

$$S_D/R = \frac{4}{5} \pi^4 \left(T/\Theta \right)^3 \quad \text{where } R \text{ is the gas constant and } \Theta$$

is the Debye temperature. Θ is of the order of 100°K or greater for salts so that $S_D/R \sim 10^{-4}$ at 1°K. We shall see that this amount is generally negligible. A second contribution to the entropy, which is constant near 1°K, is that arising

ing from the orientation of the nucleus with respect to the moment of the electrons. This comes into play, of course, only if the nucleus has a magnetic moment. However, the energy of the interaction, per ion, amounts to only about $k \cdot 10^{-2}^\circ$, so that the nuclear states are equally populated above 1°K . This hyperfine structure, however, clearly may come into play at the temperatures reached by adiabatic demagnetization.

If we omit the constant contribution of nuclear entropy, then the major contribution to the entropy in the neighborhood of 1°K is that of the electrons of the paramagnetic ions. This contribution is determined by the interaction of the electrons of the ions with the lattice, among themselves, with an external field, and with the electrons of the other paramagnetic ions. All these interactions except the last are the same for every ion, and with sufficient patience the energy levels due to them may be solved in terms of constants which usually are determined experimentally. We turn to a discussion of these contributions in the case of potassium chromium alum.

The energy levels of the electrons of the chromium ions may be examined spectroscopically insofar as the ions act independently of one another. This independence is assured at high temperatures where thermal agitation precludes cooperative effects among the paramagnetic ions. It is found from ordinary optical spectroscopy³ that, aside from low-lying levels, the first excited state is about $k \cdot 22,000^\circ$ above the

ground state. The low-lying levels may be examined using the method of microwave spectroscopy.⁴ At room temperature, it is found that there are two such levels separated by $\delta = k \cdot 12^\circ$, and each level is two-fold degenerate. The degeneracy is lifted by a magnetic field in a way consistent with the hypothesis that one level has $J = \pm 3/2$, the other $J = \pm 1/2$ with $g \sim 1.98$. Below about 160°K , a change in the microwave spectrum takes place, which is not understood. At zero field there are at least two energy-level splittings of the order of δ , indicating that not every chromium ion has the same environment at low temperatures. The specific heat arising from these splittings may be computed, but does not agree with that measured in the adiabatic demagnetization region.⁵ This disagreement may be caused by interactions among the chromium ions. Notwithstanding, experimenters⁶ usually compute the entropy arising from the low-lying levels as though there were only one splitting, the magnitude being chosen so as to agree with the specific heat data at temperatures such that kT is large compared with δ . It should be pointed out, however, that when a magnetic field splits the low-lying levels, kT is no longer large compared with the splittings. This fact makes the entropy dependent on the details of the model chosen for the low-level splittings.

We briefly review the method developed by Van Vleck et al,⁷ and refined by Bleaney et al⁴ to explain the low-lying levels. The method is to apply successive perturbations to a free chro-

mium ion. The electrons are considered to be coupled to form a resultant S and L. The effect of all surrounding matter is then taken into account by assuming that it gives rise to an effective potential, V , whose symmetry is taken as that of the point group of the chromium ion. Then perturbations of spin-orbit and of nuclear coupling are included. The assumption that the interaction of the chromium ion with the rest of the crystal may be represented by an electric potential has been criticized by Kleiner,⁸ though he feels that the success of the theory lends support to the hypothesis that the effect of the rest of the crystal may be taken into account by a potential, V .

The qualitative results of the calculation above may be found by examination of the wave functions⁴ or by the application of group theory.⁹ Hund's rule gives the lowest level of Cr^{+++} as 4F and X-ray studies¹⁰ show that the immediate environment of the Cr^{+++} ion is a distorted octahedron of water molecules. The distortion is along a different body diagonal of the cubic unit cell in the case of each of the four chromium ions in a unit cell. The potential, V , is taken as predominantly cubic with a small superposed trigonal part. The coupling of the cubic part of V with the orbit is large enough to separate the orbital states widely, leaving a state with no orbital degeneracy lowest. The average orbital moment of this state is zero. Since this is the only occupied state, magnetic properties arise only from the spin. As far as mag-

netic properties are concerned, then, we need not distinguish between J and S , in this case. The cubic part of V allows of no matrix elements to higher orbital states so that inclusion of spin-orbit coupling does not alter the fact that S may have any orientation without change of energy. The trigonal part of V does allow matrix elements of spin-orbit coupling, which give rise to the splitting δ and to the change of g from the value 2. In this case, g is not the gyromagnetic ratio but is the factor such that the change of energy with magnetic field is $g\beta S_z B$, where β is the magnetic moment of the electron and S_z is the component of spin along the field B_x at the ion. For a Cr^{+++} ion where $S = 3/2$, only one splitting δ is allowed, for a spin doublet must always remain until a magnetic field is applied, according to Kramer's Theorem.¹¹

We now return to the problem of computing the entropy of the paramagnetic salt and consider the interactions among the various ions. This problem is extremely difficult of solution as compared with the single ion problem. This situation arises because the magnetic interaction drops off only as $1/r^3$, invalidating close neighbor approximations. In addition, there may be exchange effects. Van Vleck¹² attacked this problem by expanding the partition function in powers of B_e and τ/T where $\tau/3$ is the Curie constant in the non-interacting case. He solved this problem up to terms in $(\tau/T)^4$ and to terms in B_e^2 , in the case where the crystalline electric

field is not able to split the lowest level of the multiplet. This calculation, then, is applicable only to the case of small fields, B_e , and large temperatures. At temperatures so low that terms higher than that in $(\tau/T)^2$ become significant, comparison with experiment indicates that many more terms than Van Vleck computed must be included to obtain satisfactory results.¹³ Van Vleck also computed the partition function up to the terms in $(\tau/T)^2$ and in B_e^2 , in the case where there is a crystalline field splitting of the lowest multiplet level. We see that insufficient information is available from this computation to enable one to find the entropy at large fields, even at moderately high temperature. In the past it has been customary to make use of the following line of reasoning for the solution of the problem of including magnetic interactions in the calculation of the entropy when a magnetic field is applied. We note that it is possible to compute the magnetization and thence the susceptibility, if the partition function is known, from the formula

$$M = (N/V) kT \left(\frac{\partial \ln Z}{\partial B_e} \right)_T.$$
 By susceptibility we shall refer always to the adiabatic differential susceptibility $\chi = (\partial M / \partial H)_S$. The field H is measured within the sample. We also consider the susceptibility $\chi_e = (\partial M / \partial H_e)_S$, where $H_e = B_e / \mu_0$. Since for $B_e = 0$, $M = 0$ and since $(\partial M / \partial H)_T = (\partial M / \partial H)_S + (\partial M / \partial S)_H (\partial S / \partial H)_T$, we need not distinguish between the adiabatic and isothermal susceptibility in this case. This fact is also true for χ_e .

H is used here to conform to convention although we have shown that the logical independent variable is B. However, we shall almost always be concerned with χ_e whose value would change only by a constant factor if B_e were the independent variable.

We see that Van Vleck's expansion discussed above enables us to compute the zero field susceptibility in the case where the lowest multiplet level is not split by the crystalline field. If exchange is negligible, he finds

$$M = \frac{\gamma}{3} \frac{H_e}{T - \frac{1}{2} \tau \bar{\Phi} + \frac{xQ\tau^2}{9}} \quad (3)$$

where $x = 1 + \frac{3}{8\tau(\tau+1)}$, $Q = 2V^2 N^{-2} \sum_j r_{ij}^{-6}$ (=14.4 for alums)

is a lattice sum over the distance r_{ij} between the sites of ions i and j , and $M\bar{\Phi}$ is the field at an ion site due to dipoles of moment $\frac{m}{N}$ at all other sites. The quantity $M\bar{\Phi}$ is thus the Lorentz local field¹⁴ and has the value $(1/3 - D)M$ for cubic crystalline structures, where D is the demagnetizing factor. If we neglect the term in τ^2 in (3) we see that the Van Vleck treatment of magnetic interaction gives the same result as that of Lorentz. When we apply the local field picture of Onsager,¹⁵ the results agree partially up to the term in τ^2 . The reason for only partial agreement is that Onsager's picture is only valid for a continuum, so that the coefficient $xQ/9$ must be adjusted to a suitable value to obtain agreement.¹² As these local fields persist in the literature on thermometric

measurements, they are discussed in Appendix A.

In the case in which the lowest multiplet level is split by the crystalline field, Van Vleck finds that

$$\mu_0 M = \frac{\chi_0 B_e}{1 - \chi_0 \bar{\Phi} + \alpha \chi_0^2 - 2 \alpha^{(2)} \chi_0^{-1} k T} \quad (4)$$

where χ_0 is the susceptibility if magnetic interactions are ignored, and $\alpha^{(2)}$ is a coefficient in the expansion of the partition function. Because of the difficulty in computing $\alpha^{(2)}$, Van Vleck suggests that again the Onsager approach may give a good approximation to the magnetic interaction. Clearly, the Lorentz approach may also be used to lesser accuracy. The quantity χ_0 may be computed if the splitting pattern is known.¹³

In order to solve the problem, then, of computing the entropy as a function of field and temperature, the assumption is made that the magnetic interactions may be taken into account by the local field picture. Usually the Lorentz field is used because of the ease of computation. The entropy is then computed as a function of this local field and temperature, taking into account the low level splitting. The problem of inclusion of the low level splitting has been solved for chromium alum (using the assumption of a single low level splitting) in the case of B_e along the (100) direction by Hudson¹⁶ and to terms in $(\delta/T)^2$ by Daniels and Kurti¹⁷ for any orientation, where δ is the crystalline field splitting. This

computation of the entropy before demagnetization has been most generally used. Clearly questions arise both as to the method of taking magnetic interactions into account and as to the situation regarding the low-level splitting. We remark that direct measurement of the entropy change when a magnetic field is applied is difficult experimentally, and reserve the discussion of our new entropy calculation (the asymptotic method) to Section III.

III METHODS OF MEASUREMENT OF TEMPERATURE AS A FUNCTION
OF ENTROPY

As pointed out in the introduction, the important experimental problem in finding the thermodynamic properties of paramagnetic salts is the determination of $T(S)$, the temperature as a function of entropy when no external field is present. In this section we present four methods of obtaining this information. Three of these have been applied previously and the results obtained using them are discussed. The fourth is the new method, the test of whose validity forms a major objective of this thesis. It will also be explained in detail how the new determination of $T(S)$ gives rise to an alternative and natural method for measuring the entropy, which we have called the asymptotic method. Finally, we point out that with the new method, once $T(S)$ is measured, $T(S, B_e)$ may be obtained using the data already obtained and (5), below.

We consider the measurement of $T(S)$ in the demagnetization region in the case of potassium chromium alum. This salt was chosen to test the present method because it has been studied more completely than any other salt and therefore affords a more detailed comparison among the various methods. A general review of the situation with respect to this salt has been given by de Klerk.¹⁸

In all work with paramagnetic salts below 1°K, advantage

is taken of the convenience of the zero-field susceptibility as a thermometric parameter. This is expressed by the symbol T^* , called the "magnetic temperature," and defined as the temperature inferred from the magnetic susceptibility assuming Curie's law to hold. Thus, $T^* = \lambda / \chi_e$, where $\lambda = \tau/3$ is the Curie constant and χ_e is the magnetic susceptibility measured in zero magnetic field. The function $T(S)$ is then given in the parametric form $T(T^*)$ and $T^*(S)$. When the experimental results are expressed in this form, it is possible to separate differences among observers arising from the entropy determination and from the temperature determination. It should be clear that difficulties with $T(T^*)$ arise in the demagnetization region and with $T^*(S)$ in the helium region of temperature. In conformity with the point of view adopted here that S is the independent variable, T^* is considered to be an index to the entropy. It therefore designates an entire isentropic curve, even though the temperature itself changes along this curve.

Near $T^* = .03^\circ$, χ_e becomes complex at the usual experimental frequencies of the order of 100 cps and the real part, χ_e' , goes through a maximum with respect to entropy. Clearly, χ_e' is no longer a good thermometric parameter. The temperature at which χ_e'' becomes appreciable is often called the Curie temperature. We shall not be interested here in temperatures below the Curie point. We now proceed to consider four methods of determining the relation $T(T^*)$.

1. Self-Consistent Method. This method has often been called the "theoretical method." Van Vleck's¹² expansion of the partition function gives the entropy and susceptibility in zero field, including both the effects of magnetic interaction and crystalline splitting as a function of temperature. Hebb and Purcell¹³ have explicitly calculated the entropy and the susceptibility neglecting, however, the magnetic interaction in the calculation of the susceptibility. These interactions are taken into account by a local field hypothesis. Designating the local field hypothesis by the subscript l , this information then gives $S(T)$ and $T_l^*(T)$, and thence $T(S)$ and $T(T_l^*)$. Then, $T_l^*(S)$ is obtained from adiabatic demagnetization experiments using various initial fields, and using the isothermal method to determine the entropy. The experimenter is thus in a position to use the theory to compute the final temperature in the demagnetization in two ways, i.e., from the entropy and from T_l^* . He calls the former T_{theo} and the latter T_l . If these agree it is assumed that the validity of the theoretical calculations and the local field hypothesis is established. It is found that, using the Onsager local field, the agreement is good at temperatures above $.2^\circ\text{K}$, and is not unreasonable for temperatures between $.07^\circ\text{K}$ and $.2^\circ\text{K}$. Below $.07^\circ\text{K}$, wide departures are noted.

