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MAGNETIC SUSCEPTIBILITIES of DILUTE ALLOYS of Mn and Fe in Mg and Al

by

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ABSTRACT

The ionic and electronic contributions to the total magnetic susceptibility of a non ferromagnetic metal alloy are discussed, and a review of the experimental techniques for measuring susceptibilities is given.

The presence of even small amounts of ferromagnetic impurities can have disastrous effects on the measured susceptibilities, and a method is described for correcting for such impurities when the Gouy method is used. This enabled the true susceptibility of the non ferromagnetic part of a substance to be determined with an accuracy of .1 % relative to Ge.

The room temperature values of magnetic susceptibility of the dilute alloys of Mn and Fe in Mg and Al were measured in view of obtaining information about the electronic configuration of the transition elements in solution. A localized d electron picture rather than a d band picture was found to be adequate. The measured effective Bohr magneton numbers yielded two possible electronic configurations for the solute atoms. The possibility of distinguishing between these is discussed in terms of the corresponding change in population of the conduction band and its influence on the electronic susceptibility.

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CHAPTER I

INTRODUCTION

A minimum in the dependence of resistivity on temperature was discovered by de Haas and van den Berg (1934) and was later found in a variety of dilute alloys (MacDonald and Pearson 1955). A resistance maximum was reported by Gerritsen and Linde (1951-52-53) in dilute alloys of Mn in Cu, Ag or Au and of Cr in Au. In conjunction with this, the magneto resistance of most of the above alloys was anomalous ; the resistance decreased in a magnetic field below a critical temperature which was in the neighborhood of the temperature at which the maximum occurred. Gerritsen was thus led to the following classification :

1. Alloys with a normal temperature dependence of resistivity and a normal magneto resistance ;
2. Alloys with a minimum in the resistance and a normal magneto resistance ;
3. Alloys with a maximum and consequently a minimum in the resistance and a negative magneto resistance.

Korringa and Gerritsen (1953) offered an explanation for case (3). They postulated that the introduction of impurities may result in extra electronic states which are spatially localized but have energies near the Fermi energy. This would give rise to anomalies in the resistance and magneto resistance. Schmitt (1956)

then suggested that the anomalous electrical behaviour could be a result of a cooperative interaction taking place between the magnetic impurity ions. Thus a cooperative interaction may be taking place either between the conduction electrons and/or the impurity ions. Since the total magnetic susceptibility of a metal is proportional to the density of states of the conduction electrons at the Fermi level and to the spectroscopic state of the impurity ion, a study of the magnetic properties should give valuable additional information about these alloys.

Owen, Browne, Knight and Kittel (1956) conducted experiments aimed at studying the magnetic properties of dilute alloys of Mn in Cu. From their susceptibility and spin resonance data, they suggest that an antiferromagnetic state with a ferromagnetic interaction is present below a certain critical temperature. Owen, Browne, Arp and Kip (1957) did some preliminary work on alloys of Mn in Ag and Mg. Magnetic susceptibility measurements on dilute Cu Sn and Cu Fe alloys (F.T. Hedgcock 1956) showed an anomalous paramagnetism in the neighborhood of the temperature of the observed resistance minimum in these alloys. Jacobs & Schmitt extended their work on the Cu Mn system (1957) to the Cu Co system (1959) ; the Cu Co alloys had a resistance minimum but no maximum and showed no evidence of a cooperative magnetic transition at low temperatures but exhibited deviations from a Curie Weiss law.

Most of the alloys studied with the intention of investigating anomalous electrical and magnetic behaviour at low temperatures

have been dilute alloys of transition metals in monovalent metals. It was thought of interest to investigate the dilute alloys of transition metals in the divalent and trivalent metals Mg and Al.

Work is presently being carried out in this laboratory on the resistivity, electron spin resonance and relative magnetic susceptibilities at low temperatures of the Mg Mn, Al Mn, Al Fe, Mg Fe systems. The present thesis is concerned with the absolute magnetic susceptibilities at room temperatures with the view of complementing the above work, and obtaining information about the spectroscopic state of the impurity ion from the dependence of susceptibility on concentration.

Another value of magnetic susceptibility measurements lies in the fact that it is a very sensitive tool for the detection of ferromagnetic impurities. Such impurities are often difficult to remove and to detect and can have disastrous effects as far as significant results are concerned. From susceptibility measurements it is possible to estimate the amount of ferromagnetic impurity present in the alloys.

CHAPTER II

THEORY

MAGNETIC SUSCEPTIBILITIES

There are three main types of magnetism : dia-, para- and ferromagnetism.

Substances exhibiting dia- or paramagnetism have a magnetization that is in general proportional to the field. The magnetic force on the substance is in the same direction as the field gradient $\frac{\partial H}{\partial r}$ for paramagnetics and in the opposite for diamagnetics. If I is the intensity of magnetization acquired in a field H , the volume susceptibility k and the mass susceptibility χ are defined by

$$k = \frac{I}{H} \qquad\qquad \chi = \frac{I}{\rho H}$$

where ρ is the density. The differences in behaviour of dia- and paramagnetics in magnetic fields may be formally accounted for by attributing a negative susceptibility to diamagnetics and a positive to paramagnetics.

Substances exhibiting ferromagnetism are qualitatively distinguished magnetically from other substances by the fact that they may acquire a relatively high magnetization in weak magnetic fields, and possess a remanent magnetization in zero magnetic field.

In general for ferromagnetics, there is not a linear relation between the magnetization and the field strength. The susceptibility, defined formally as the ratio of the intensity of magnetization to the field strength $\frac{\partial I}{\partial H}$, therefore varies with the field, so that the magnetic characteristics of a ferromagnetic cannot be specified in so simple a manner as can those of dia- and paramagnetics.

Diamagnetism is associated with the tendency of electrical charges which are present in all atoms, to shield partially the interior of an atom from an applied magnetic field. The application of a magnetic field induces a current which gives rise to a magnetic moment in the opposite direction to the field.

Paramagnetism exists only if the orbital electrons in an atom have a resultant angular momentum. If the atom is considered to have a permanent magnetic moment, an applied field will tend to orientate the moments in the direction of the field.

Free electrons which are present in metals and semiconductors give rise to both a dia- and paramagnetic susceptibility. Thus the total susceptibility of a non ferromagnetic metal alloy may be considered to be made up of four terms :

$$\chi_T = \chi_{ion}^{+} + \chi_{ion}^{-} + \chi_e^{+} + \chi_e^{-} \quad \ldots\ldots \quad (II - 1)$$

where χ_{ion}^{+} = paramagnetic susceptibility of the ionic core,

χ_{ion}^{-} = diamagnetic susceptibility of the ionic core,

χ_{e}^{+} = paramagnetic susceptibility of the conduction electrons,

χ_{e}^{-} = diamagnetic susceptibility of the conduction electrons.

The χ_{ion}^{-} term is always present since it arises from the existence of electrical charges in the atoms. The other terms may or may not be present depending on the nature of the alloy.

The substances studied in the present investigation are dilute alloys of Mg Mn, Al Mn, Al Fe, Mg Fe, the largest concentration of transition element being .1%. The ionic cores of Al and Mg have no resultant magnetic moment and hence do not contribute to the χ_{ion}^{+} term. The ionic cores of Mn and Fe do have a resultant magnetic moment and therefore give a paramagnetic contribution to the susceptibility. The χ_{ion}^{+} term of the alloy is equal to the concentration of transition element times its paramagnetic ionic susceptibility (= c . χ_{ion}^{+} Fe or Mn). However, the value of χ_{ion}^{+} for Fe or Mn may depend on the solvent to which it is added (see Chapter V). The other three terms χ_{ion}^{-}, χ_{e}^{+}, χ_{e}^{-}, are present in the metals Al and Mg. It is required to know how these terms are affected by putting small concentrations of Fe and Mn into solution in the metals. For this a discussion of the individual terms is necessary. It will be shown that small concentrations of Fe and Mn will have a negligible effect on the value of the sum $\chi_{ion}^{-} + \chi_{e}^{+} + \chi_{e}^{-}$ which is the total susceptibility of the solvent metal. Thus the susceptibility of the dilute alloys studied can be expressed as :

$$\chi_{T \text{ alloy}} = \chi_{T \text{ solvent metal}} + c\,\chi_{ion}^{+}{}_{\text{transition element}} \qquad \ldots \text{(II - 2)}$$

where $\chi_{T \text{ alloy}}$ = total susceptibility of the alloy,

$\chi_{T \text{ solvent metal}}$ = total susceptibility of the solvent metal,

c = concentration of transition element,

χ_{ion}^{+} transition element = paramagnetic susceptibility of the ionic core of the transition element in solution in the solvent.

By measuring the total susceptibility of the solvent and of the alloys, it is possible to determine the value of χ_{ion}^{+} of the transition element when in solution in a particular solvent.

A discussion of the four terms contributing to the total susceptibility of a non ferromagnetic substance will now be given ; firstly, from the point of view of free atoms and electrons to get some insight into the nature of the individual terms ; and secondly, from the point of view of solids in which one would normally expect the ions and electrons to be influenced by the electric and magnetic fields of their neighbours.

MAGNETIC SUSCEPTIBILITIES OF FREE ATOMS

Langevin's derivation of the diamagnetic moment of free atoms assumes the Larmor theorem which states that : for an atom in a magnetic field the motion of the electron is to the first order in H, the same as the possible motion in the absence of the field except for the superposition of a precession of angular frequency ω_L of the electron orbit about the magnetic field (see figure 1),

$$\omega_L = -\frac{eH}{2mc}$$

The equivalent diamagnetic current is

$$I = - \frac{Ze}{2\pi c} \quad \frac{eH}{2mc} \qquad \text{in e.m.u.}$$

Ampère's law states that the magnetic moment μ of a current loop is given by the product of the current times the area of the loop

$$\mu = - \frac{Z e^2 H}{4 m c^2} \quad \bar{\rho}^2$$

for Z electrons, where $\bar{\rho}^2 = \bar{x}^2 + \bar{y}^2$ is the average of the square of the perpendicular distance of the electron from the field axis (see figure 1). It can be seen that $\bar{\rho}^2 = \frac{2}{3} \bar{r}^2$ for a spherically symmetrical charge distribution, where $\bar{r}^2 = \bar{x}^2 + \bar{y}^2 + \bar{z}^2$ is the mean square distance from the nucleus.