2. Calorimetric Method. At zero external field, $dU = dQ$ and so $T = \frac{dQ}{dT^*} \frac{dT^*}{dS}$. The second factor is obtained from demagnetization experiments. The first is obtained by noting the

change in T^* when a certain amount of heat is added. The experimental difficulty is in adding the heat. We consider three methods:

a) External Heating. Heating by contact with an electrical resistance coil is the standard method for calorimetry at higher temperatures. This method, or an equivalent, remains applicable at temperatures greater than about $.2^\circ\text{K}$. It fails at lower temperatures not only because the thermal conductivity decreases,¹⁹ but because a given temperature difference is a larger percentage of the temperature being measured.

b) Gamma Ray Heating. Since the absorption coefficient is small, it is possible to achieve reasonably uniform heating. It must be assumed that the absorption coefficient is independent of temperature. Unless the absorption coefficient and the strength of the source are known the heating must be calibrated in a region where the heat capacity of the sample is known. This situation pertains in the helium region of temperature but the heat capacity is so low that the warming rate is large. Smaller heating rates are unfeasible because they must be large in comparison with the residual heat leak into the sample due to imperfect thermal isolation. The only satisfactory method of calibration of the gamma ray heating is to make a comparison with a thermometric measurement in the region of $.3^\circ\text{K} - .5^\circ\text{K}$, achieved by the theoretical

method or by external heating. Lastly, it must be mentioned that this method has been criticized because of the disruption of the crystal by the gamma rays and because of the possibility of non-equilibrium situations arising.²¹

c) Magnetic Heating. Below the Curie point hysteresis sets in. It is possible, then, to supply heat at a rate which may be established by magnetic measurements. These, however, are not easily made and inaccuracies have led to unexplained deviations among various workers using this method, which at first sight seems to be the most straightforward.⁶ This method is naturally restricted to temperatures below the Curie point. The difficulty of attaining thermal equilibrium between various parts of the sample may account for part of the discrepancy. The use of paramagnetic relaxation at high frequencies does not seem to have been explored, although much is known about such relaxation in the helium temperature region.

3. Garrett's Susceptibility Method.²² If we expand the magnetization along an isotherm as a power series in H_e , we may write

$$M = \chi H_e + \psi H_e^3 + \dots$$

where the quadratic term vanishes by symmetry. Remembering that the temperature changes when a magnetic field is applied, one may compute²² the susceptibility when a small field H_e is applied adiabatically and find

$$\chi_e = \left(\frac{\partial M}{\partial H_e} \right)_s = \chi \left[1 - \left(\frac{3}{2} \Xi - \frac{3\psi}{\chi} \right) H_e^2 + \dots \right]$$

where

$$\Xi = \frac{\mu_0 V}{\chi} \frac{d\chi}{dT} \frac{d\chi}{dS}.$$

The temperature may be determined if it is known at one point from

$$\Delta T = \int \frac{\mu_0 V d\chi}{\chi \Xi (dS/d\chi)}$$

where Ξ is determined experimentally by measuring the change in χ_e when a small field is applied adiabatically and ψ is estimated theoretically. The correction due to ψ is small at high temperatures. DeKlerk¹⁸ calculated some temperatures using this method, but does not publish them as they do not agree with other temperature determinations. He finds that the Ξ values, which he obtains from Garrett's work,²³ are too large. This would be the case if the field, H_e , used were too large. The trouble with the method is that very small fields must be used. The change in susceptibility with field then is not large compared to the change due to heat leak within the time of measurement.

4. Magnetic Method. From the Maxwell relation

$\left(\frac{\partial T}{\partial B_e} \right)_s = - \left(\frac{\partial m}{\partial S} \right)_{B_e}$, temperature changes can then be determined from

$$T_f - T_i = - \int_{B_{e,i}}^{B_{e,f}} \left(\frac{\partial m}{\partial S} \right)_{B_e} (dB_e)_s$$

where the subscripts i and f refer to the initial and final conditions of T and B_e along an adiabat. In the case of an adiabatic demagnetization

$$T_f - T_i = - \frac{\partial}{\partial S} \int_{B_{e1}}^0 \mathcal{M} dB_e \quad (5)$$

A knowledge of $\mathcal{M}(B_e, S)$ suffices to determine the final temperature. This information can be obtained by purely magnetic methods if the entropy is known before the demagnetization. If, however, T_i is 1°K and T_f is of the order of $.05^\circ\text{K}$, a small percentage error in the determination of the right-hand side of (5) would spoil the determination of T_f .

This difficulty in the determination of $T_f = T(S)$ is avoided by applying a method developed by Professor M. A. Herlin,²⁴ which compares the behavior of the actual salt sample to that of a corresponding ideal paramagnetic gas. Consider the ideal paramagnetic gas for which the energy levels are given by $mg\beta B_e$, where m is the magnetic quantum number. The partition function of the ideal paramagnetic gas is a function of $g\beta B_e/kT$ and therefore of B_e/T alone. The values of S and \mathcal{M} derived from this partition function are thus also functions of B_e/T alone. Then \mathcal{M} is a function of S alone and independent of B_e . We write $\mathcal{M} = \mathcal{M}_I(S)$ in this case. In an adiabatic demagnetization, where S is constant, \mathcal{M} remains constant as does B_e/T . The explanation for this behavior is that the entropy and the magnetization are both measures of the alignment of the dipoles. As the field decreases,

the decrease in its aligning effect must be compensated by a decrease in the disaligning effect of the thermal excitation. This means a drop in temperature and, since B_e/T is constant, when the field goes to zero the temperature must also go to zero.

Now consider the situation in an actual paramagnetic salt. Here the entropy may be reduced through interactions within the salt and not through the agency of the magnetic field alone. In an adiabatic demagnetization the magnetization may then vanish with the field, and the temperature drops to a final value above zero. (The salts which are of interest for magnetic cooling are not generally ferromagnetic, so that remanent magnetization at $B_e = 0$ is not expected.) When a large field is applied, however, the energy of interaction of each ionic dipole within the salt with the external field becomes large compared to internal interaction energies. The behavior of the actual salt then approaches that of the ideal. Curves of magnetization vs. field at constant entropy would then start at the origin, but at high fields approach an asymptotic value characteristic of an ideal salt at the same entropy. This asymptotic value is not that arising from magnetic saturation but from the increase in temperature resulting from the increase in the field. This behavior is exemplified in our experimental curves, Figure 14, where the range of the experimental curves brings the magnetization to within 12% of the computed asymptotic, or ideal value, for the mag-

netization.

We now compare our actual salt with the ideal. Let $m = m_I - m_c$ define m_c where m is the magnetization of the real salt. Then (5) gives

$$T_f = T_i + \frac{\partial}{\partial s} \int_0^{B_{e1}} m_I \downarrow B_e + \frac{\partial}{\partial s} \int_{B_{e1}}^0 m_c \downarrow B_e.$$

If the salt were ideal, T_f would be zero so the first two terms on the right cancel if the initial field, B_{e1} , is such that the ideal and actual salt have the same temperature.

This situation pertains as $B_{e1} \rightarrow \infty$. We thus have

$$T_f = \frac{\partial}{\partial s} \int_{\infty}^0 m_c \downarrow B_e. \quad (6)$$

Equation (6), which is equivalent to (1) in the Introduction, gives the final temperature in terms of magnetic quantities measured non-calorimetrically, just as does (5). However, the objection of the loss of accuracy upon subtracting two nearly equal numbers has been removed. The magnetic method, which has previously been useful only for finding temperature changes in small fields, becomes a practical procedure in the study of the transition of paramagnetic substances to the ordered state characteristic of absolute zero. The experimental comparison of the results of this method with those of the methods described earlier will be seen to give satisfactory agreement. Reservations to this statement may be ascribed to uncertainties applying to all methods in some degree.

The data required in the application of the magnetic method is expressed by the function $m_c(B_e, S)$. We recall that the entropy is labeled by T^* for experimental convenience so actually we find $m_c(B_e, T^*)$ and $T^*(S)$. The function $m_c(B_e, T^*)$ is found from experiment for values of B_e less than (in the case of the present experiment) 2000 gauss. At larger fields the extrapolation of Appendix B is used. This extrapolation assumes that magnetic interactions may be taken into account by the Lorentz local field and assumes a general form for the effect of the interactions between a magnetic ion and the non-magnetic constituents of the salt on the entropy. At very large fields the actual salt approaches ideality and so $m \rightarrow m_I$, the ideal magnetization at the same entropy. Since m_I is a function of S alone, S can be evaluated when m_I has been found. We have called this method the asymptotic method of entropy determination.

We point out some aspects of this method.

- 1) There are no constants which have to be determined in the demagnetization region, such as the splitting δ or a heating rate.
- 2) The question of magnetic interactions does not enter except in the extrapolation. One would hope to carry the measurements in the magnetic field to such a large field that the extrapolation would account for a very small portion of m_I . It would not be advantageous, however, to go to such

high fields and therefore temperatures that the lattice entropy is appreciable. For a demagnetization from 10 kilogauss, measurements of m up to about 5000 gauss would be quite satisfactory. As noted, the present experiment fell somewhat short of this goal as measurements could be made only in fields up to 2000 gauss. Even in this case, however, the extrapolation accounted for only 12% of the value of the asymptotic magnetization.

3) The entropy determination does not depend on holding the magnetic field and temperature constant while the salt is being isolated from the helium bath prior to demagnetization.

4) We would expect the theory not to enter so heavily when the entropy is found as a function of the magnetization instead of B_e/T . The expectation is founded on the fact that both the magnetization and the entropy are measures of the amount of alignment of the dipoles, whereas B_e/T is merely a measure of the strength of one possible aligning mechanism. Other aligning mechanisms arise from interactions within the sample.

5) We see that with the asymptotic method of entropy determination, there is only small reliance on a model of the low-level splittings. This model enters only into the extrapolation to large magnetic fields, and could therefore, with suitable experimental techniques, be avoided. With

the isothermal method, on the other hand, the use of a model is essential to calculate deviations from the behavior of an ideal salt. It is possible that, although the customary models give only small deviations from the ideal, large deviations may occur.

IV EXPERIMENTAL ARRANGEMENT

In order to measure temperatures by the magnetic method it is necessary to measure the magnetization as a function of field and entropy. The field was produced by a liquid-nitrogen-cooled, iron-free magnet. At a given field the susceptibility was measured with the aid of a mutual-inductance coil surrounding the sample and a Hartshorn mutual-inductance bridge. This data was taken for a range of entropy values as the sample warmed up due to the unavoidable heat leak. Each value of the entropy was identified by the susceptibility at zero field at that entropy. The actual value of the entropy was later determined from the high-field magnetization at that entropy. This experiment was repeated at various fields. These data were sufficient to plot the susceptibility as a function of field at various values of the entropy. At fields greater than 2000 gauss extrapolation as explained in Appendix B was used. Integration of these curves yielded the required data.

Some of the apparatus is shown in cross section in Figure 1. The sample S is suspended by a nylon thread from a bakelite holder, mounted with radiation shields, and is held in place by the glass weight W. The region around the sample may be maintained at a high vacuum by pumping through tube P. The entire assembly may be removed through a ground glass stopper at the top of P. The sample chamber is maintained at a low temperature by the helium bath H contained in the inner

dewar I. The temperature of this bath may be lowered by pumping and is controlled either by maintaining the pressure above H constant (by controlling the pumping speed) or by keeping a resistance thermometer at a constant temperature (by adding heat to H while simultaneously pumping). The magnet M is supplied with current through leads L, while the mutual inductance coil C consists of primary C_1 and secondary C_2 . The lower part of the apparatus is cooled by the liquid-nitrogen bath N contained in outer dewar O. As this dewar is not sufficiently long to provide for cooling of the entire inner dewar, the region above the ring seal of this dewar is cooled by 5/8" copper rods R which are fitted to the inner dewar by a tightly fitting yoke.

Figure 2 is a block diagram of the measuring apparatus. Mutual inductances which are enclosed in dotted lines are actually coaxial coils, although they are shown separated for clarity. The apparatus of Figure 2 consists of the Hartshorn bridge and the magnet M, together with its control equipment. This magnet is used both to perform the demagnetization and to provide the steady field in which the susceptibility is measured. We show in Appendix C that the susceptibility is a linear function of the mutual inductance, μ_c , of the coil c, which surrounds the sample S. A current is established in the primary by the power amplifier. Mutual inductors Σ and V and resistor R_3 are varied until the detector shows no secondary current. The value $\mu_I + \mu_V$ of the mutual inductance of the

mutual inductors Σ and V in series is then a measure of the real part of μ_C , and the value of R_3 a measure of the imaginary part of μ_C . The imaginary part at the frequency, fields, and entropies used in this experiment does not arise from properties of the sample but from circulating currents in metal which must be placed near to the sample.

We consider now, in detail, the components of the equipment.

The primary current is derived from a power amplifier capable of delivering about 5 watts without serious distortion. This amplifier is driven by a multivibrator source of $33\frac{1}{3}$ cps which is synchronized with an accurately controlled 100 cps signal supplied by the MIT electrical engineering department. The output of this source is filtered to such an extent that the overtone content is about 5%.

The mutual inductor C surrounding the sample, and the calibrated variable mutual inductors, Σ and V , were designed with the following criteria in mind:

- 1) The change in μ_C with susceptibility must be great enough to allow the necessary measurements to be made.
- 2) The alternating field at the sample must not be so large that the susceptibility changes appreciably over this range of field.
- 3) The secondary must be so designed that the voltage induced at the line frequency shall not be so large as to

saturate the detecting equipment.

4) The capacitance between the primary and the secondary must be kept small, to avoid the introduction of secondary currents arising from this capacitance.

5) Similarly, shunting capacitances in either the primary or secondary circuit should be avoided. These capacitances have much less disturbing effect than those of 4).

6) The secondary circuit should not change in position as the inductors Σ and V are varied. This precaution minimizes the effects of stray fields on the calibration of Σ and V .

Criterion 5) is met by making coils of one layer only. This requirement does not conflict seriously with 1) as the lower impedance level achieved by using small numbers of turns allows of a smaller thermal noise level. The small mutual inductance values thus attained also make the fulfilling of 2), 3), and 4) easier. Condition 4) is met, in the case of Σ and V , by sufficient spacing of the primary and secondary coils. In the case of C , large spacing is not possible, as the space inside the magnet is too valuable. Therefore, a grounded metal foil in the form of a cylinder with a longitudinal slit was placed between the primary and secondary of C . Condition 3) is met by making all secondaries astatic. This term is used to mean that, for any secondary turn, there is nearby one of the same area, wound in the opposite sense. It was felt that 2)

would be satisfactorily met if the alternating field at the salt were restricted to one gauss, peak to peak.

The design proceeded as follows. It was decided that a sphere of chrome alum 7 mm in diameter would have a sufficiently large heat capacity to allow long warmup times. The secondary which surrounded the sample might be wound of #44 formex insulated magnet wire. One turn per millimeter was considered convenient for the corresponding primary. It was estimated that at the secondary impedance of about 10 ohms imposed by these conditions, 10^{-9} volts might be detected with a band width of one cps consistent with rapid measurements. These conditions, together with 2), dictated that the smallest unit of mutual inductance should be 5×10^{-11} henry. Variable inductors Σ and V were designed with this value in mind. The details of C are given in Figure 3. The secondary, surrounded by the grounded metal foil, is wound on a piece of cigarette paper which slips on the tube containing the sample. The astatic secondary is wound of five sections in such a way that the mutual inductance between it and the magnet is small. The primary is in liquid nitrogen, inside the magnet.

The inductor V is continuously variable. It consists of two coplanar, astatic, secondary windings mounted side by side, with a primary which slides in a parallel plane. The primary leads travel through mercury puddles which are connected to the rest of the primary circuit. The geometrical factors, indicated in Figure 4, are so adjusted that the third and fifth

derivatives of mutual inductance, with respect to displacement of the primary from the center, vanish. Since the even derivatives vanish by symmetry, the mutual inductance is a nearly linear function of distance over a wide region. The variation in mutual inductance due to $1/2''$ of travel of the primary in the linear region is about 5×10^{-9} henry and is called one turn. With the help of a vernier, .01 turn is easily read. The mutual inductor V is calibrated by finding the change of displacement corresponding to a certain change of mutual inductance for all positions of the primary. These data are then summed to yield the curve of mutual inductance vs. displacement of Figure 5. The zero of mutual inductance is chosen arbitrarily.

The mutual inductor Σ is stepwise variable. It consists of four secondary turns placed as a magnetic octupole inside various primary windings through which the primary current may be reversed. These windings are so placed that a reversal of the current through them leads to a change of mutual inductance of about 2, 4, 8, 16; 20, 40, 80, 160, and 320 turns. These steps are calibrated with the help of V. The dimensions of Σ are shown in Figure 6.

The resistive network connected with R_3 in Figure 2 is used to balance the imaginary part of the mutual inductance. Since the imaginary part is not used for quantitative measurements, no special precaution is taken concerning the values of the resistances.

The detector consists of a transformer with a voltage step up of 500 feeding a battery operated preamplifier using 3 type 5678 tubes, with a final cathode follower output. This output is put through a low pass filter and attenuator in order to prevent intermodulation distortion in the selective amplifier which follows. This amplifier has three stages, each of which incorporates degenerative feedback at frequencies remote from the passed frequency. The over-all bandwidth is about 2 cps. The output is displayed on an oscilloscope which is synchronized to the $33\text{-}1/3$ cps source in such a way that the unbalance due to the real and the imaginary part of the mutual inductance may each be conveniently observed.

The magnet is powered by two submarine batteries which may be connected so as to give either 2 or 4 volts. The current is controlled by the resistors R_2 which consist of two $3/8$ " Kovar tubes cooled by water running through them. It is to be noted that one resistor is in parallel and one in series so that the magnet current may be adjusted to any value up to that provided by the full voltage. The current is read as the voltage drop across a shunt, as measured by a meter or potentiometer. The field is inferred from the current, as calibrated by a Sensitive Research fluxmeter which was in turn calibrated in a magnet whose field was known from proton resonance experiments. The calibration yielded $B = .1773 I$ webers/sq. meter, where the current I is measured in an arbitrary unit.

The magnet itself is constructed of two concentric stacks

of annular copper disks. A radial slit is cut in each one, and its end is soldered to the next disk; .00025"-thick mylar is used as insulation. The inner and outer sections are connected in series. The inside diameter is 2.03 cm, the outside diameter 10.84 cm, and the length 6.62 cm. Somewhat thicker disks are used in the center so that at low currents the field is uniform $\pm .2\%$ for 1 cm along the axis. This error figure represents the limits to which it was possible to measure the homogeneity of the field. 10 kilogauss may be obtained with the expenditure of 800 watts in the liquid nitrogen coolant. Greatly larger fields are not possible as the coolant is circulated by convection only. There is additional loss of nitrogen from heat flow down the 5/8" copper rods serving as leads. About 100 liters of liquid nitrogen are consumed in a 15-hour run, including about 10 demagnetizations.

The mutual inductance μ_3 is included for the following reason. The current in the primary of the measuring coil C induces a voltage in the magnet through μ_2 . The alternating current thus induced would depend on the setting of R_2 . This situation would be undesirable as the alternating field arising from this current would be part of the field at the sample. To avoid this difficulty, μ_3 is made equal but opposite in sign to μ_2 .

The sample consisted of a spherical crystal .280" in diameter of potassium chromium alum. The commercial salt was

allowed to crystallize from a solution in a dish at room temperature. As a thermostat was not used the resulting crystal was by no means free of imperfections. The crystal was mounted to a polystyrene rod with coil dope in such a way that a cubic axis of the crystal was along the axis of the rod. A hemisphere was then machined of the crystal with a lathe. This hemispherical end was again mounted in a polystyrene rod and the other end of the crystal was machined to complete the sphere. The rod in which the sample was mounted was then cut off near the sample and another piece of polystyrene rod was used to close over the freshly machined end of the crystal. The crystal was thus mounted in a polystyrene cylinder about .4" long and .3" in diameter. Coil dope was used to seal up this capsule and was reapplied after every run to maintain the seal. Nevertheless, deterioration of the surface of the sample was evident after four runs. A cubic axis of the crystal was thus along the axis of the polystyrene cylinder. This axis was mounted parallel to the magnetic field.

The sample was suspended by nylon threads from a 1/8" bakelite rod 8" long which had three pairs of radiation shields mounted on it. The top view of one of these shields is shown in Figure 7. The upper two pairs were brass while the lower pair was bakelite. The lower 9" of the pumping tube, together with the sample chamber, was enclosed with carbon paper held in place by black photographic masking tape. A glass weight, used to keep the nylon threads taut, fitted snugly in the sample cham-

ber which was 12 mm glass tubing 5" long sealed off at the bottom. The pumping tube was 15-mm tubing. The assembly was positioned by the lowest radiation shield's resting on the necked portion between the sample chamber and the pumping tube. This tube is connected to an oil diffusion pump (Diffusion Products Industries GF20A) whose action may be stopped with a stopcock. Figure 8 schematically shows the arrangement. A small amount of helium gas from V_2 may be admitted to the sample chamber via the volume V_1 , which is of such a size that when 30 mm of Hg pressure of helium gas in V_1 is allowed to expand into the pumping system the final pressure is about 10^{-4} mm of Hg. This expansion is performed when the sample chamber is immersed in liquid helium so that the volume ratio is actually not so large as 3×10^5 . The volume V_2 is large compared to V_1 so that a supply of helium gas at about 30 mm of Hg pressure may be maintained in V_2 during a run.

The inner dewar was 34" long, vacuum-jacketed for the lower 30". The bottom 4" was narrowed to an outside diameter of 20 mm, inside diameter of 15 mm. The body of the dewar was 32 mm inside diameter. The outer dewar was 6-1/8" in inside diameter and 24" long. The upper portions of the inner dewar were cooled by copper rods as has already been explained. Both dewars were silvered, leaving slits, not only to provide visual access to the helium bath but also to preclude the pos-

sibility of circulating currents in the silvering.

The temperature of the helium bath was lowered by pumping on it. At the lowest pressures the vapors above the liquid helium were removed by a Diffusion Products Industries MB200 booster pump backed by a Kinney DVD 8810 mechanical pump of 40 liters per second capacity. At higher pressures the mechanical pump alone was used.

The pressure over the helium bath was measured by a mercury manometer, a McLeod gauge, or a differential oil manometer, which were connected to the pumping line which connected the dewar with the booster pump. This pressure, and thence the temperature of the bath, could be maintained constant with the help of a "barostat." This consists of a valve in the pumping line which is actuated by a magnet which is controlled by contacts in the differential oil manometer, aided by an amplifier. A bleeder valve is used at lower pressures when greater pumping speeds are required. At still lower pressures the adjustment of the bleeder valve becomes so critical that the use of the barostat is unfeasible.

In the latter case the temperature of the bath was measured directly with a carbon resistance thermometer connected in an alternating current bridge.¹² The output of this bridge was applied to a phase sensitive detector whose output was rectified and amplified. Adjustment of this amplifier was possible such that the current from it to a heater in the bath might have any prescribed value when the bath was too cold and

any other prescribed value when the bath was too warm. The average temperature of the bath may be changed by adjusting the value of the variable resistor in the bridge.

V PROCEDURE FOR AN EXPERIMENTAL RUN

The secondary of the measuring coil was placed at a convenient position on the sample chamber. The length of the thread supporting the sample was adjusted so as to position the sample at the center of the secondary. After the inner dewar was mounted the magnet, with the primary of the measuring coil already placed within, was slipped onto the inner dewar and adjusted to a position such that the mutual inductance between the magnet and the secondary of the measuring coil was a minimum. This procedure was used to minimize pickup in the secondary due to vertical vibration of the magnet.

The vacuum space of the inner dewar was flushed several times with air to remove any helium which might have diffused in during the previous run. About 0.1 mm of Hg pressure of air was allowed to remain in the vacuum space to provide for a heat-transfer gas during precooling. (This gas froze out upon introduction of the liquid helium.) The sample assembly was then positioned and, after pumping with the forepump to a pressure of about 0.1 mm of Hg in the sample chamber and inside the inner dewar, liquid nitrogen was piped into the outer dewar. An effort was made to cool immediately after pumping out the sample chamber so that the crystal might not lose water of crystallization through any faults in the polystyrene capsule. The sample was isolated from the pump until it had cooled sufficiently, so that there was no danger of its losing

water. When this temperature was reached the diffusion pump was turned on. Shortly before the liquid helium was to be introduced, gaseous helium was introduced into the inner dewar. At the same time, V_2 was filled with helium to a pressure of 30 mm of Hg. Liquid helium was then transferred into the inner dewar.

While the barostat maintained the pressure over the helium bath near, but below, atmospheric pressure a measurement of μ_C was made. The temperature of the sample was at this time high, but not known exactly. Its susceptibility was therefore small. The measurement of μ_C thus made was used only as a guide. After closing off the diffusion pump with a stopcock, exchange gas at a pressure of about 0.1 micron of Hg was introduced to the sample chamber through the intermediary of V_1 . After equilibrium obtained (about 5 minutes) μ_C was again measured. The barostat was then successively set to maintain different pressures, while at each pressure μ_C was measured. About a dozen such measurements were made. At bath temperatures below 1.6°K the resistance-thermometer and heater temperature control was used instead of the barostat. On many runs, however, no readings were taken below 1.6°K. It was observed that equilibrium was attained within five seconds to within .002°, after the bath temperature was changed. The preceding data were used to calibrate the measuring coil.

The temperature of the bath was then reduced as much as

possible (to about 1°K) and the magnet turned on to a field of about 10 kilogauss. After about 2 minutes the diffusion pump was turned on to pump the exchange gas from around the sample. After pumping about 3 minutes the temperature of the bath was allowed to rise to about 1.3°K for 5 minutes. This procedure was of value in desorbing (outgassing) much of the helium gas absorbed on the walls of the sample chamber. The bath was then reduced to its lowest temperature again for two minutes and the magnet then turned off by varying R_2 . The demagnetization required about 10 seconds. Allowing a longer time for any of the foregoing procedures did not appreciably reduce the thermal leak, but using shorter times increased it.

After demagnetization the following procedure was repeated until the sample warmed up to $T^* = .18^{\circ}$. With zero field applied, μ_C was measured. Having fixed R_2 , the magnet was turned on over a period of about 2 seconds using R_1 . Then μ_C was again measured along with the magnet current I . The magnet was next turned off, again using R_1 , and μ_C was measured again. The switch S_2 was then closed and the magnet current increased to give a field of about 4500 gauss. This field was maintained for ten seconds and then reduced to zero. The purpose of this remagnetization was to re-establish temperature homogeneity throughout the sample. The time at which each measurement of μ_C was made was recorded mechanically to the nearest .01 minute. This procedure was then repeated. The alternating magnetic field at the sample was 0.6 gauss, rms.

After the sample reached $T^* = .18^\circ$, exchange gas was introduced and a calibration point in the helium region of temperature was taken to check that there had been no change in the relative positions of the coils of C. Another demagnetization was then carried out and a new value of steady field was applied in making the measurements described in the last paragraph.

After three or four demagnetizations, the helium was exhausted. The dewar was refilled with liquid helium and the entire procedure repeated. Four or five calibration points were taken in the helium region of temperatures on fillings after the first.