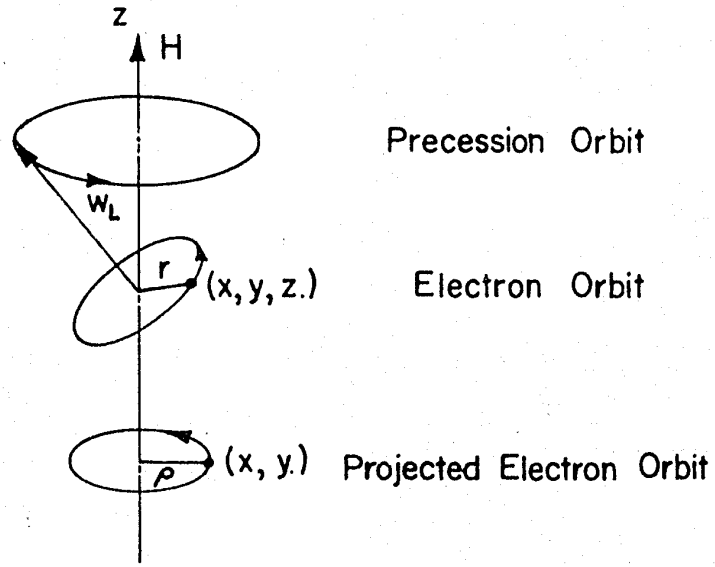


Fig. 1

Larmor Precession and Diamagnetism

The diamagnetic susceptibility per unit mass for N atoms per unit mass is then given by

$$\chi = - \frac{Z e^2 N}{6 m c^2} \bar{r}^2 \quad \ldots\ldots\ldots \quad (II - 3)$$

From this expression it is seen that the diamagnetic effect is temperature independent and is a universal property of all atoms.

The paramagnetism of an atom requires that the atom possess a resultant orbital angular momentum. The atom will then have a resultant magnetic moment.

An electron in a circular orbit of radius r and angular velocity ω_o is equivalent to a current $I = \frac{e \omega_o}{2 \pi}$. According to Ampère's law stated previously there is a magnetic moment associated with this current loop :

$$\mu = \frac{I \times \text{area}}{c} = \frac{e \omega_o r^2}{2 c} \qquad \text{in e.m.u.}$$

or

$$\mu = \frac{e}{2 m c} \times \text{angular momentum.}$$

An applied magnetic field will tend to orientate the moments in the direction of the field and this tendency will be counteracted by the thermal motions of the atoms. There will be an equilibrium distribution of the magnetic moments with respect to the field at any temperature T. If the equilibrium distribution can be determined, an expression for the susceptibility may be deduced. Before deriving the Langevin expression for paramagnetism, it is necessary to review some concepts of quantum theory.

VECTOR MODEL OF THE ATOM

Using the vector model of the atom, four quantum numbers are needed to describe the behaviour of an atom in a magnetic field:

- the total quantum number $n = 1, 2, 3, \ldots\ldots$
- the orbital angular momentum quantum number $\ell = 0, 1, \ldots (n-1)$
- the spin magnetic quantum number m_s which represents the projection of the spin vector s along the direction of the field ; $m_s = \frac{1}{2}$ ou $-\frac{1}{2}$
- the orbital magnetic quantum number m which represents the projection of the ℓ vector along the direction of the field ; $m_\ell = \ell, \ell-1, \ldots 0, \ldots -\ell$.

The angular momentum associated with an electron moving in a circular orbit is an integral multiple "n" of $\frac{h}{2\pi}$ and the corresponding magnetic moment is an integral multiple "n" of $\frac{he}{4\pi m}$ (in e.m.u.) ($\equiv \mu_B$, the Bohr magneton).

The Pauli principle states that only one electron in a given atom can possess a particular set of values for the four quantum numbers n, ℓ, m_ℓ, m_s .

For a multielectron atom, let us assume that the orbital and spin momenta are "coupled" to form a resultant orbital and spin momentum of the total electrons in the atom. The Russell Saunders coupling is the useful one in magnetism : the various ℓ vectors combine to form a resultant $L = 1, 2, 3, \ldots\ldots$

and the s vectors a resultant $S = 0, \frac{1}{2}, 1, \frac{3}{2} \ldots$ They can be combined to form a resultant $J = 0, \frac{1}{2}, 1, \frac{3}{2} \ldots$. There are $2S + 1$ ways in which L and S may combine if $L \gg S$, giving the multiplicity of energy levels, since the energy associated with a particular atom depends on the value of J. Thus for given L and S vectors there are certain energy states available ; the "allowed" energy states correspond to a multiplet. The energy separation between the outermost components of a multiplet is known as the overall width. Multiplets are said to be wide or narrow depending on whether the energy of transition between two successive states ($h\nu(J\,J')$) is very large or very small with respect to kT. For wide multiplets, $h\nu(J\,J') \gg kT$ nearly all the atoms will be in their lowest energy state since there is not sufficient thermal energy to excite them to a higher state. For narrow multiplets $h\nu(J\,J') \ll kT$, the atoms must be in a variety of energy states.

To determine the resultant L, S or J vectors for an atom or ion in the "ground" state, Hund has devised a set of rules. Firstly, the spin momenta combine to give the maximum value of S consistent with the Pauli principle. Secondly, when the maximum value of S has been thus determined, the orbital momenta combine in a like manner to give the maximum value of L. Thirdly, for an incomplete shell of electrons, the lowest term has $J = L - S$ when the shell is less than half occupied, and $J = L + S$ when the shell is more than half occupied.

If an atom is in a state J, one would expect the magnetic moment to be $M_J \mu_B$ where M_J is the projection of J along the

direction of the field. However, the magnetic moment is actually found to be $g M_J \mu_B$, where g, the Landé splitting factor, is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

The splitting factor was initially introduced empirically by Landé, and was later given a theoretical basis in wave mechanics.

We are now in a position to calculate the paramagnetic susceptibility of an atomic system. On the application of a magnetic field H, an atom of magnetic moment $M_J g \mu_B$ will have a magnetic energy $M_J g \mu_B H$. For normal fields and at room temperatures, $M_J g \mu_B H$ is generally much smaller than the thermal energy kT (a field of 10^5 gauss corresponds to a temperature of $\sim 10^\circ$ K). Hence, if kT is insufficient to excite an atom to a higher energy state, $M_J g \mu_B$ will be also, and we will neglect the influence of $M_J g \mu_B$ on the energy state of the atom.

There are two extreme cases in the calculation of paramagnetic susceptibilities, one for very wide multiplets and the other for very narrow multiplets.

For wide multiplets, $h\nu(J\,J') \gg kT$, the atomic system can be said to have a value of J corresponding to the ground state, since the thermal energy is insufficient to excite the atoms to higher energy states. On the application of a magnetic field the J vector precesses about the lines of force giving components of magnetic moment $M_J g \mu_B$ parallel to H,

where $M_J = J, J-1, \ldots -J$. The magnetic potential energy of an atom in a particular M_J state is $- M_J \, g \mu_B \, H$. In a system of independent atoms, the probability that an atom will have a particular value of M_J, assuming Maxwell Boltzmann statistics, is given by

$$\frac{e^{M_J \, g \mu_B \, H \, / \, kT}}{\sum_{M_J = -J}^{J} e^{M_J \, g \mu_B \, H \, / \, kT}}$$

Multiplying this expression by $M_J \, g\mu_B$ and summing over all possible M_J states will give the average magnetic moment of an atom. Hence the total magnetic moment M_H of N atoms per unit mass will be given by

$$M_H = \frac{N \sum_{M_J = -J}^{J} (M_J \, g \mu_B) \, e^{M_J \, g \mu_B \, H \, / \, kT}}{\sum_{M_J = -J}^{J} e^{M_J \, g \mu_B \, H \, / \, kT}}$$

If we expand the exponential and assume $\mu_B \, H \ll kT$, this expression gives

$$M_H = \frac{N \, g^2 \, J \, (J + 1) \, \mu_B^{\,2} \, H}{3 \, kT}$$

The susceptibility is then

$$= \frac{N \, g^2 \, J \, (J + 1) \, \mu_B^{\,2}}{3 \, kT} \quad \ldots\ldots \quad (II - 4)$$

From this expression, it is seen that the paramagnetic susceptibility is inversely proportional to the temperature, and is dependent on the spectroscopic state of the atomic system.

A convenient parameter to define is the effective magneton number of the system p eff and it is defined by the relation

$$g \sqrt{J(J+1)}\, \mu_B = p_{eff}\, \mu_B$$

The effective magnetic moment being then $\mu_{eff} = p_{eff}\, \mu_B$

Thus

$$\chi = \frac{N (p_{eff}\, \mu_B)^2}{3kT} \quad .... \quad (II - 5)$$

Now let us consider the case of narrow multiplets $h\nu\ (J\ J') \ll kT$. The thermal energy will now excite the atoms to many different J states : the L and S vectors are constantly changing their coupling to give a different resultant J. On the application of a magnetic field it is reasonable to assume that the coupling of L and S is small compared with that of either L or S with the magnetic field. Hence we can consider the orbital and spin momenta to be separately quantized giving projections M_L and M_S along the direction of the lines of force

$$M = L, L-1, ... -L \qquad (g_L = 1)$$

$$M_S = S, S-1, ... -S \qquad (g = 2)$$

If we now assume that the average magnetic moment of an atom is equal to the sum of the average magnetic moments due to M_L and M_S, then the magnetic moment M_H of N atoms per unit mass

will be given by

$$M_H = \frac{N\mu_B \sum_{M_L=-L}^{L} M_L \, e^{M_L \mu_B H / kT}}{\sum_{M_L=-L}^{L} e^{M_L \mu_B H / kT}} + \frac{N\mu_B \sum_{M_S=-S}^{S} 2M_S \, e^{2M_S \mu_B H / kT}}{\sum_{M_S=-S}^{S} e^{2M_S \mu_B H / kT}}$$

Assuming as before that the Maxwell Boltzmann law holds.

If $\mu H \ll kT$ this expression gives

$$M_H = N\mu_B \left[\frac{L(L+1)\mu_B H}{3kT} + \frac{4S(S+1)\mu_B H}{3kT} \right]$$

and the susceptibility is then

$$\chi = \frac{N (p_{eff} \mu_B)^2}{3kT}$$

where the effective magneton number p_{eff} is now given by

$$p_{eff} = \sqrt{L(L+1) + 4S(S+1)} \quad \ldots\ldots \quad (II-6)$$

It was observed experimentally by Curie that many paramagnetics approximately obeyed the law which bears his name

$$\chi = \frac{C}{T} \qquad (C = \text{Curie constant})$$

The inverse proportionality of χ to the absolute temperature is in agreement with the theoretical formulae derived above. However,

the Curie law is not obeyed for independent atoms when the multiplet width $h\nu$ (J J') is comparable to kT. This has been discussed by Van Vleck and usually in such cases the theoretical calculation of χ is very difficult.