About ten demagnetizations took enough time nearly to exhaust the supply of liquid helium which was available on one day. At this time the sample was removed and the polystyrene capsule painted with coil dope to seal any cracks which appeared under thermal stress. Readings of μ_C were then made at various values of field.

VI LIMITATIONS IMPOSED BY THE EQUIPMENT

Before discussing the evaluation of the data it will be useful to have an understanding of why the data had to be taken in the manner in which they were.

It would be desirable to make the measurements of susceptibility at all fields at a given entropy on one demagnetization. The unavoidable warm-up rate precluded this. It was originally supposed that, using our pumping system to isolate the sample from the helium bath, the residual heat leak might be reduced to the value of 4 ergs per minute obtained by Malaker,²⁵ who originally used our system of mounting the sample. When it was found that the heat leak was actually about 20 ergs per minute it was realized that the likely cause was our smaller scale. Whereas the pumping rate decreases as r^4 , where r is the radius of the pumping line, the amount of helium gas to be pumped depends mostly on the wall area from which the gas is desorbed. This area decreases only as r . We see, then, that when warm-up times are considered, small systems have this disadvantage in addition to the necessarily small heat capacity of the sample.

Some experiments were carried out on the vacuum which might be attained in the sample chamber. An additional tube was brought up from the sample chamber and attached to an ionization gauge. The pressure in the line through which the chamber was pumped was likewise measured. The pressure as

read at the gauges differed by a factor of ten throughout the pumping procedure, the lower pressure being observed in the line which was being pumped. Other information was obtained by observing warm-up rates of the sample. If the sample chamber was not outgassed according to the procedure described above, the warmup rate was about doubled. If the sample chamber was not outgassed and a fluctuation in the booster pump action caused the temperature in the bath to rise, the warm-up rate was increased many-fold. If an ionization gauge was used to measure the pressure in the pumping line during a run the warm-up rate was about doubled.

It was not possible, using the present apparatus, to measure the susceptibility in large fields. This situation arose because vibration of the magnet induced a noise voltage in the secondary of the measuring coil. This vibration stemmed from two causes. The first was the mechanical pumps, whose effect was greatly reduced by mechanically decoupling them from the dewar system. The second cause was the boiling of the liquid nitrogen coolant around the magnet. No feasible method of preventing vibrations caused by the boiling came to mind. The following limitation on measurements in magnetic fields was therefore imposed. Up to about 2 kilogauss, there was no serious reduction in sensitivity; at higher fields the sensitivity was rapidly reduced, the reduction being about a factor of 200 at 10 kilogauss over the zero-field condition.

We were thus forced to make an extrapolation at high fields and were prevented from measuring the entropy in the helium region with the aid of the formula

$$\Delta S = \int_0^{\theta_e} \left(\frac{\partial m}{\partial T} \right)_{\theta_e} (d\theta_e)_T.$$

It was found that, even with R_2 untouched, there were small variations in the magnet current, attributed to changes in resistance of the leads into the nitrogen as the nitrogen level dropped. These changes were just large enough to be detected on the meter used to read the magnet current. Later runs used a potentiometer to measure the current and a correction was applied for the variation in current.

The viscous pressure drop between the surface of the liquid helium and the point at which the pressure was measured was increased by the presence of the pumping tube to the sample by a factor of 8 over the drop which would be observed in the case of an unobstructed dewar of the same size. This increased pressure drop was aggravated by our inability to cool the top of the inner dewar effectively. A warmer inner dewar increases both the volume and viscosity of the gas passing through it, as well as increasing the heat leak. These difficulties, then, limit the lowest temperatures attainable and the accuracy of pressure measurements at the surface of the liquid helium.

As changes in the behavior of samples from run to run have been observed,^{6,26} it would be desirable to make all meas-

urements without allowing the sample to come greatly above helium temperatures, thus avoiding the thermal shocks which occur between runs. As noted, however, only about 10 demagnetizations could be made with the liquid helium available at one time and this much data was insufficient to give an accurate magnetization curve. In addition, about 20 hours was needed to obtain this data, after which time the efficiency of the observer is greatly reduced. Several coolings were therefore required to take the complete set of data.

VII EVALUATION OF THE DATA

As shown in Appendix C, both the real and imaginary parts of μ_C vary with susceptibility. We concern ourselves only with the real part, but to save writing use no special notation. For each calibration we fit the results to a straight line

$$\mu_C = A + B/T \quad (7)$$

of μ_C plotted against $1/T$. We then define an experimental susceptibility, χ_e by

$$\mu_C = A + B\chi_e \quad (8)$$

The quantity χ_e is then proportional to the susceptibility, which is given by Curie's law in the helium region of temperatures. It was found that, on any one run, B is a constant, near to 21 turn-deg, but that A may change if the coils of μ_C are disturbed. The parameter A never changed by more than 0.4 turn during a run. The parameters A and B also depended on the magnetic field as μ_3 could be adjusted only in magnitude, not in phase. The change of A with field was measured and found to be 0.2 turn at the largest field used (2000 gauss). B was again assumed to be constant within the experimental accuracy. The quantity χ_e is determined from (8), using appropriate values of A and B for that run.

Above the λ -point, the values of T in (7) were determined from the pressure in the liquid helium near the sample. The pressure was taken as the pressure in the pumping line increased

by the hydrostatic pressure of the liquid helium. Below the λ -point, thermal equilibrium was assumed and the hydrostatic pressure was not included. The pressures were converted to temperatures using the Agreed Scale.²⁷ Below $T=1.6^\circ\text{K}$, deviations from (7) were observed. It was assumed that these corresponded to a pressure drop along the dewar as we should not expect deviations from Curie's Law at this high a temperature.¹⁶ Figure 9 is a typical calibration curve.

For each current I in the magnet, χ_ϵ was determined as a function of T^* as follows. The "magnetic temperature" T^* was used as a measure of the entropy, which was evaluated later. The value of $\chi_{\epsilon_0} = 1/T^*$ was measured before and after the measurement of χ_ϵ . The value of χ_{ϵ_0} at the time of the measurement of χ_ϵ was then found by linear interpolation. It was then possible to plot $\chi_\epsilon(T^*)$. However, for small I , χ_ϵ was known to about 5 parts in 10^5 , so that such a plot would not be convenient. For small I , then, $\chi_{\epsilon_0} - \chi_\epsilon$ is a convenient quantity to plot, as illustrated by Figure 10. At large I , χ_ϵ is small and may be plotted directly, as exemplified in Figure 11. At intermediate fields neither procedure is satisfactory. We then plot some slowly varying function of χ_ϵ and T^* against T^* . Figure 12 illustrates such a procedure. In practice, the quantity $B\chi_\epsilon = \mu_\epsilon - A$ was used instead of χ_ϵ . The results were later divided by B , as the greatest inaccuracy of calibration was in the value of B . Any later corrections, which might be realized,

could then easily be applied.

From these curves the value of χ_e at any T^* can be read for the various values of I used. Thence plots of χ_e vs. I at constant entropy (labeled by the value of T^* corresponding to that entropy) are constructed. Again accuracy is gained by plotting differences. In Figure 13 we plot

$$\chi_e - \frac{\chi_{e0}}{1 + (I/I_1)^2}$$

for the values of T^* included. The parameter I_1 is different for each value of T^* as indicated in Table 1. The curves are drawn to fit the points, but errors enter on the scale to which the curves are drawn. The points of Figure 13 represent the results of two runs which seemed to agree well with each other. A third run gave points at high fields which did not agree with these two. It was felt that this disagreement was associated with the variation from run to run which other workers have observed below the Curie point.^{6,26} It was necessary to use this latter run to provide the following extrapolation. At low fields (< 500 gauss) all runs agreed. At large I it was found that the experimental points approached a curve of the form

$$\chi_e = \frac{\chi_2}{[1 + (I/I_2)^2]^{3/2}}$$

(See Appendix B.) Then χ_2 and I_2 were chosen so as to fit the values of χ_e measured at the three largest fields used ($I = 0.9943, 1.1068, 1.2143$) and are given in Table 1. In

all cases, (9) was used for fields given by $I > 1$; the experimental points were used for fields given by $I < 1$.

We define $M_E(I) = \int_0^I \chi_E dI$. Thus M_E is proportional

to the magnetization of the sample and is evaluated by applying Simpson's rule to the curves of Figure 13 and adding the values obtained analytically for the part of χ_E expressed analytically. The curve of M_E vs. I is given in Figure 14.

As $I \rightarrow \infty$, M_E is found to approach a limit $M_{E\infty}$, as given in Table 1. Finally, we define the function $F_E = \int_0^{\infty} [M_{E\infty} - M_E] dI$

which is also evaluated by a combination of Simpson's rule and analytical formulas and is tabulated in Table 1.

We now wish to make connection between the experimental quantities and absolute values. We assume that the susceptibility in the helium region is given by Curie's law

$$\chi_E = \frac{\tau}{3T} = \frac{\mu_0 N g^2 J(J+1) \beta^2}{3VKT} \quad (10)$$

where $g = 2$ and $J = S = 3/2$ for the case of chromium alum.

Then

$$\frac{V}{\mu_0 N \beta} \chi_E = \frac{g^2 J(J+1) \beta}{3KT} = \frac{3.3627}{T} = 3.3627 \chi_E$$

and

$$\frac{m}{N\beta} = \int \chi_E dB_E = \int (3.3627) \chi_E (.1773) dI = .5962 M_E.$$

The quantity $\frac{m_{\infty}}{N\beta} = .5962 M_{E\infty}$ is given in Table 1.

Similarly,

$$F = \frac{1}{N} \int [\mathcal{M}_m - \mathcal{M}] d\theta_e = (.5962)(.1773)(9.2838 \times 10^{-29}) F_E \\ = .9813 \times 10^{-29} F_E.$$

The tables of Hull and Hull²⁸ were used to compute the entropy. These give $f = 3 B_{3/2}(\frac{3}{2} x)$ as a function of x , where $B_{3/2}$ is the Brillouin function with $J=3/2$. For an ideal paramagnetic gas

$$\frac{\mathcal{M}}{N\beta} = J g B_J \left(\frac{J g \beta \theta_e}{kT} \right).$$

If $g=2$ and $x = \frac{g \beta \theta_e}{kT}$, $f = \frac{9\mathcal{M}}{N\beta}$. Making this associa-

tion, the values of x given in Table 1 were computed. The values of S/R of Table 1 and Figure 15, for an ideal salt subjected to this value of x , were then read from the tables of Hull and Hull. Values of $S/N = k \cdot S/R$ are also given in Table 1.

The quantity F was then associated with the integral in (6), and F is plotted as a function of S/N in Figure 16. The slopes were determined graphically and their negatives are plotted as T in Figure 17 as a function of T^* .

VIII CONCLUSIONSDetermination of the Thermodynamic Properties

Since the primary objective of this thesis was to establish a new method of measuring the thermodynamic properties of a paramagnetic salt in the demagnetization region, we wish to compare our work with that of others. In addition, some previously undetermined properties of the particular salt studied have been measured, which are discussed later in their connection with theory.

The important result of measurements in the demagnetization region is embodied in the function $T(S)$, the temperature as a function of entropy when there is no external field. The experimental index of the entropy is T^* , so that actually one must determine $S(T^*)$ and then $T(T^*)$. The methods which have been applied to the solution of these two problems for potassium chromium alum are summarized in the following table:

| <u>Laboratory</u> | <u>Sample</u> | <u>Entropy</u> | <u>Temperature</u> | <u>References</u> |
|---|---------------------------|-------------------|---|-------------------|
| Oxford | Powder | Isothermal Method | Gamma Ray Heating | 5, 17, 18 |
| Leiden and National Bureau of Standards | Powder and Single Crystal | Isothermal Method | Self-Consistent (Theoretical) Method and Magnetic Heating | 6, 18, 26, 29, 30 |
| Present work | Single Crystal | Asymptotic Method | Magnetic Method | |

We typify the previous work by that of Bleaney⁵ at Oxford and of de Klerk, et al.²⁹ at Leiden. The isothermal method of entropy determination consists of computation in the helium region of temperature. The asymptotic method makes use of the fact that at high fields the isentropic magnetization approaches that of an ideal paramagnetic gas. Since the zero-field magnetic properties of chromium alum are very nearly isotropic, we expect Bleaney's results on a powder sample to agree with those on single crystals.

The comparison with the results of other workers is given in the form of graphs of $S(T^*)$ (Figure 15) and $T(T^*)$ (Figure 17). For completeness we give the result $T(S)$ in Figure 18. Making the comparison for the entropy we see that Bleaney's results lie above ours by a constant amount. Results of other workers roughly agree with those of Bleaney or lie somewhat higher, as exemplified by those of de Klerk. As the slope of our $S(T^*)$ curve then agrees with that of others, we may proceed to a consideration of the temperature agreement. The difference in the absolute value may not be ignored, however, and is discussed later. Making the comparison for the temperature, we see that all results are in rough agreement. That the differences noted actually constitute rough agreement is substantiated by the fact that if the g -factor for our sample were as small as 1.96, our results would be brought into agreement with those of Bleaney. As it has been suggested³⁰ that the g -factor might be this low at high fields, and con-

sidering the possibility of calibration errors, the differences between our results and those of Bleaney must be discounted with our present state of knowledge about the salt. The results of de Klerk are given by the self-consistent method, which does not give complete internal agreement at the entropies used in this experiment and are omitted from further discussion.

We take this agreement of temperature determinations to indicate that the magnetic method, expressed by Equation (1) or equivalently Equation (6), has a satisfactory basis and is in actual fact practical. Since entropy differences are used in the application of (1), the asymptotic method of entropy determination is thought to give valid entropy differences.

The agreement so far as the absolute value of the entropy is concerned is not good. We first dispose of the possibility that the disagreement arises from instrumentation errors, and then discuss other possibilities among which no decision can be made at present.