INFLUENCE OF A CRYSTALLINE FIELD ON PARAMAGNETIC SUBSTANCES

Suppose now that instead of considering the particles to be free, we consider them to be acted upon by the electric fields of the neighbouring particles. This is what we would normally expect in the case of solids. It is found that if an electric field acts upon an atomic system, the orbital motion of each electron is affected while the spin which is an intrinsic property of the electron is not. If the electric field is sufficiently strong to break down the L S coupling, then the L vector will precess about the field giving a projection M_L upon it where $M_L = L, L-1, \ldots -L$. Now on the application of an external magnetic field, if the orbital momenta remain fixed under the influence of the internal field they will not orientate with respect to the external field. The orbital momenta are then said to be "quenched". The spin momenta are not affected by internal electric fields and they may orientate with respect to the external field. When the orbital momenta are completely quenched, we would expect the effective magneton number p eff given by equation (II-6) to be replaced by

$$p \text{ eff} = \sqrt{4 S (S + 1)}$$

When quenching is incomplete the value of p_{eff} should lie between

$$\sqrt{4S(S+1)} \quad \text{and} \quad \sqrt{L(L+1) + 4S(S+1)}$$

It is observed experimentally that the great majority of paramagnetic solids, instead of obeying a simple Curie law, obey a Curie-Weiss law :

$$\chi = \frac{C}{T - \theta} \qquad \ldots\ldots\ldots\ldots \quad (II - 7)$$

where θ , the Weiss constant, varies widely for different substances ; it is a measure of the amount of interaction between the particles due to the molecular fields present.

MAGNETIC SUSCEPTIBILITIES OF CONDUCTION ELECTRONS IN A METAL

A number of important physical properties of some metals, in particular the simple monovalent metals, are understood in terms of the free electron theory, which states that the valence electrons of the constituent atoms of the metal are able to move about freely through the volume of the metal. One would normally expect then that the paramagnetic susceptibility of the conduction electrons would be given by equation (II - 4) in which $L = 0$, $S = \frac{1}{2}$, $g = 2$, i.e.

$$\chi = \frac{N \mu_B^2}{kT} \qquad \ldots\ldots \quad (II - 8)$$

However, it is observed experimentally that the susceptibility is approximately independent of temperature and of the order of $\frac{1}{100}$ th of the value given by equation (II - 8) at room temperature.

Equation (II - 4) was derived assuming the Maxwell Boltzmann statistics to be valid for the assembly of particles under consideration. Pauli showed that for conduction electrons in a metal, it was necessary to apply the Fermi Dirac statistics which take into account the requirements of the Pauli exclusion principle.

Free electrons moving in a constant potential may be described by plane waves with wave functions $\Psi \sim e^{i k.r}$ where k is the wave vector. Their energy values are given by $E = \frac{\hbar^2}{2m} k^2$ and are distributed quasi continuously from zero to infinity.

Each energy level can only accommodate a certain number of electrons consistent with the Pauli exclusion principle. At absolute zero, all the energy levels below a certain level will be filled and all the levels above it will be empty. This dividing level is known as the Fermi energy $E_F(o)$.

$E_F(o) = \frac{\hbar^2}{2m} (3 \pi^2 N)^{2/3}$ where N is the electron concentration. A convenient parameter is the Fermi temperature defined as $T_F = E_F / k$. At a temperature T, only those electrons within $\sim kT$ of the Fermi level will be able to orientate themselves with respect to an applied magnetic field. Thus only the fraction $\sim T / T_F$ of the total number of electrons should be counted as contributing to the susceptibility. The paramagnetic susceptibility of conduction electrons is known as the Pauli spin paramagnetism and is given by :

$$\chi = \frac{3 N \mu_B^2}{2 kT_F} \quad \ldots\ldots \quad (II - 9)$$

where T_F is the Fermi temperature and is of the order of 10^4 to 10^5 ^oK . Equation (II -9) is $\sim \frac{1}{100}^{th}$ of the value of Equation (II - 8) and is independent of temperature, as required experimentally.

Since a magnetic field causes electrons to move in spiral paths, Landau (1930) has shown that there is also a diamagnetic effect produced by the conduction electrons which is 1/3 of the Pauli paramagnetism.

$$\chi = \frac{- N \mu_B^2}{2 k T_F} \quad \ldots\ldots\ldots \quad (II - 10)$$

Thus the total susceptibility of the conduction electrons is

$$\chi = \frac{N \mu_B^2}{k T_F}$$

This can also be written $\chi = \frac{2}{3} \mu_B^2 g(E_F)$ where $g(E_F)$ = density of states at the Fermi level = number of states per unit energy range per unit volume.

INFLUENCE OF A PERIODIC POTENTIAL ON THE MAGNETIC SUSCEPTIBILITIES OF CONDUCTION ELECTRONS

The free electron model of metals outlined above gives a good insight into some of the magnetic properties of metals. It is, however, a crude approximation, for no account has been taken of the periodic potential of the solid in which the electrons move.

A characteristic feature of wave propagation in periodic structures is Bragg reflection which occurs for electron waves in crystals. An important consequence of Bragg reflection is that it leads to the existence of energy gaps in the distribution in energy of the conduction electrons. That is, there may arise a substantial region of energy in which solutions of the wave equation do not exist. Bloch was thus led to the band theory of solids. Energy versus wave vector curves are shown below for a free electron and for an electron in a monatomic linear lattice.

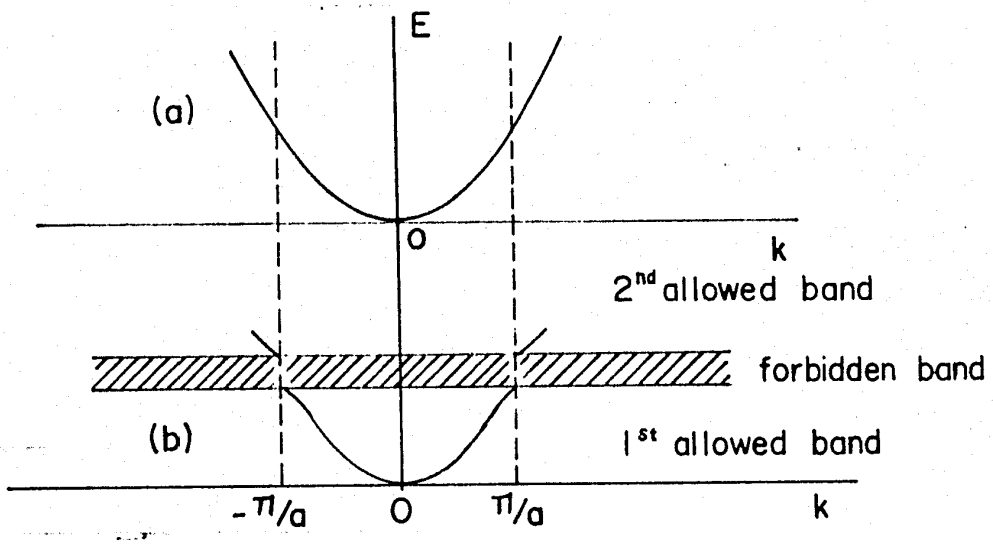


Fig. 2

Energy versus wave vector

(a) for a free electron

(b) for an electron in a monatomic linear lattice of lattice constant "a"

The variation of E with k may be emphasized by a rather unfamiliar expression for mass

$$m = \frac{\hbar^2}{\partial^2 E / \partial k^2}$$

obtained from the relation $E = \frac{\hbar^2}{2m} k^2$ for free electrons by taking the second derivative of E with respect to k.

The effect of the periodic potential on the conduction electrons may be taken into account by defining an effective mass m^*

$$m^* = \frac{\hbar^2}{\partial^2 E / \partial k^2}$$

where now $\partial^2 E / \partial k^2$ is obtained from the E versus k curve of electrons moving in the periodic potential. Assume that in the portion of interest all the states in the band may be described by the same value of the effective mass m^*. Then the results obtained from the free electron model are valid if we simply replace m by m^*.

Consider the expressions for the susceptibilities of conduction electrons given by equations (II - 9 and 10) in which

$$k T_F = E_F = \frac{\hbar^2}{2m} (3 \pi^2 N)^{2/3}$$

$$\mu_B = \frac{he}{4 \pi m}$$

In the Pauli spin susceptibility, the magnetic moment μ_B is due to spin only which is not affected by the periodic potential and hence m in μ_B is not replaced by m^*.

In the Landau diamagnetism μ_B is due to the spiral motion of the electrons in the metal and is affected by the periodic potential. It is therefore necessary to replace m by m^*.

In both these cases, the mass in E_F is replaced by m^*. Hence

$$\chi_{\text{Pauli}} \sim m^* \qquad \ldots\ldots\ldots \qquad (\text{II - 11})$$

$$\chi_{\text{Landau}} \sim \frac{1}{m^*} \qquad \ldots\ldots\ldots \qquad (\text{II - 12})$$

From these relations it is seen that high paramagnetic electron susceptibilities occur when $\frac{m^*}{m} \gg 1$, and high diamagnetic electron susceptibilities occur when $\frac{m^*}{m} \ll 1$.

MAGNETIC SUSCEPTIBILITY OF A DILUTE ALLOY

The total susceptibility of a non ferromagnetic metal can be considered to be made up of four terms as stated in equation (II - 1). We have discussed above each of the individual terms and are now in a position to justify the use of equation (II - 2) for dilute alloys of transition elements in metals.

From equations II - 3, 5, 7, 9, 10, 11, 12,

$$\chi^{-}_{\text{ion}} = \frac{- Z e^2 N \bar{r}^2}{6 m c^2} \simeq 10^{-7}$$

$$\chi^{+}_{\text{ion}} = \frac{C}{T - \theta} = \frac{N (p \text{ eff } \mu_B)^2}{3 k (T - \theta)} \simeq 10^{-4}$$

$$\chi_e^+ = \frac{3}{2} \frac{N \mu_B^2}{k T_F} \simeq 10^{-6} \quad \text{and} \sim m^*$$

$$\chi_e^- = -\frac{1}{2} \frac{N \mu^2}{k T_F} \simeq 10^{-6} \quad \text{and} \sim \frac{1}{m^*}$$

The added impurity can influence the electronic terms of the alloy in two ways : by changing the total number of conduction electrons, thus shifting the Fermi level ; or by changing the "periodic" potential and thus the effective mass. The impurity will influence the χ_{ion}^- term through its dependence on $\bar{r}^2$. The contribution of the χ_{ion}^+ term to the alloy is $c\ \chi_{ion}^+$ where c is the concentration of transition element.

Owing to the small concentrations of impurity ($<$ .1 %) and to the relative order of magnitude of the terms (χ_{ion}^+ is 10^2 and 10^3 times larger than the other terms), we can assume that the χ_{ion}^-, χ_e^+ and χ_e^- terms of the solvent metal are negligibly changed by the added impurity. Hence :

$$\chi_{T\ \text{alloy}} = \chi_{T\ \text{solvent metal}} + {}^c\chi_{ion\ \text{transition element}}^+$$

CHAPTER III

METHODS of MEASURING SUSCEPTIBILITIES - APPARATUS

The magnetic force which acts upon a weakly magnetic substance can be found by considering the change in potential energy which results from the introduction of the substance in a magnetic field.