The greatest experimental errors arise in the measurement of B in (7) (the calibration constant of the mutual inductance coil), and the calibration of the field B_0 in terms of the current I . It is estimated that each of these errors is at most 1/2%. It seems unlikely that the g -factor is much less than 1.98 at zero field, a difference of 1% from the value 2 chosen in Curie's law (10). As g enters into (10) as g^2 , the total possible error from these causes is 3%, an insufficient amount

to account for the 7% reduction in our values of χ_m , which would be necessary to make our entropies agree with those of deKlerk, et al. It should be noticed that a variation in g would lead to an alteration of the entropy computed by the isothermal method though not so great an alteration as in our case.

We must consider the possibility that the extrapolation to large fields (9) is in error. As, at fields below 2000 gauss, χ_E falls off more rapidly than a function of the form (9), we might expect that our extrapolation leads to too large values of asymptotic magnetization $M_{E\infty}$. Typically, the extrapolation accounts for about 12% of the value of $M_{E\infty}$. As noted, this amount would have to be reduced to 5% to obtain agreement with deKlerk, et al. Although the possibility cannot be excluded, it seems unlikely that such a large error in extrapolation would be possible.

Another possibility for the non-agreement of entropy values is an error in the theoretical basis for the computation of entropy. In the case of the asymptotic method, the greatest possibility for error arises from the extrapolation to very large fields. In the case of the direct calculation of the entropy near 1°K (the isothermal method), a knowledge of the structure of the low-lying energy levels is necessary. The magnetic interactions must also be taken into account. As has been pointed out, it is impossible to make these correc-

tions correctly at present. However, the heat capacity near 1°K at zero field is known⁵ to be about $.016R/T^2$ so that the entropy reduction from the free spin case is $\Delta S/R = .008$ at zero applied field. It seems unlikely that this value would be greater with an applied field, as $\Delta S/R$ vanishes in the limit of very large fields. A correction of the order of $\Delta S/R \approx .01$ is not large enough to bring about agreement of the values in Figure 15.

Finally, the difference among our results at high fields on different runs must be recalled. These differences may be correlated with those noticed below the Curie point^{6,26} in $T^*(S)$ and in the high-temperature specific heat. The former is attributed to the rate of cooling to liquid helium temperatures and the latter to aging of the sample over a period of time. Definitive experimental information is, however, lacking on this point of non-reproducibility from run to run.

Comparison with Theory

The theoretical problem occasioned by the interactions among magnetic ions at low temperatures has been attacked by two methods. One, valid in the high-temperature limit, is to compute the partition function as a series in τ/T , where $\tau/3$ is the Curie constant. This expansion has been discussed in Section III where we have shown that it is the basis for the isothermal method of entropy determination near 1°K.

This expansion breaks down, however, at temperatures reached by adiabatic demagnetization. Bleaney⁵ has shown in detail that the zero-field specific heat below 0.5°K cannot be fitted to a curve given by this approximation. The other theoretical approach is to evaluate the low-lying energy levels of the system of interacting magnetic ions. It is difficult, however, to evaluate even the ground state, so this method has fallen short, up to now, of settling the theoretical situation up to temperatures where the series expansion method holds. Some progress, however, has been made along these lines by considering spin-waves or by introducing an order parameter. These approaches do not seem to be valid at temperatures as high as 0.1°K . The temperatures achieved in the present experiment thus lay between those covered by the two theoretical approaches.

It should be noticed, however, that in principle complete specific-heat data, at a given external magnetic field, yields the energy-level structure at that field. In practice, it is possible only to choose a model for the energy-level structure and see if it gives results which agree with experiment. As the thermodynamic behavior at high magnetic fields is not sensitive to the structure of the model chosen, the most significant comparison is with data at low fields. The data obtained in the present experiment (with the help of (2)), are sufficient to determine the complete thermodynamic properties at low fields with good accuracy. Inasmuch as no agreement with

theory can be obtained even at zero field,⁵ it is fruitless to make comparisons at other fields at the present time. When further theories are proposed, they may now be compared with data over a wide range of fields (in the limited region of entropy covered in the present experiment) whereas previously the emphasis has been only on the zero-field behavior.

IX SUGGESTIONS FOR FURTHER WORK

To carry out a complete program toward understanding the interactions among magnetic ions imbedded in a crystal, one would like to propose theoretical models and compare the equilibrium and the transport properties predicted by them with the properties measured experimentally. We consider only the experimental problems connected with the measurement of the equilibrium properties.

The present work has pointed up the value of two new methods of measuring the thermodynamic properties of a paramagnetic salt. The measurement of the entropy still is not beyond question. One would like, then, to establish the entropy measurements.

It would be desirable to modify the equipment so that measurements might be made in large fields. Then the extrapolation (9) could be made to account for a smaller fraction of the asymptotic magnetization (and hence of the entropy determined by the asymptotic method) and also might be made more accurately. It should be possible to make these measurements in large external fields, in spite of the high noise level, by use of a very narrow band width detector. The long time that would then be necessary to measure the susceptibility would not be a serious difficulty for two reasons. 1) At large fields the change of susceptibility with entropy is small. 2) For a given heat leak, the rate of entropy increase is

smaller at high fields than at low fields as the temperature is higher.

One could then check these findings by measuring the entropy change when a magnetic field is applied isothermally in the helium region of temperature. This problem is not so simple experimentally as it is necessary to measure the heat evolved instead of the heat added as in ordinary calorimetry. One might, however, provide the sample with a thermometer and heater. Then, after magnetizing isothermally, isolate the sample and demagnetize isothermally, keeping the temperature constant with the aid of the heater. The entropy, when the magnetic field was applied, would then be determined. This calorimetric method of measuring the entropy would require more complicated apparatus than is required for the application of the asymptotic method. The hope would be to establish the asymptotic method calorimetrically and then rely on the asymptotic method.

If a large magnetic field were available for making the demagnetization, one could attain the very low-temperature region where there is greatest disagreement among experimenters as to the value of the temperature and where the greatest theoretical interest lies. Similarly, the use of a salt for which the low-lying levels of the individual ions are well known would be of greater theoretical interest, for then the problem of magnetic interactions among the ions might be more easily distin-

guished from that of the interactions of the ions with their immediate surroundings.

In the region below the Curie point, relaxation effects make the determination of the equilibrium magnetization by alternating current methods difficult. It would not be out of the question, however, to design an apparatus which measures the magnetization by moving the sample at constant magnetization.

LOCAL-FIELD APPROXIMATIONS

We set ourselves the problem of finding the connection between $H_e = B_e/\mu_0$, the external field, and $H_l = B_l/\mu_0$, the field actually acting on a magnetic ion. We consider only ellipsoids, for which $H = H_e - DM$ where $H = \frac{B}{\mu_0} - M$ is the field inside the sample, and D is the demagnetizing factor. We now wish to relate H_l with H .

Lorentz approaches this problem by assuming that the magnetization arises from dipoles of magnetic moment $p = m/N$ located at each ion site. This assumption, though valid for induced moments, is clearly invalid for permanent dipole moments. He computes the field at a dipole, which is chosen as the origin of coordinates, by summing the contributions of dipoles within a sphere around the origin, and computing the contribution of other dipoles by macroscopic magnetostatics. The latter contribution is H diminished by the field arising from dipoles in a sphere, $-\frac{M}{3}$. The summed contribution is zero if the point group is cubic, since the z -component of field at the origin of a z -directed dipole is $\frac{p(3z^2 - r^2)}{r^5}$, and $\sum x^2 = \sum y^2 = \sum z^2 = \sum r^2/3$. Thus the field at the dipole is $H_l = H_L = H + \frac{M}{3}$.

Onsager avoids making the error of computing the reaction of a dipole on itself by conceiving of a continuum of permea-

bility μ with a spherical cavity of permeability μ_0 into which a dipole is placed. The change in field when the dipole is inserted has no orienting effect. We solve this problem with the condition that the field at large distances is H . We find that $H_d = H_{on} = 3H/[2 + \mu_0/\mu]$.

We define
$$T_L^* = \frac{\tau}{3\chi_d} \quad (A1)$$

where $\chi_d = M/H_d$ and $\tau/3$ is the Curie constant. We consider only low fields so that $\partial M/\partial H = M/H$. Substituting $\chi_e = M/H_e$, we find

$$T_L^* = \frac{\tau}{3} \frac{1 + (1/3 - D)\chi_e}{\chi_e} \quad (A2)$$

$$T_{on}^* = \frac{\tau}{3} \frac{(1 - D\chi_e)[1 + (1 - D)\chi_e]}{\chi_e + \frac{2-3D}{3}\chi_e^2}$$

$$= \frac{(T_L^* + \frac{2\tau}{9})(T_L^* - \frac{\tau}{9})}{T_L^* + \frac{\tau}{9}} \quad (A3)$$

If the sample is a sphere, we have $T_L^* = \tau/3\chi_e$. This fact leads to the popularity of using spherical samples for adiabatic demagnetization experiments.

Van Vleck's⁵ calculation gives

$$\chi_e = \frac{\tau}{3} \frac{1}{T - \frac{1}{2}\tau(1/3 - D) + \frac{\tau^2(1/3 - D)^2}{9T}} \quad (A4)$$

which is equivalent to (4) of the text where κ and Q are defined. We call this temperature T_V^* and might imagine a corresponding local field given by (A1). It is most convenient to eliminate χ_e between (A4) and (A2) yielding

$$T_L^* = T_V^* \left[1 + \frac{\kappa Q \tau^2}{9 T_V^{*2}} \right]. \quad (\text{A5})$$

APPENDIX BLARGE-FIELD SUSCEPTIBILITY

We wish to compute the form of susceptibility curves at large fields, along an isentrope. We use

$$\left(\frac{\partial \eta}{\partial B_e}\right)_s = \left(\frac{\partial \eta}{\partial B_e}\right)_T + \left(\frac{\partial \eta}{\partial T}\right)_{B_e} \left(\frac{\partial T}{\partial B_e}\right)_s$$

$$= \left(\frac{\partial \eta}{\partial B_e}\right)_T - \frac{\left(\frac{\partial \eta}{\partial T}\right)_{B_e}^2}{\left(\frac{\partial S}{\partial T}\right)_{B_e}} \quad (B1)$$

The form of Daniels and Kurti's¹⁷ result is that to first approximation, we may write

$$S = Nk \left[\ln z - y B_T(y) - \frac{a(y)}{2 T^2} \right] \quad (B2)$$

and

$$\eta = N g J \beta B_T(y) \quad (B3)$$

where $y = \frac{g J \beta B_l}{k T}$, z is the ionic partition function derived from energy levels $m y / J$, and B_J is a Brillion function. Since z is the ionic partition function, a local-field hypotheses is required to take account of magnetic interactions, as indicated by the use of B_l in y . We now restrict ourselves to the use of the Lorentz local field and a spherical sample so that $B_l = B_e$. The terms in (B1) are then easily computed and we find

$$\left(\frac{\partial \eta}{\partial B_e}\right)_s = \frac{N(g J \beta)^2}{k T} \left\{ \frac{1}{B_T'(y)} + \frac{1}{a + y a'/2} \right\} \quad (B4)$$

At large fields, with constant entropy, $y \rightarrow y_\infty$. At this entropy, we let

$$\frac{a(y)}{2T^2} = G(y) - G(y_\infty)$$

and expand $u=1/y$ in a Taylor series in $V = \frac{k}{\mathcal{J}\beta B_e}$. We find

$$v^2 = 2v^2 \frac{G(\frac{1}{v}) - G(y_\infty)}{a(\frac{1}{v})}$$

$$\left(\frac{dv}{dv}\right)_{v=y_\infty} = 0$$

$$\left(\frac{d^2v}{dv^2}\right)_{v=y_\infty} = \frac{a(y_\infty)}{y_\infty B_T'(y_\infty)}$$

so that

$$\frac{kT}{\mathcal{J}\beta B_e} = \frac{1}{y_\infty} + \frac{1}{2} \frac{k^2 a(y_\infty)}{y_\infty B_T'(y_\infty) (\mathcal{J}\beta)^2 B_e^2} \quad (B5)$$

Substituting in (B4) we find

$$\left(\frac{\partial m}{\partial B_e}\right)_s = \frac{Nk^2 \left(a + \frac{ya'}{2}\right) y_\infty}{\mathcal{J}\beta \left[B_e + \frac{ak^2}{2(\mathcal{J}\beta)^2 B_T'(y_\infty) B_e} \right] \left[B_e^2 + \frac{k^2 \left(a + \frac{ya'}{2}\right)}{(\mathcal{J}\beta)^2 B_T'(y)} \right]} \quad (B6)$$

$$\left(\frac{\partial \frac{m}{N\beta}}{\partial B_e}\right)_s = \frac{\left(\frac{k}{\beta}\right)^2 \left(a + \frac{ya'}{2}\right) \frac{y_\infty}{\mathcal{J}\beta}}{B_e^3 + \frac{k^2 (3a + ya') B_e}{2(\mathcal{J}\beta)^2 B_T'(y_\infty)} + \frac{k^4 a \left(a + \frac{ya'}{2}\right)}{2(\mathcal{J}\beta)^4 [B_T'(y_\infty)]^2 B_e}} \quad (B7)$$

where we have let $y = y_\infty$ in the argument. (B7) is somewhat inconvenient for extrapolation, and we compare it with

a function of the form

$$\frac{\chi}{\mu_0 N \beta} = \frac{\chi_0}{[1 + (B_e/B_{e0})^2]^{3/2}} = \frac{\chi_0 B_{e0}^3}{B_e^3 + \frac{3}{2} B_{e0}^2 B_e + \frac{3}{8} \frac{B_{e0}^4}{B_e} + \dots} \quad (\text{B8})$$

By suitable choice of B_{e0} and χ_0 , (B8) agrees with (B7), except for a factor 3/4 in the last term in the denominator if $a \gg y_{\bullet} a'$, which is the case for the results of Daniels and Kurti in the region of y_{\bullet} used in the present experiment. (B8) was used as the extrapolation formula in the present work.