In Figure 3, the unbroken lines represent the lines of force of a magnetic field and the broken line is a direction along which the small body O of permeability μ_2 and volume V is free to move. If the body is situated in a region of permeability μ_1, then the change in potential energy is

$$- \frac{(\mu_2 - \mu_1)}{8\pi} H^2 v$$ and the force which tends to move the body along the direction z is given by

$$F_z = - \frac{d}{dz} \left[\left(\frac{-\mu_2 + \mu_1}{8\pi} \right) H^2 v \right]$$

where $\mu_2 = 1 + 4\pi k_2$

$\mu_1 = 1 + 4\pi k_1$

where k_2 and k_1 are the respective volume susceptibilities of the substance and the surrounding medium. The force can be written

$$F_z = \frac{k_2 - k_1}{2} \frac{dH^2}{dz} V \quad \ldots\ldots \text{(III - 1)}$$

(Ref. Bates).

There are two main methods for the determination of susceptibilities, the Gouy and the Curie methods. The magnetic force is measured by means of a sensitive balance and in the Curie method the susceptibility is calculated from equation (III - 1). This equation may be integrated when a long specimen is used and this is known as the Gouy method.

In the Gouy method, the substance to be investigated is provided in the form of a rod of uniform cross section A, and positioned in a magnetic field as shown in Figure 4.

From equation (III - 1), the magnetic force in the z direction on an elemental volume dv is given by

$$dF_z = \frac{k_2 - k_1}{2} \left[\frac{dH_x^2}{dz} + \frac{dH_y^2}{dz} + \frac{dH_z^2}{dz} \right] A\, dz$$

From considerations of symmetry, the terms $\frac{dH_x^2}{dz}$ and $\frac{dH_z^2}{dz}$ are very small and can be neglected. On integrating dF_z between $H_y = H_{max}$ and H_{min} we obtain for the total magnetic force F_z on the specimen

$$F_z = \frac{k_2 - k_1}{2} A \left(H_{max}^2 - H_{min}^2 \right) \quad \ldots\ldots (III - 2)$$

where $F_z = mg$ = the difference in weight measured on the balance with and without the magnetic field acting on the specimen.

In the Curie method, the substance to be investigated has a small volume v and is suspended in a magnetic field as shown in Figure 5. The force F_z is given by

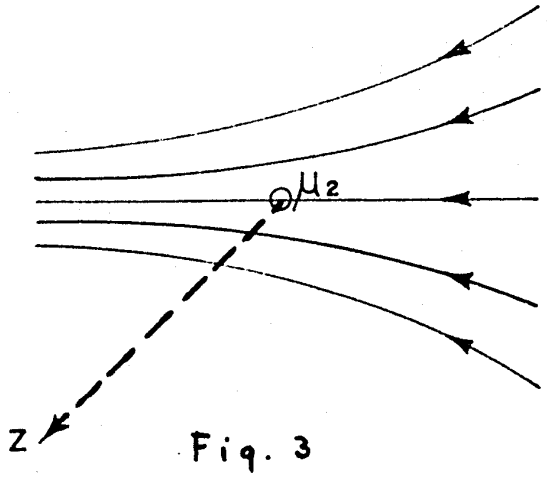


Fig. 3

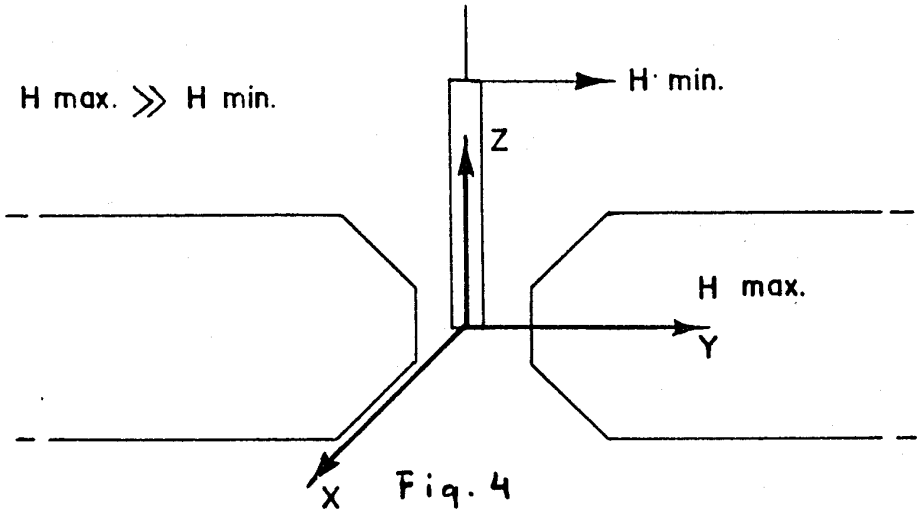


Fig. 4
Gouy Method

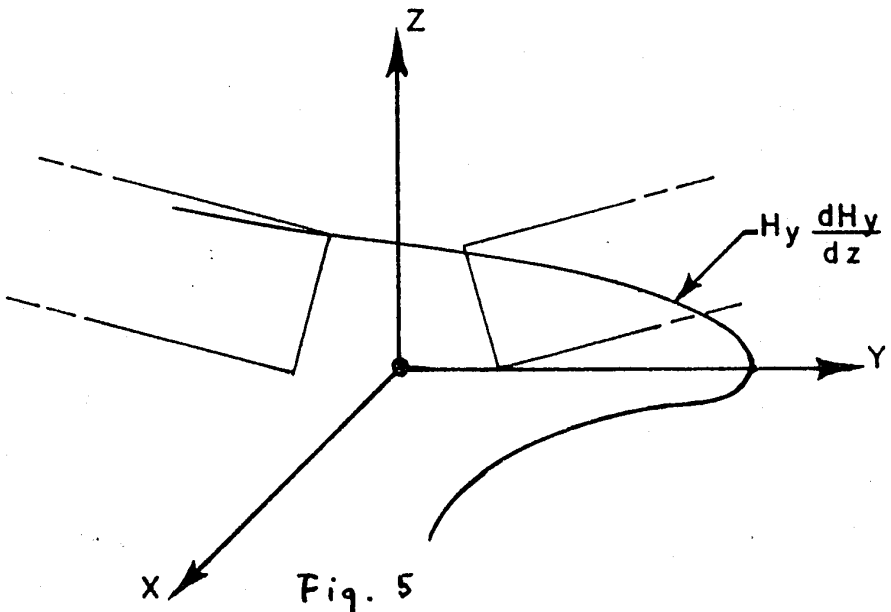


Fig. 5
Curie Method

$$F_z = (k_2 - k_1)\, v\, H_y \frac{dH_y}{dz} \quad \ldots\ldots\ldots (III - 3)$$

where we have again neglected the $\frac{dH_x^2}{dz}$ and $\frac{dH_z^2}{dz}$ terms. The method requires that the curve of $H_y \frac{dH_y}{dz}$ against x (see Figure 5) shall exhibit a reasonably flat maximum so that the value is fairly constant over a short distance ; otherwise, serious errors may arise through failure to maintain the body in a standard position. This defect may be avoided by using pole tips of special design so that the force is fairly constant over distances of as much as 1 to 2 cms.

Usually, Hy and $\frac{dH_y}{dz}$ are of the order of 10^4 gauss and 10^3 gauss per cm. respectively.

The Gouy method is generally more sensitive than the Curie method for the force on a substance can be made larger as long as there is a sufficient quantity of substance available. This was the case for the substances investigated presently and hence the Gouy method was chosen.

To calculate the susceptibility K_2 of a substance from equation (III - 2), it is necessary to know the value of k_1 which in this case is the susceptibility of air and is of the order of 5 % of the susceptibilities measured. A precise determination of k_1 is difficult since it varies with atmospheric conditions. A 3 degree change in temperature or a 1 % change in barometric pressure will cause a 1 % change in k_1 . It was therefore thought preferable to eliminate k_1 from equation (III - 2) by evacuating the surrounding atmosphere of the sample.

DESCRIPTION OF APPARATUS

Photographs of the apparatus are shown in Plates I and II.

The magnetic force was measured with a microbalance (George Westphal Company of Canada). It is an equal arm balance with a capacity of 30 gms per pan. Two rider scales ranging from .1 to 10 mgs. (II A) and from 0.01 to .3 mgs (II B) and an optical system enable readings to be estimated to the nearest microgram.

The microbalance and suspended sample were enclosed in a case (I A) that could be evacuated. The open case, shown in Plate II, can be made vacuum tight by means of the front plate and a large O ring seal. O ring seals were used throughout the construction to permit adjustment of the riders after the case had been evacuated (Fig. 7). The range of the rider scales, 10 mgs, was the limit of the maximum change in weight that could be measured when the case was evacuated.

An electronic current regulator (I B) (F.T. Hedgcock and F. Hunt, 1956) stabilized the magnetic field of the electromagnet (I_c). The magnet current is varied by adjusting the exciter current of a d.c. generator as supplied from an unregulated power supply. The bias voltage on control triodes fixes the current supplied to the exciter coils of the generator. A 1 ohm resistor in series with the magnet coils provides an error voltage which is applied to the cathode of the first half of a twin triode. If the output current changes, the voltage change across the 1 ohm resistor

PLATE I

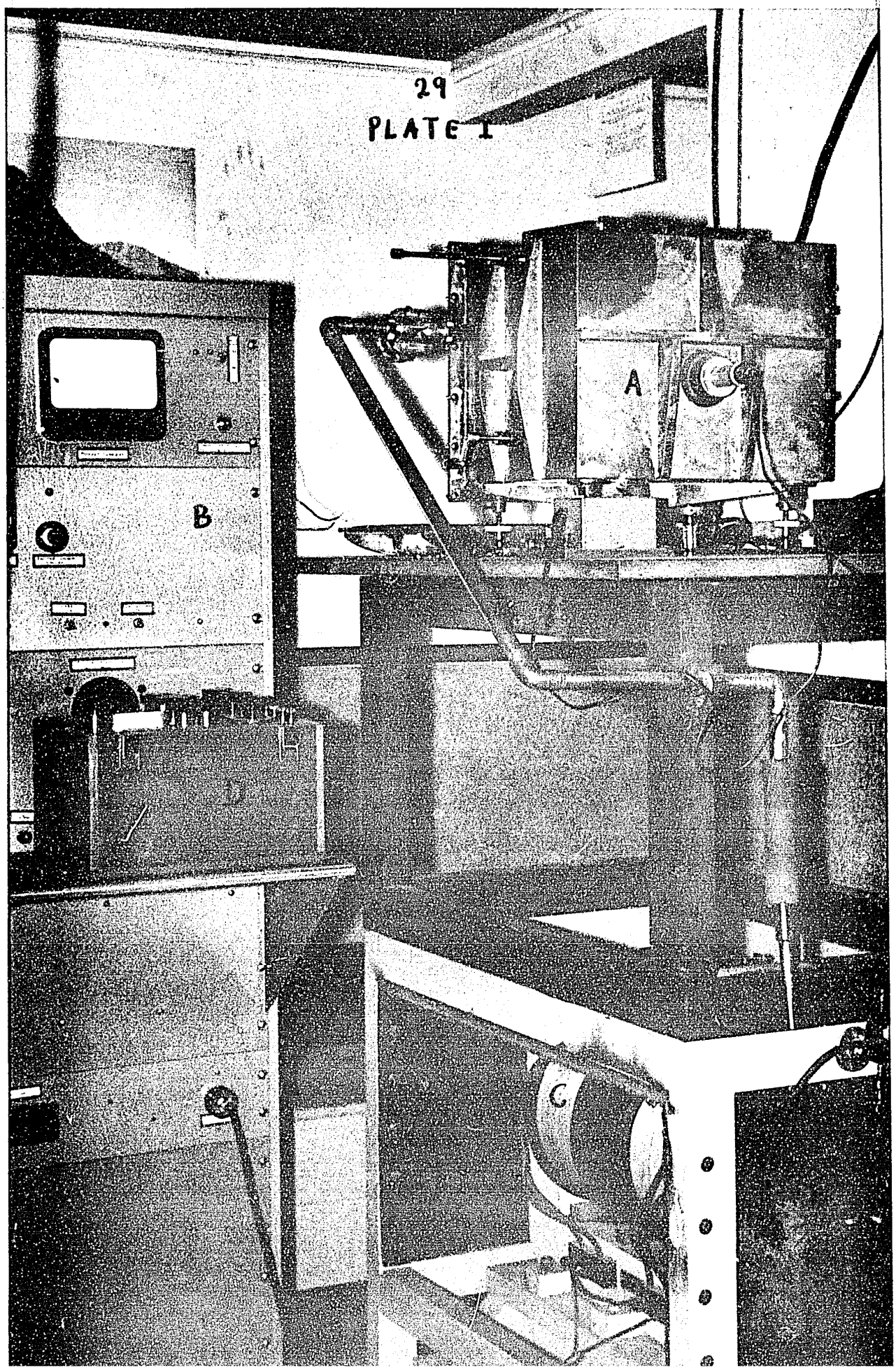
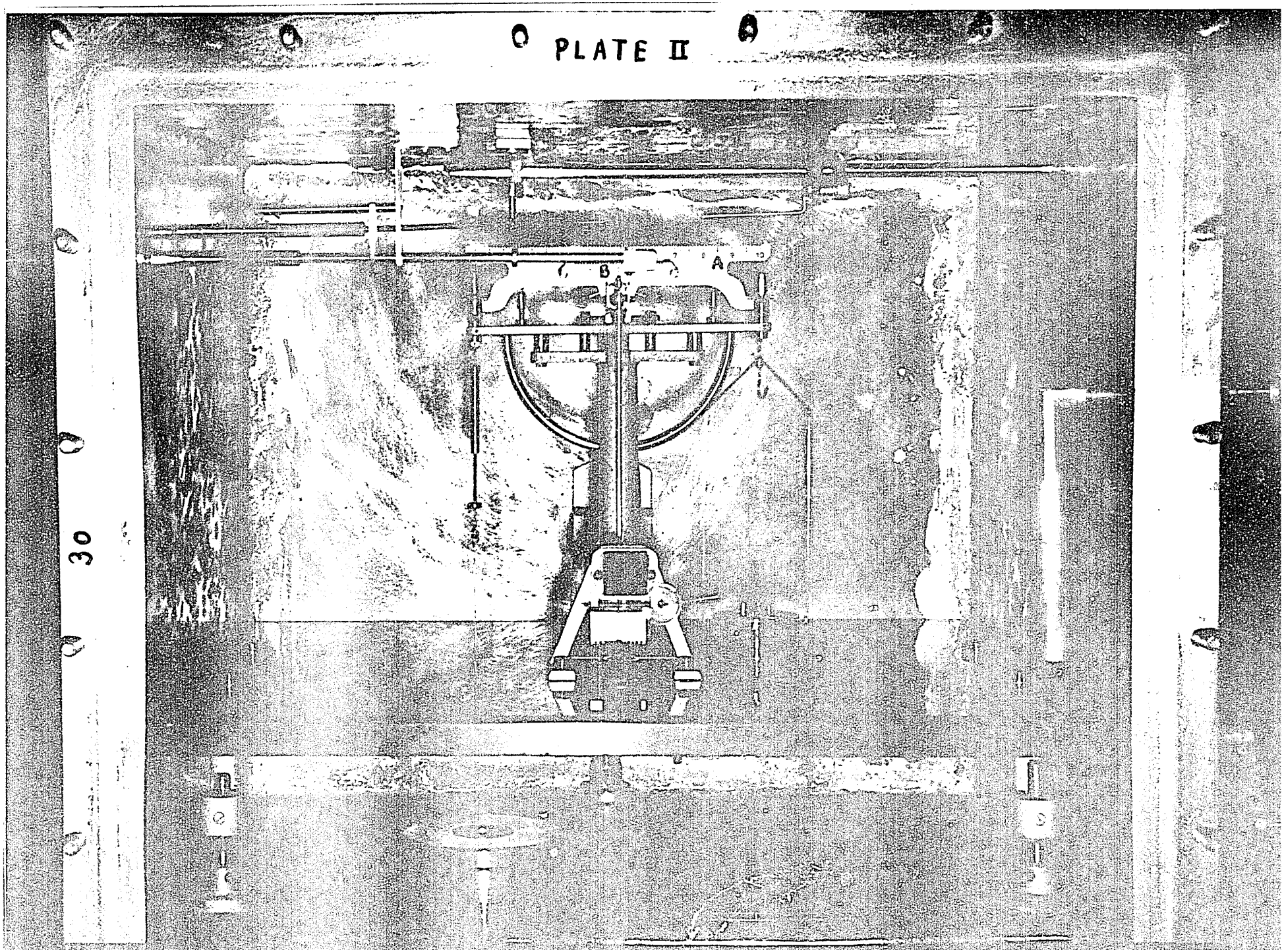


PLATE II



gives rise to an amplified voltage at the grid of the control triode. This voltage change tends to restore the magnet current to the original value as determined by the setting of the (twin triode) grid voltage. For better accuracy, the current was read by means of a potentiometer (I D).

The microbalance was sensitive to stray magnetic fields and in order to eliminate this effect it was necessary to shield the magnet with 1/4 inch steel plate (I E) and to raise the balance three feet above the magnet.

In order to absorb vibrations that might be transmitted to the balance, grooved rubber pads (commercially known as isomode pads) were placed between the balance system and its support.

CALIBRATION AND OPERATION OF THE MICROBALANCE

The sensitivity of the optical scale was measured by moving the riders and observing the corresponding deflection (Fig. 6). The sensitivity was found to decrease towards the ends of the optical scale, varying from 2.2. μgs/div at the center (hatched part of graph) to 2.8 μ gs/div at the 100 division mark. It is always possible to adjust the optical scale reading to $\pm$ 5 μgs since the sensitivity of the rider scale is 10 μ gs/div. For loads of 1, 5 and 10 gms the sensitivity was found to be the same and equal to 2.2 μ gs/div at the center of the scale. For loads greater than 10 gms, the movement of the balance became sticky.

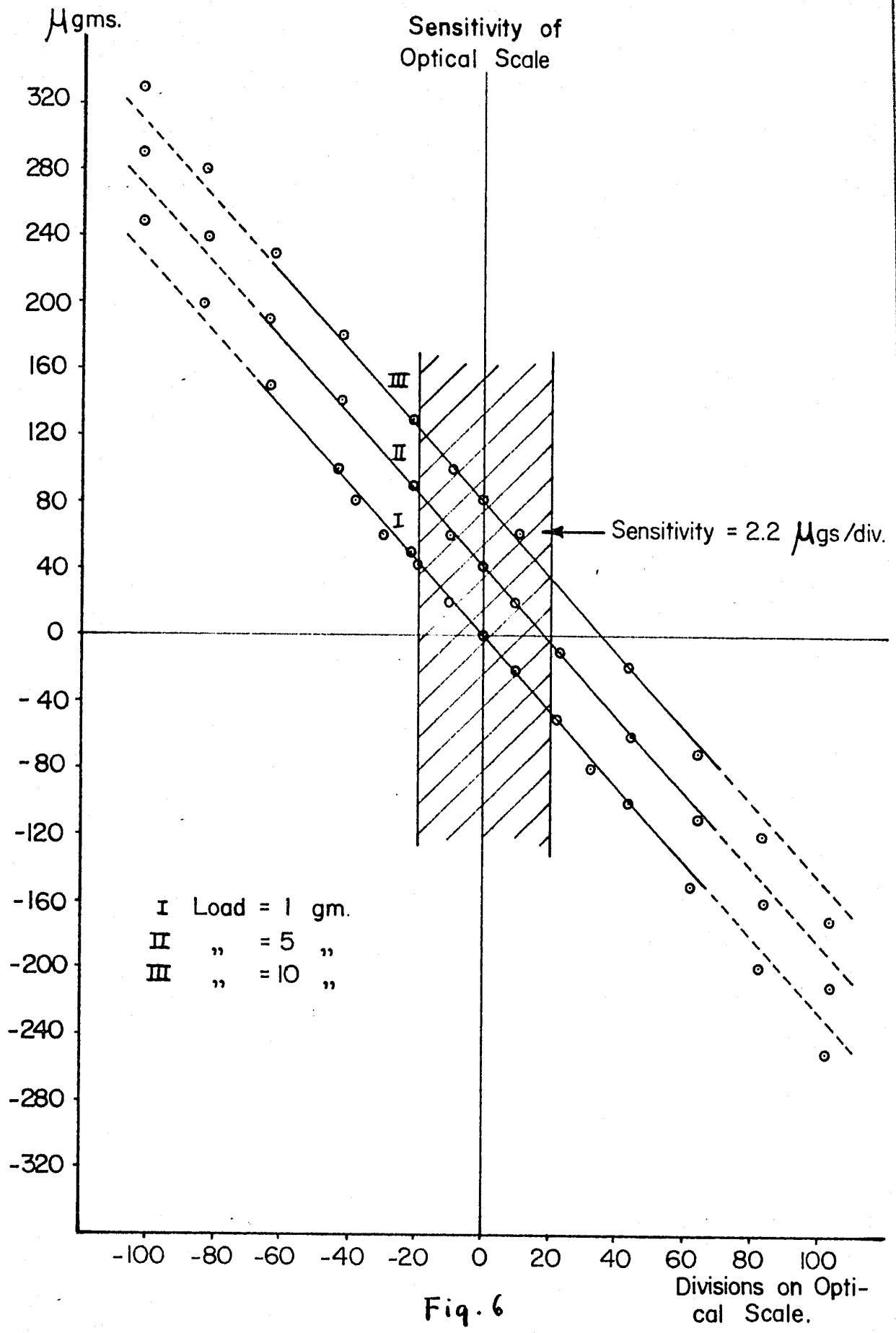
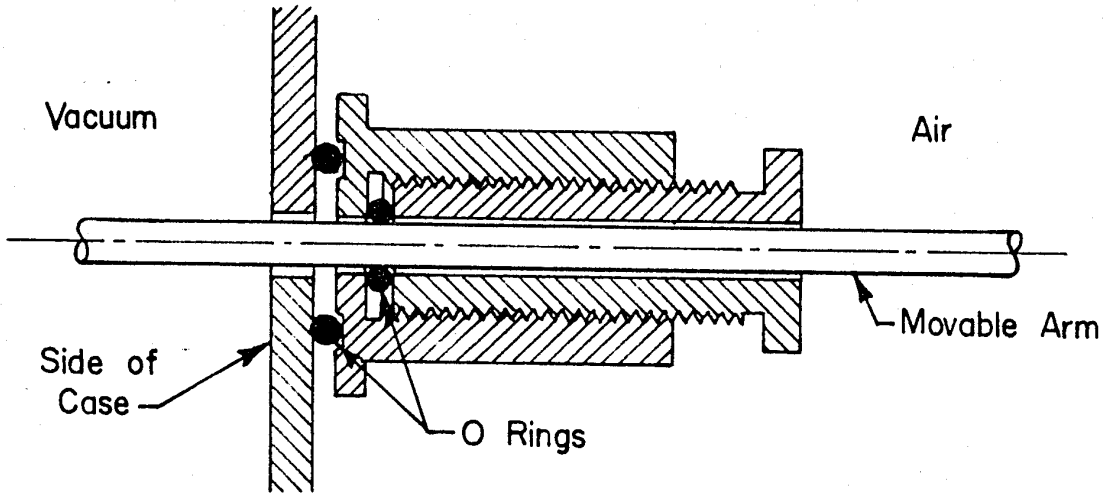