APPENDIX CDEPENDENCE OF MUTUAL INDUCTANCE ON SUSCEPTIBILITY

We wish to show that the mutual inductance of a pair of coils surrounding a sample is a linear function of the susceptibility of that sample. The flux intercepting the secondary coil is then of the form

$$\phi = a B_0 + b M$$

where a and b are geometrical constants. B_0 is the field which would be present if the sample were not and M is the magnetization of the sample. The assumption has been made that the distribution of B_0 does not change with M . The equipment for the present experiment was designed to make this assumption valid. The voltage induced in the secondary is then

$$\begin{aligned} E &= - \frac{d\phi}{dt} = - a \frac{dB_0}{dt} - b \frac{dM}{dt} \\ &= - \left(a + b \frac{dM}{dB_0} \right) \frac{dB_0}{dt} \\ &= - \left(a + b \frac{dM}{dB_0} \right) \left(c \frac{di}{dt} + d i \right) \end{aligned}$$

where i is the primary current, assumed sinusoidal, and c and d are geometrical constants. The last equality arises from the fact that any current induced by i , and thence the field B_0 , may be expressed as a linear combination of i and

di/dt . If we compare this expression with that defining the mutual inductance $\mu = \mu' + j\mu''$ ($j = \sqrt{-1}$),

$$E = \mu' \frac{di}{dt} + \mu'' i$$

we see that both the real and imaginary parts of the mutual inductance are linear functions of the susceptibility dM/dB_0 of the sample.

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TABLE 1

Some Parameters at Each of the Entropies Used

| T* | <u>.10</u> | <u>.11</u> | <u>.12</u> | <u>.13</u> | <u>.14</u> | <u>.15</u> | <u>.16</u> | <u>.17</u> | <u>.18</u> |
|----------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| I ₁ | .240 | .251 | .262 | .273 | .284 | .295 | .306 | .317 | .328 |
| X ₂ | 3.622 | 3.634 | 3.660 | 3.684 | 3.694 | 3.676 | 3.624 | 3.574 | 3.522 |
| I ₂ | .682 | .670 | .658 | .647 | .637 | .629 | .623 | .617 | .611 |
| M _{E∞} | 3.7247 | 3.5395 | 3.3760 | 3.2298 | 3.0961 | 2.9697 | 2.8519 | 2.7384 | 2.6305 |
| F _E | 1.8631 | 1.7914 | 1.7276 | 1.6674 | 1.6099 | 1.5529 | 1.4980 | 1.4436 | 1.3905 |
| m _w /Nβ | 2.2206 | 2.1102 | 2.0128 | 1.9256 | 1.8459 | 1.7705 | 1.7003 | 1.6326 | 1.5683 |
| F×10 ²⁴ | 1.8282 | 1.7579 | 1.6953 | 1.6362 | 1.5798 | 1.5239 | 1.4700 | 1.4166 | 1.3645 |
| x | 1.21712 | 1.10811 | 1.02266 | .95298 | .89380 | .84145 | .79518 | .75248 | .71364 |
| S/R | .81761 | .88170 | .93359 | .97664 | 1.01340 | 1.04607 | 1.07477 | 1.10101 | 1.12463 |
| S/N×10 ²³ | 1.1286 | 1.2171 | 1.2887 | 1.3482 | 1.3999 | 1.4440 | 1.4836 | 1.5198 | 1.5524 |

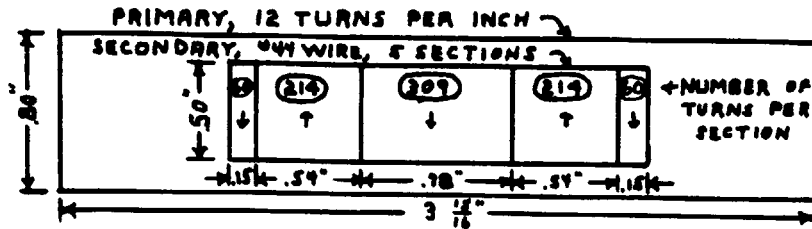


FIGURE 3 - MUTUAL INDUCTOR C

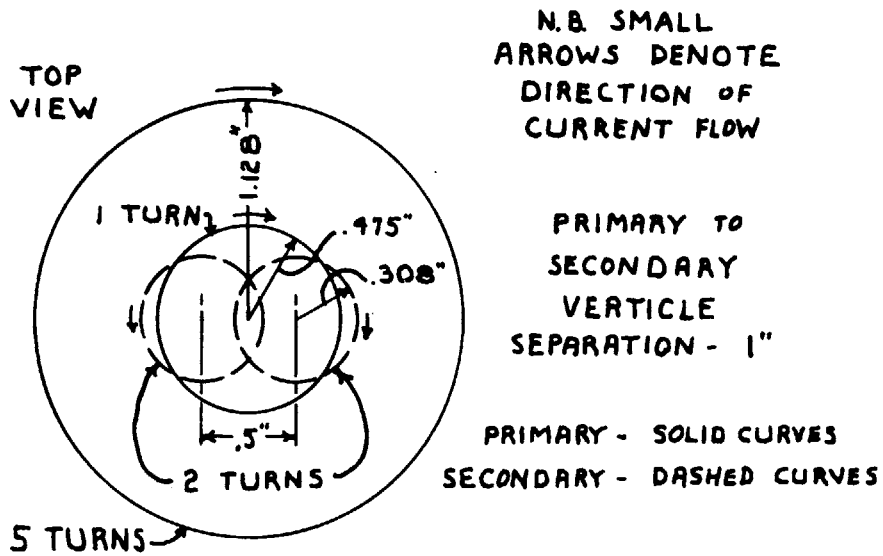


FIGURE 4 - MUTUAL INDUCTOR V

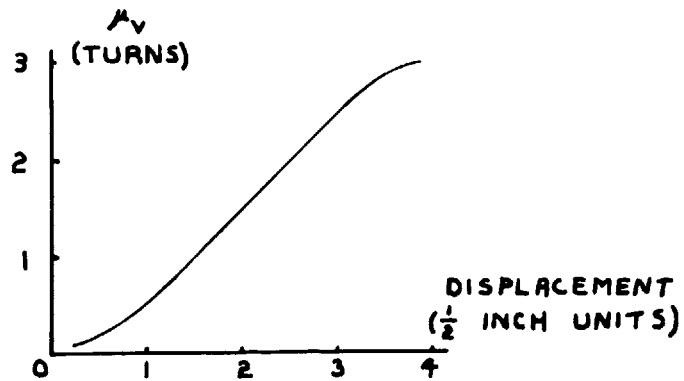


FIGURE 5 - μ_v VS. DISPLACEMENT

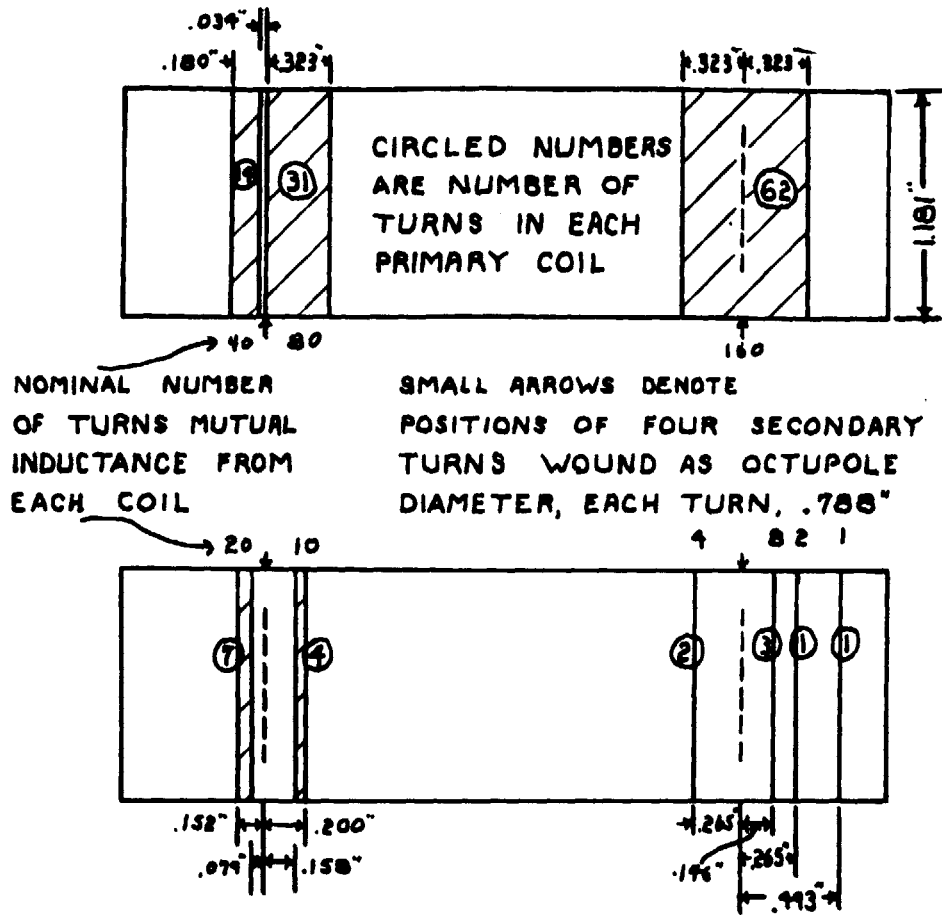
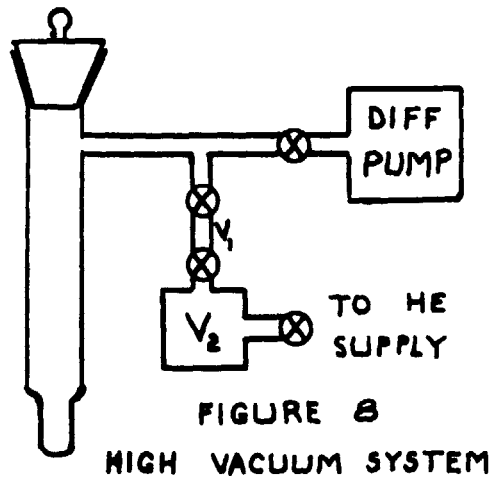
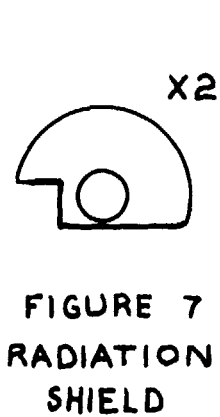