μgms.
Sensitivity of
Optical Scale
320
280
240
200
160
120
80
40
0
-40
-80
-120
-160
-200
-240
-280
-320
III
II
I
Sensitivity = 2.2 μgs/div.
I Load = 1 gm.
II " = 5 "
III " = 10 "
-100 -80 -60 -40 -20 0 20 40 60 80 100
Divisions on Optical Scale.

Fig. 6

However, in the present investigation the loads were always less than 10 gms.

The operation of the present microbalance differed from that of an ordinary one for two reasons : first, the balance case was evacuated and second, magnetic damping was present in varying degrees.

Evacuation of the case generally simplified the operation of the balance. It eliminated the disturbing effect of air currents, the necessity to correct for the buoyancy of air, and the possible changes in weight due to absorption of moisture on humid days. Evacuation also eliminated the source of error due to convection currents induced by differences in temperature of the balance and the sample : there convection currents can buoy up the sample and cause significant errors in the force readings. There was, however, one spurious effect due to evacuation. When the balance case is evacuated, there is a cooling of the balance due to the expanding air, followed by a gradual return to thermal equilibrium. These temperature changes cause the zero point to shift : $\sim$ + 500 μ gs during evacuation, followed by a return drift of $\sim$ - 10 μ gs per hour. A typical plot of the zero point drift after evacuation as a function of time is given in Fig. 8. It is seen to be linear and can be corrected for if necessary. The measurements of magnetic force were done within an hour and were of the order of 10 mgs. The error introduced by this zero point drift is therefore only $\sim$ 0.1 %.



O Ring Seals

Fig. 7

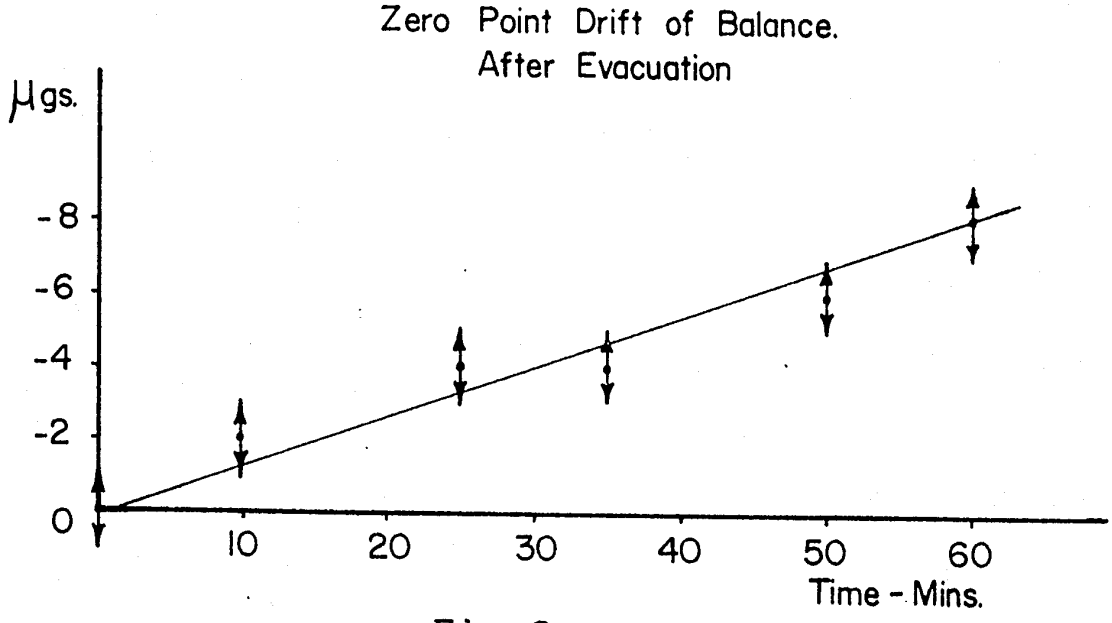


Fig. 8

Magnetic damping was present in varying degrees depending on the field strength and the conductivity of the sample. The effect of the magnetic damping on the amplitude of oscillations of the balance is shown in Fig. 9 of amplitude of swing as a function of time for a Mg sample in different magnetic fields (the balance case was evacuated). It can be seen that with no magnetic damping it takes a relatively long time for the balance to come to rest and hence the method of successive swings could be used to determine the rest point. For moderate magnetic fields, the magnetic damping is sufficient to bring the balance to rest quickly and as can be seen in Fig. 10, the rest point is independent of the amplitude of the initial swing. The balance is always adjusted to bring the samples to rest in the same position in the magnetic field, thus eliminating any errors that might arise from different positions in the magnetic field.

ACCURACY IN THE DETERMINATION OF THE SUSCEPTIBILITY

The accuracy with which k can be calculated from equation (III - 2) depends on the accuracy with which F, A and $(H^2_{max} - H^2_{min})$ can be determined.

An effective average cross sectional area can be obtained from the average measured diameter, ($\sim$ .5 cm), of the sample or by replacing A k in equation (III-2) by $\frac{m\chi}{\ell}$ where χ, m and ℓ are the mass susceptibility, mass and length of the sample. Depending

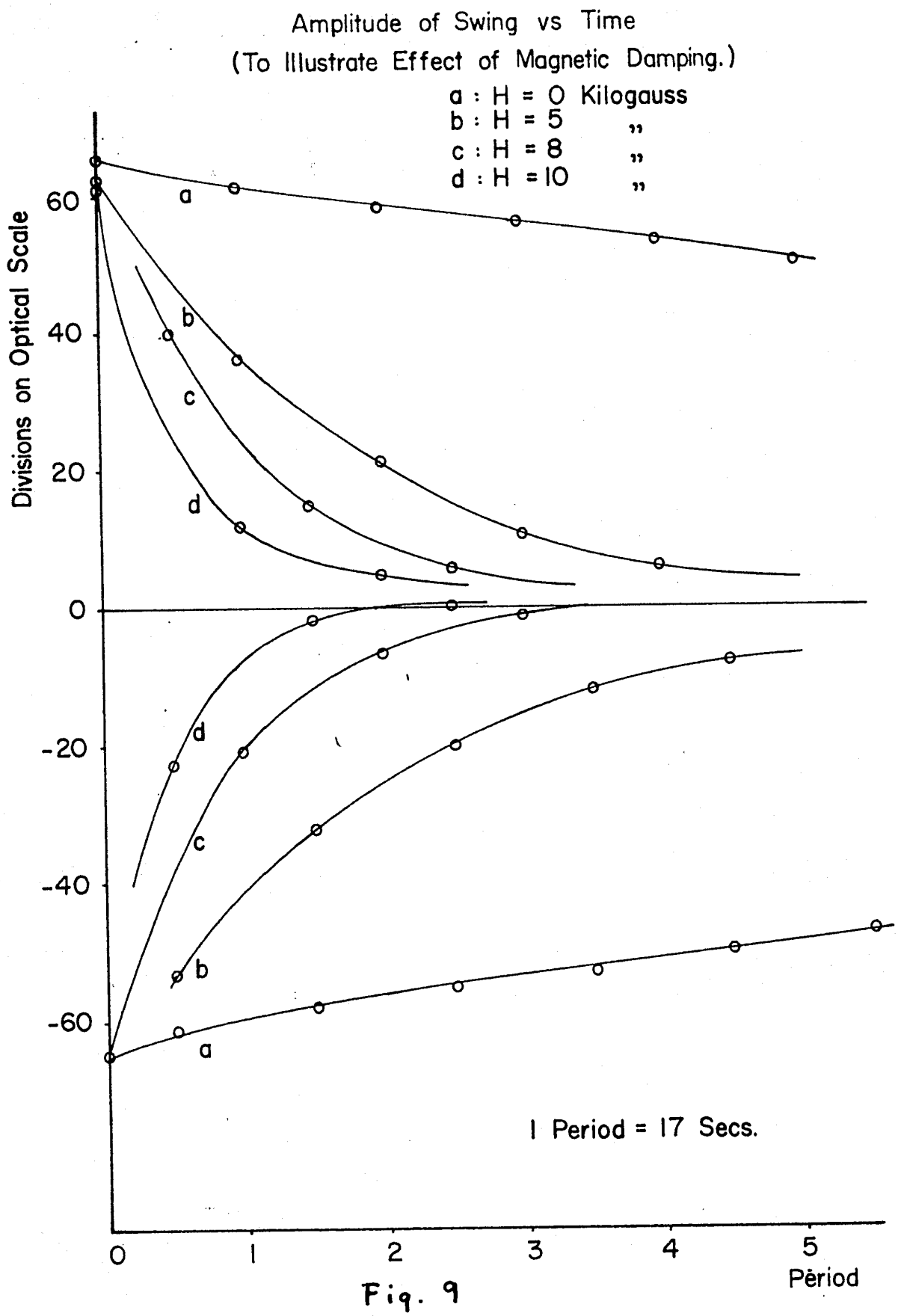

Amplitude of Swing vs Time
(To Illustrate Effect of Magnetic Damping.)
a : H = 0 Kilogauss
b : H = 5 "
c : H = 8 "
d : H = 10 "
Divisions on Optical Scale
60
40
20
0
-20
-40
-60
a
b
c
d
1 Period = 17 Secs.
0
1
2
3
4
5
Period

Fig. 9

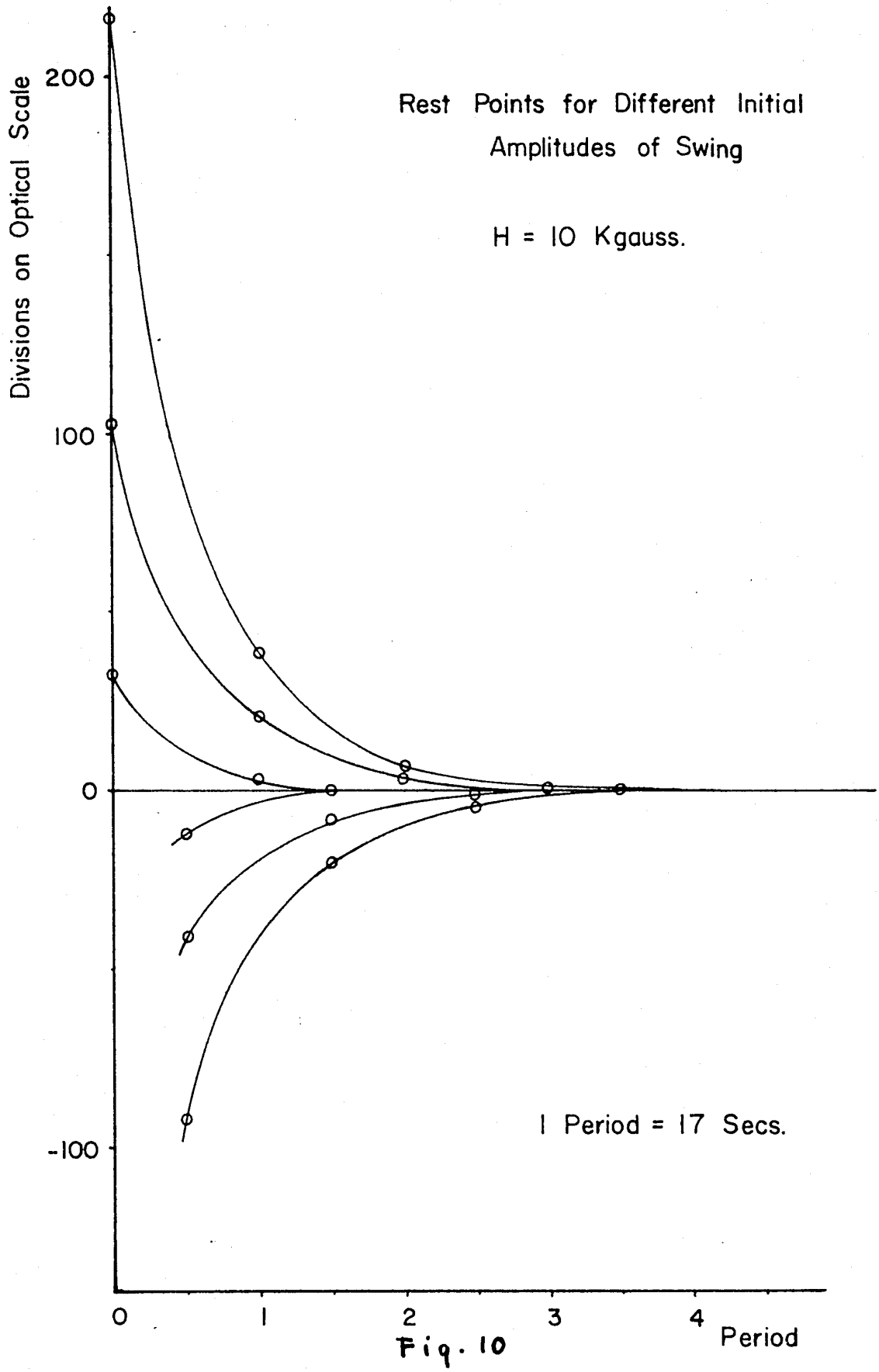

Rest Points for Different Initial Amplitudes of Swing
H = 10 Kgauss.
1 Period = 17 Secs.
Divisions on Optical Scale
200
100
0
-100
0
1
2
3
4
Period

Fig. 10

on the sample, the maximum deviation from the average diameter varied from .1 % to .5 %. For deviations of $\sim$ .1 % the second method is more accurate because $l \sim 6.6$ cms and $m \sim 1$ to 10 gms can be determined to at least .05 %.

Because of the inability to compensate for forces $>$10 mgms without re-evacuating the case, the pole separation was fixed such that F was $\sim$ 10 mgs. For the samples investigated, a gap of 2.9 cms was found to be suitable. The force was reproducible to within $\pm$ 2 μgs.

Since the samples were of the same length, it was desired to position them so that the fields H_{max} and H_{min} at their ends would be the same, thus necessitating only one determination of $(H^2_{max} - H^2_{min})$. As can be seen in Fig. 11 of force as a function of distance, the positioning is not overly critical for $(H^2_{max} - H^2_{min})$ is found to be constant over a region of $\sim$ 2 mms.

Fluxmeter readings of field profile and of H_{max} and H_{min} as a function of magnet current are given in Figures 12 and 13. A fluxmeter determination of $(H^2_{max} - H^2_{min})$ is only accurate to $\sim$ 1 % and since this represents the largest error in the calculation of χ, a more accurate determination was desired. A proton resonance calibration of field was impossible because the field is not uniform over a large enough volume. Since the microbalance was the most sensitive device available for detecting fields, it was decided to calibrate $(H^2_{max} - H^2_{min})$ as a function of the force measured on a sample of known susceptibility.

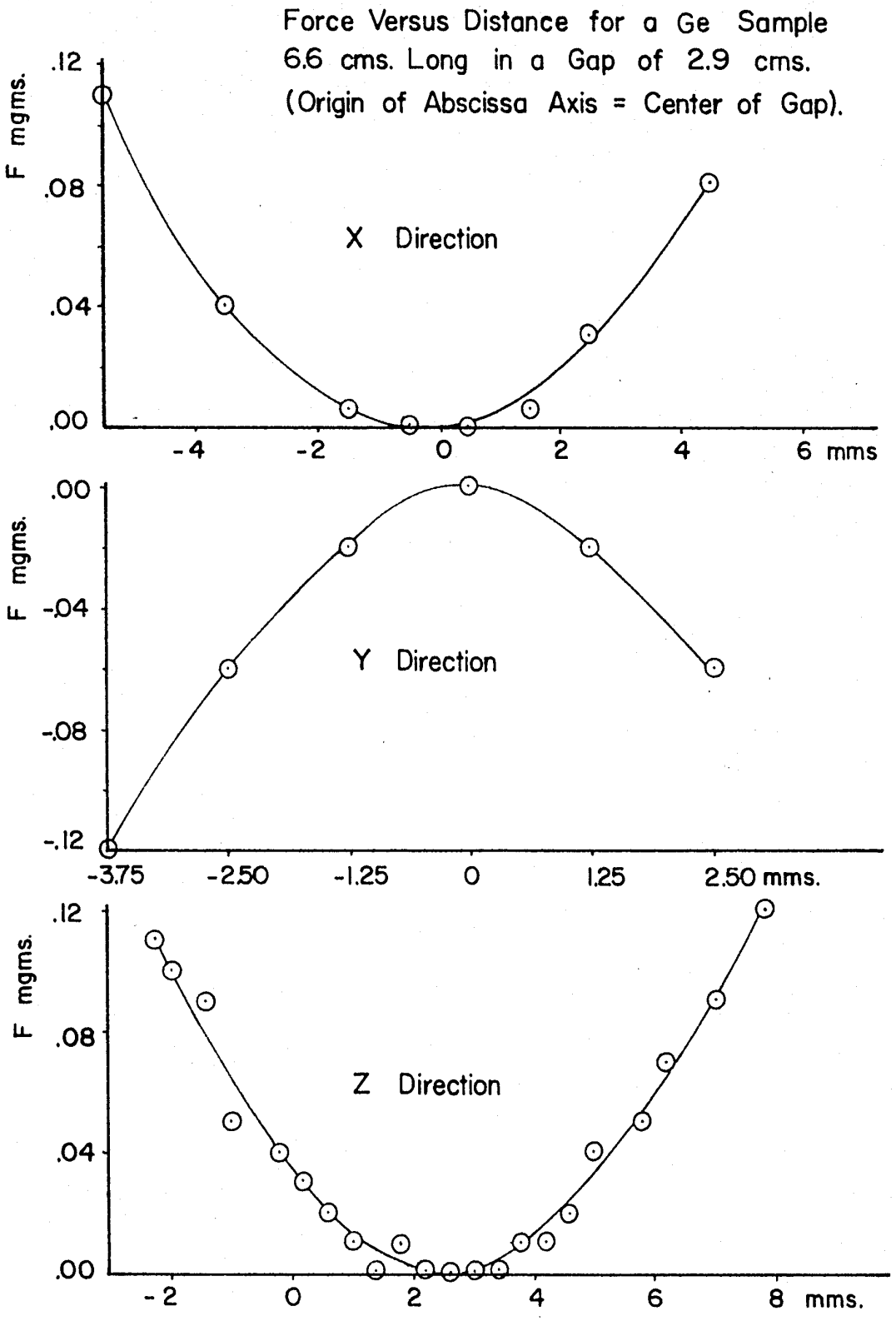

Force Versus Distance for a Ge Sample
6.6 cms. Long in a Gap of 2.9 cms.
(Origin of Abscissa Axis = Center of Gap).
F mgms.
.12
.08
.04
.00
X Direction
-4
-2
0
2
4
6 mms
F mgms.
.00
-.04
-.08
-.12
Y Direction
-3.75
-2.50
-1.25
0
1.25
2.50 mms.
F mgms.
.12
.08
.04
.00
Z Direction
-2
0
2
4
6
8 mms.