FIGURE 6- MUTUAL INDUCTOR Σ



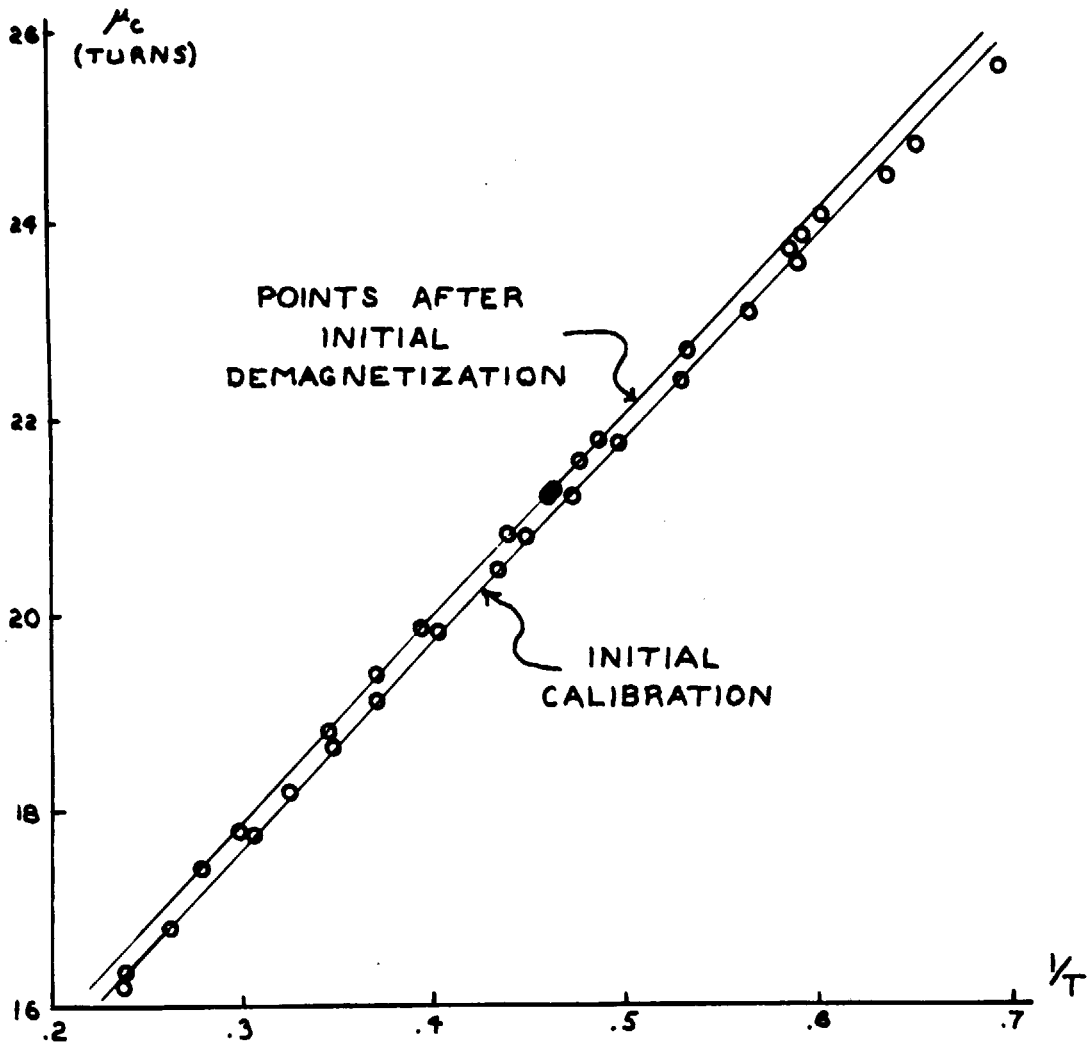


FIGURE 9 - TYPICAL CALIBRATION CURVE

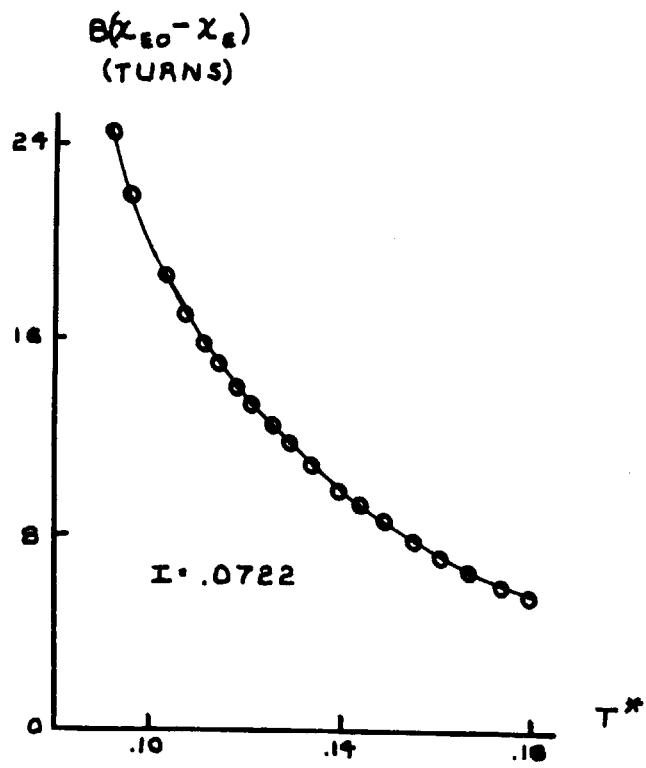


FIGURE 10 - TYPICAL DATA AT LOW FIELDS

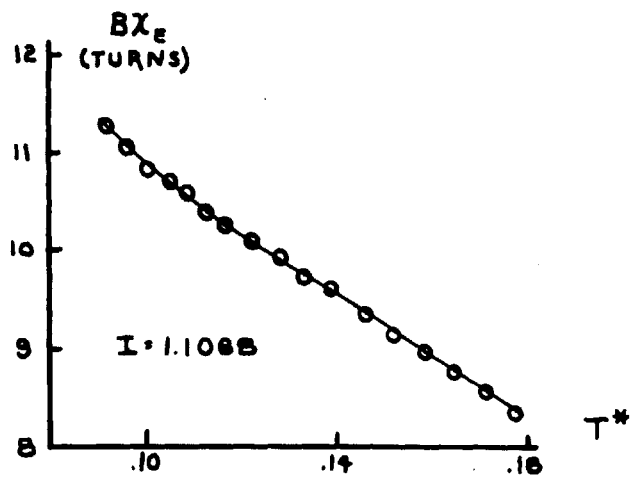


FIGURE 11 - TYPICAL DATA AT HIGH FIELDS

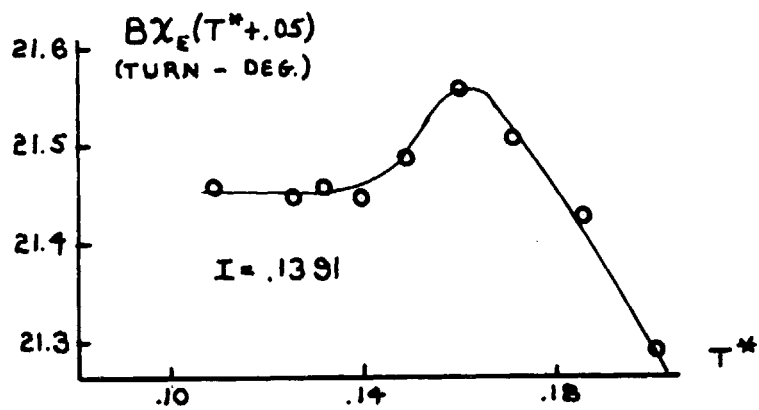
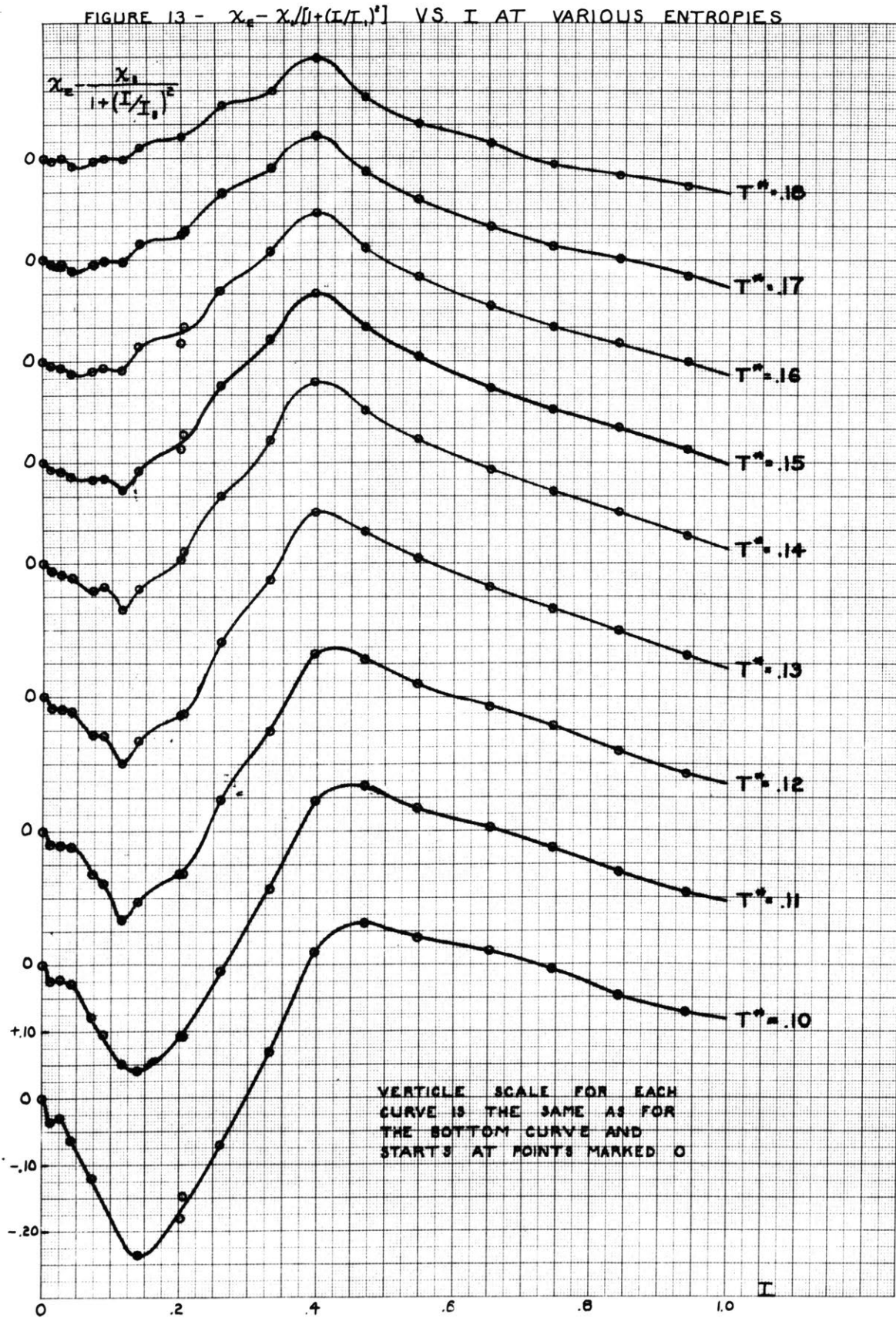
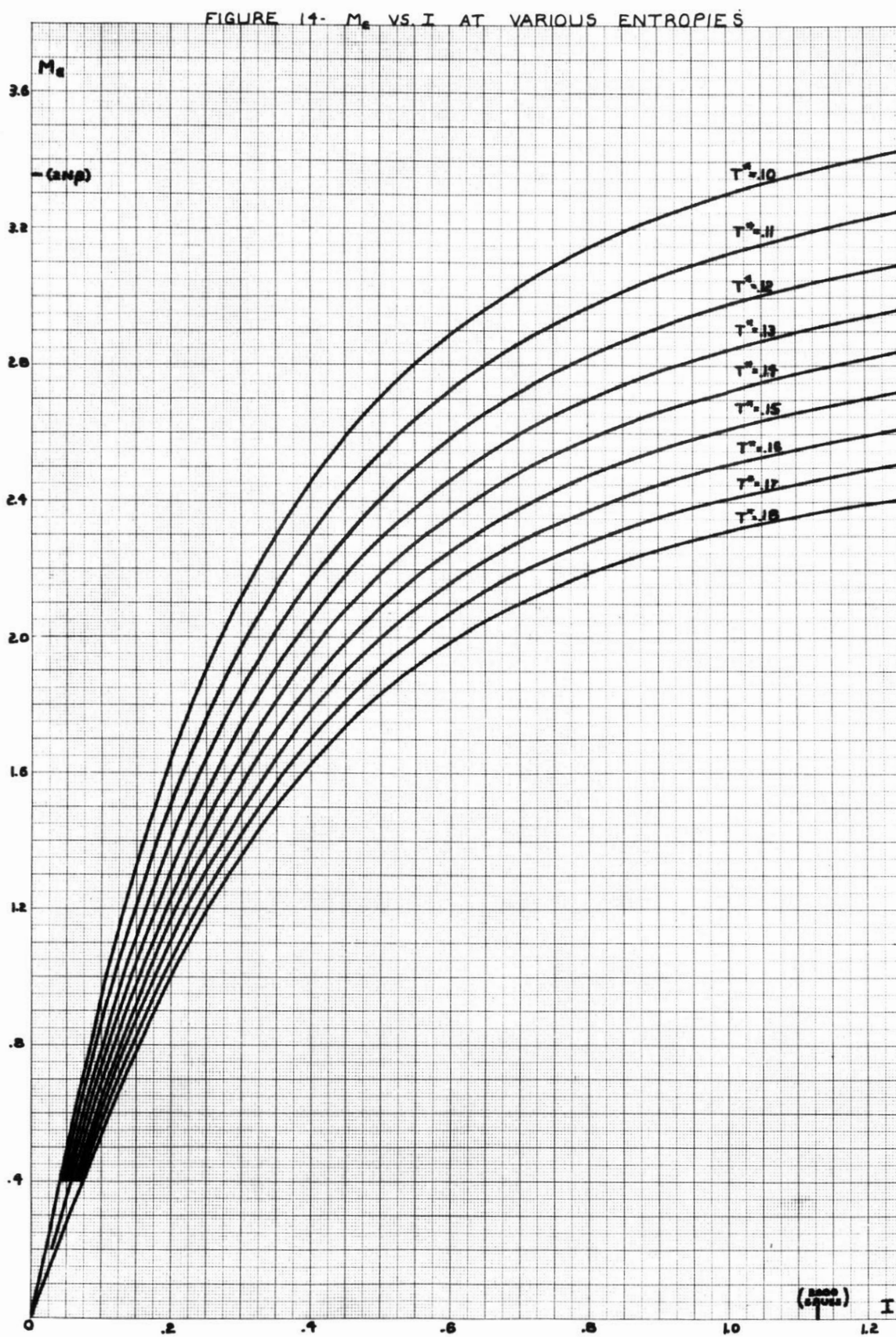


FIGURE 12 - TYPICAL DATA AT MODERATE FIELDS





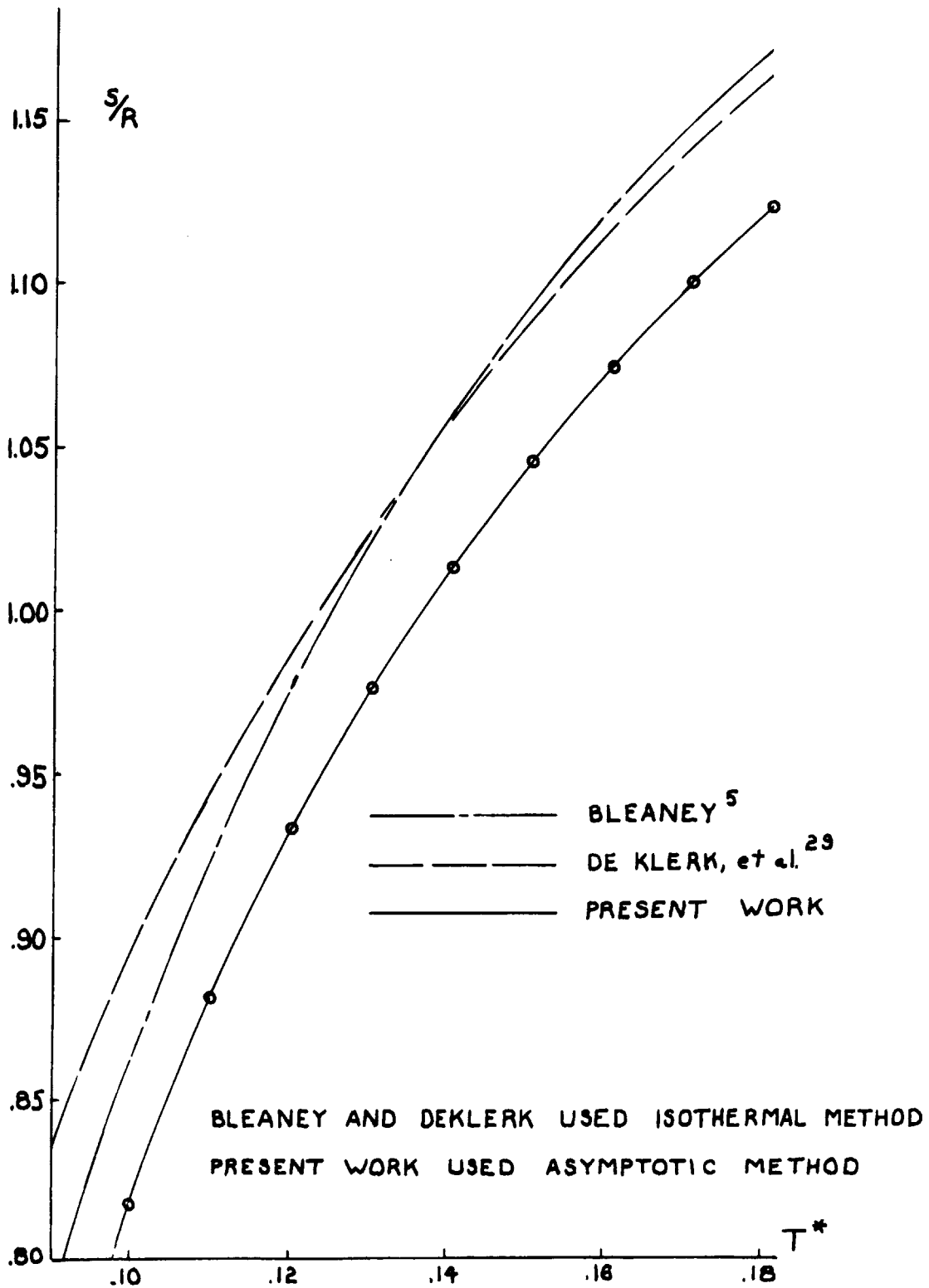


FIGURE 15 - $\frac{S}{R}$ VS. T^*

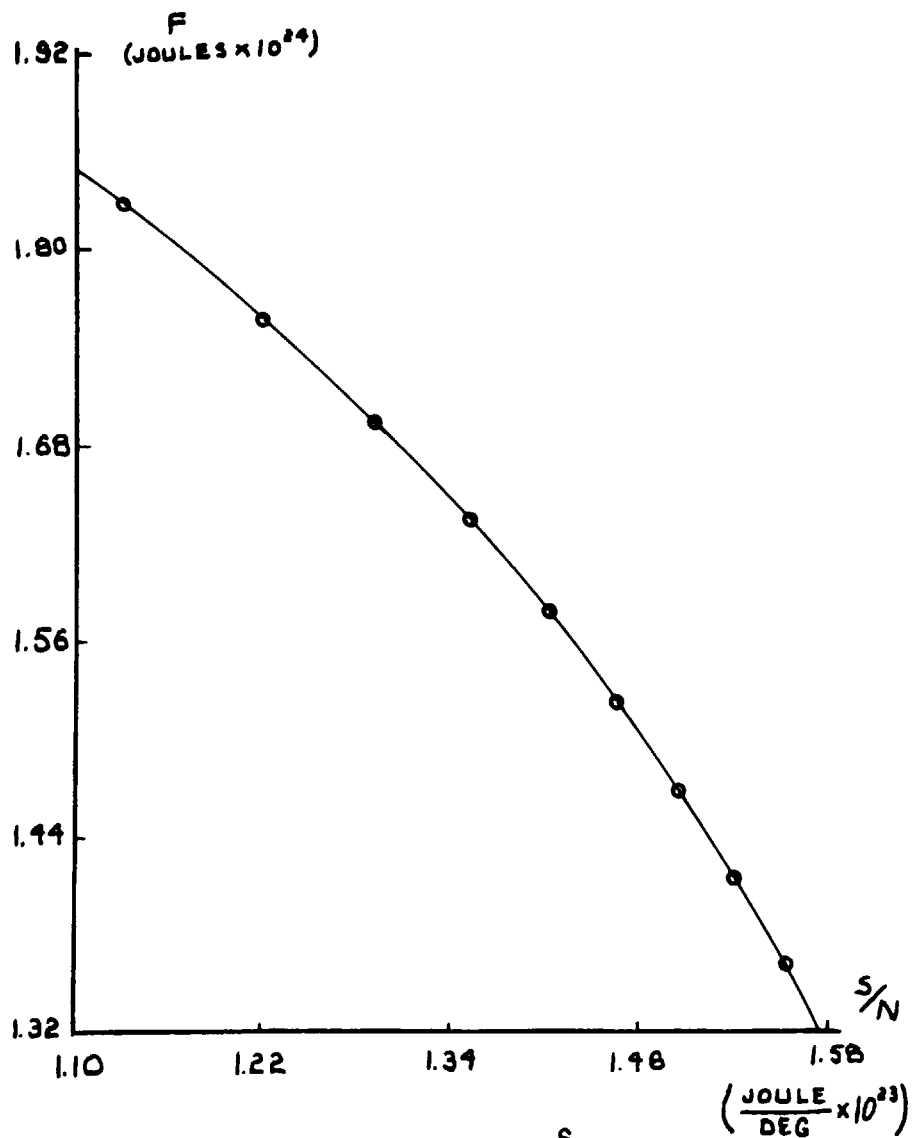


FIGURE 16- F VS. $\frac{S}{N}$
(SLOPE EQUALS $-T$)

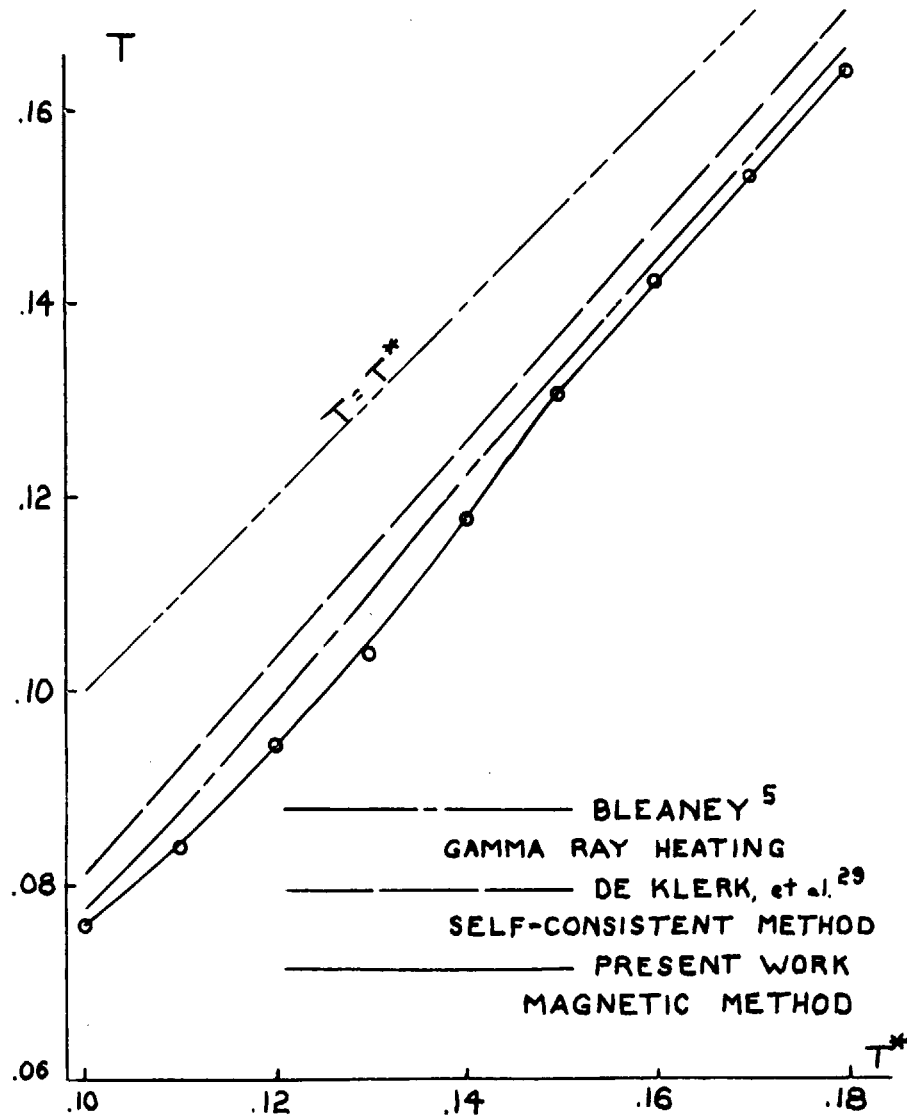


FIGURE 17 - T VS. T^* ($B_e = 0$)

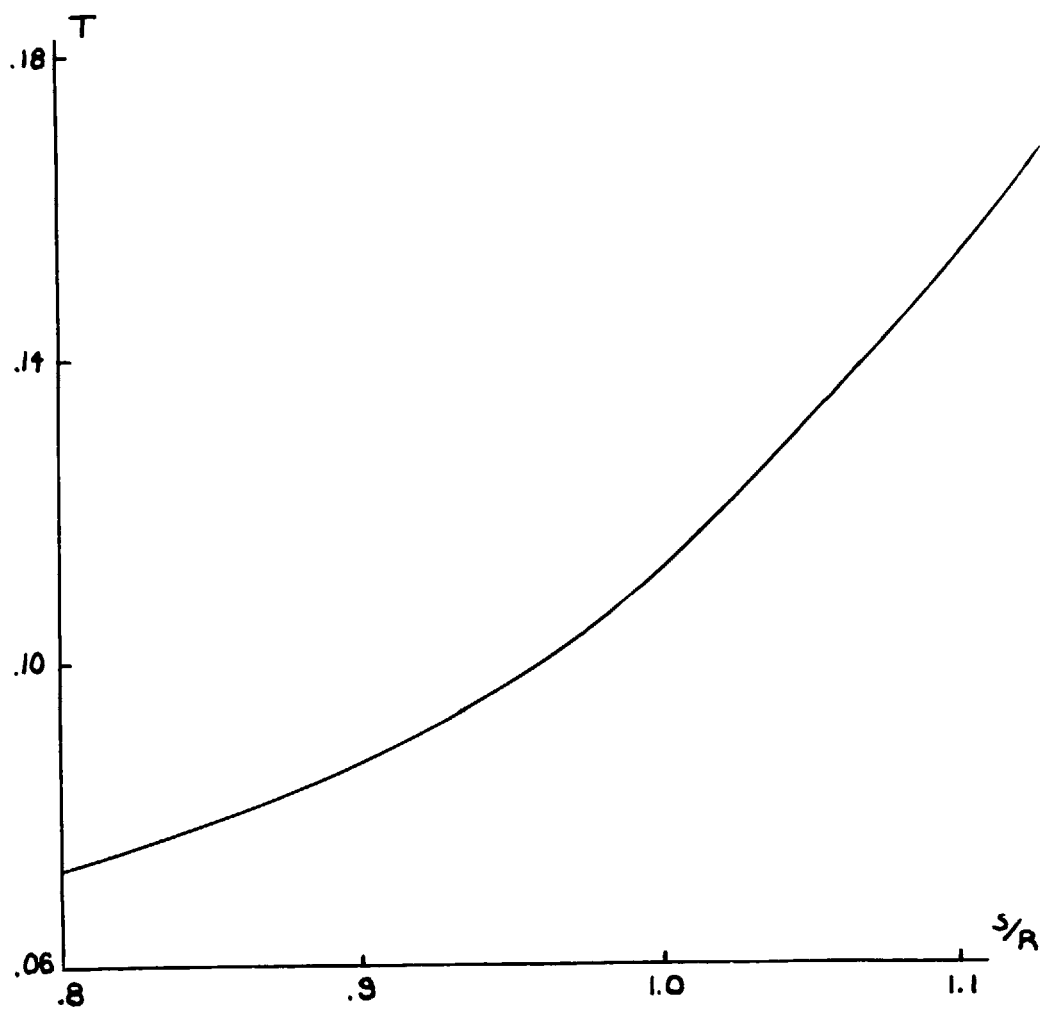


FIGURE 18 - T VS. $\frac{S}{R}$ ($B_0 = 0$)

BIOGRAPHICAL NOTE

The author was born on November 14, 1929 in New Haven, Connecticut. After attending schools in Connecticut, Kansas, and Maryland he graduated from the Bethesda-Chevy Chase High School, Chevy Chase, Maryland, in 1946. He worked for three summers at the National Bureau of Standards, 1944-1946. From 1946 to 1950 he pursued undergraduate study leading to an S.B. in physics at the Massachusetts Institute of Technology where he was awarded undergraduate scholarship aid and was elected to Sigma Xi in his senior year. Since 1950 he has pursued graduate study at the Massachusetts Institute of Technology, leading to a degree of Doctor of Philosophy. During his first year of graduate study he was awarded scholarship aid and has since held an appointment as Research Assistant in the Research Laboratory of Electronics. He took the opportunity to teach an undergraduate course during the tenure of this appointment.