Fig. 11

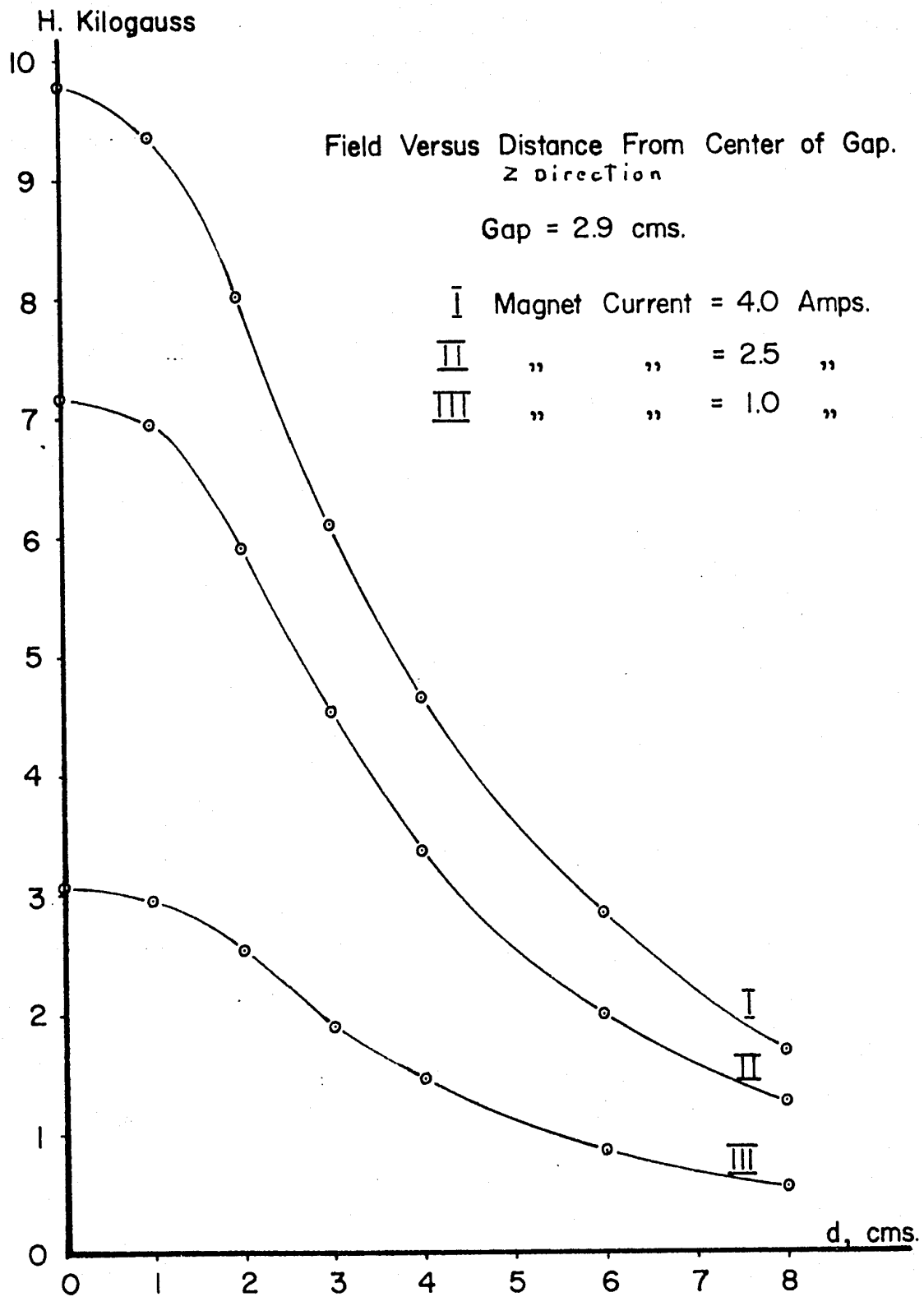

H. Kilogauss
10
9
8
7
6
5
4
3
2
1
0
Field Versus Distance From Center of Gap.
z direction
Gap = 2.9 cms.
I Magnet Current = 4.0 Amps.
II " " = 2.5 "
III " " = 1.0 "
I
II
III
d, cms.
0 1 2 3 4 5 6 7 8

Fig. 12

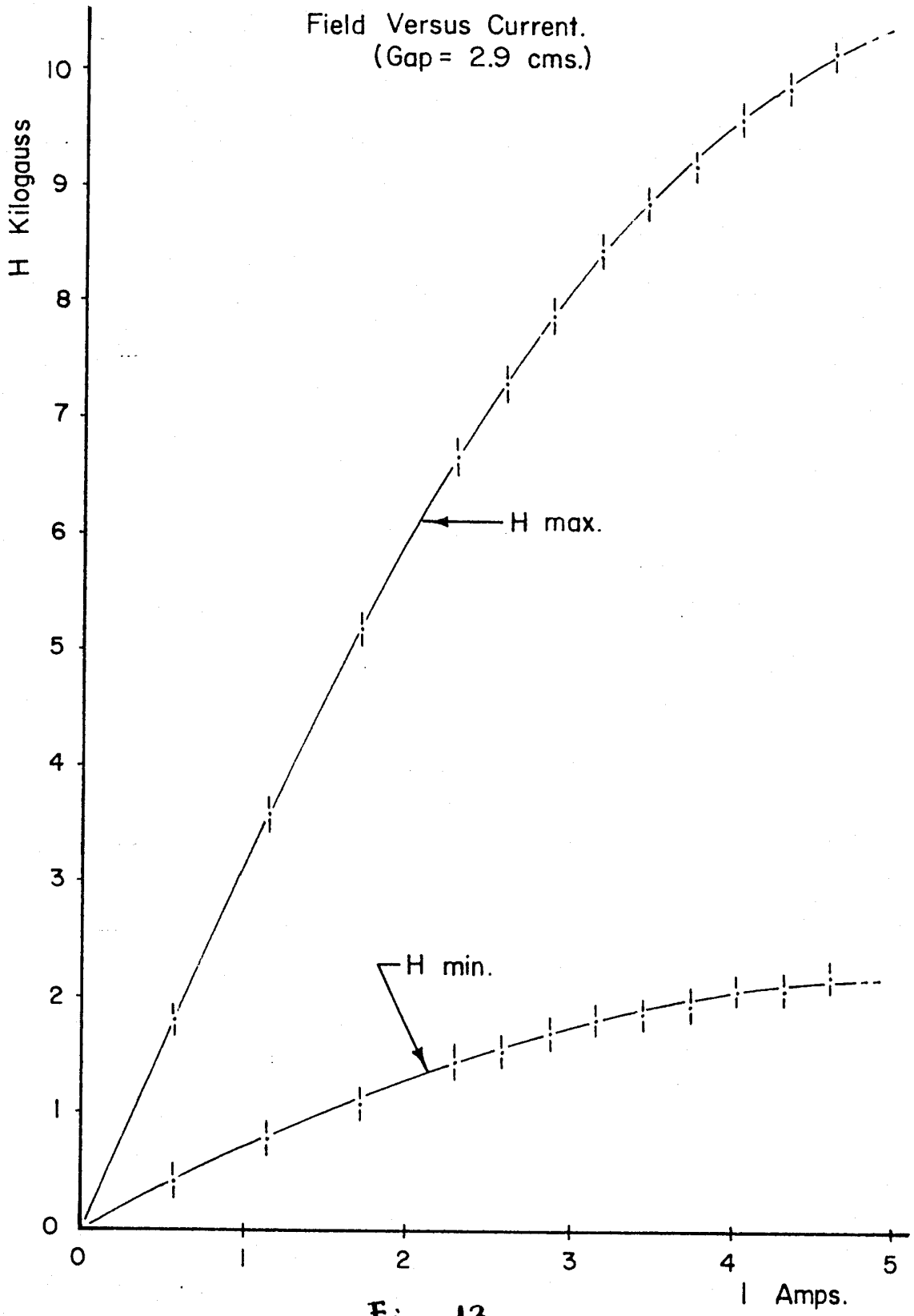

Field Versus Current.
(Gap = 2.9 cms.)
H Kilogauss
10
9
8
7
6
5
4
3
2
1
0
H max.
H min.
0
1
2
3
4
5
I Amps.

Fig. 13

In choosing a calibration substance several characteristics were desired : - a solid substance that could hang freely in the magnetic field and hence eliminate the necessity to correct for the susceptibility of a container ; - a substance that would give a magnetic force of $\sim$ the same order of magnitude as the samples investigated ; - a substance that can be obtained free of ferromagnetic impurities because the presence of such impurities can be disastrous as far as reliable results are concerned (see Chapter IV). Zone refined Ge was found to satisfy these requirements.

The susceptibility χ_x of a sample (x) relative to Ge is given by

$$\chi_x = \frac{F\,\alpha}{F\,Ge}\ \chi_{Ge}\ \left(\frac{m}{l}\right)_{Ge}\ \left(\frac{l}{m}\right)_x \quad \ldots \text{(III - 4)}$$

where the accuracy of $F \sim .1\ \%$

where the accuracy of $l,m \sim .05\ \%$

where the accuracy of $\chi_{Ge} \sim .5\ \%$.

Hence χ_x can be determined absolutely to within $\sim .7\ \%$ and relatively to Ge to within $\sim .1\ \%$.

CHAPTER IV

CORRECTION FOR FERROMAGNETIC IMPURITIES IN THE GOUY METHOD

Ferromagnetics are qualitatively distinguished magnetically from other substances by the fact that they may acquire a relatively high magnetization in weak fields. For example in a field of $\sim$ 1000 gauss, the intensity of magnetization per unit mass M of a diamagnetic may be $\sim 10^{-6}$, of a paramagnetic $\sim 10^{-3}$ and of a ferromagnetic $\sim 10^{2}$. Let us consider the effect of a ferromagnetic impurity in a non ferrous sample. The magnetic force on a substance of mass Δm is $\Delta F_x = \Delta m \, M \frac{\partial H}{\partial x}$. Thus, even if a ferromagnetic is present in a sample in very small amounts, it may contribute significantly to the total force measured since its intensity of magnetization is so high. The total force F_T measured on a sample will be equal to the sum of the forces on the non ferrous part and on the ferromagnetic part of the sample : $F_T = F_{nf} + F_f$. If it is possible to evaluate F_f, then $F_T - F_f$ will give the force on the non ferrous part of the sample which we require to determine the true susceptibility of the non ferrous material.

There are several ways in which ferromagnetic impurities may be present in a sample : 1) they may be in solution in the solvent ; 2) they may have formed an intermetallic compound with the solvent ; 3) they may be precipitated in particles. The behaviour

of the ferrous impurity will be different depending on the physical state in which it exists in the solvent. Let us consider each of the above cases.

1. Ferrous Impurities in Solution

An atomic system that behaves ferromagnetically has energy shell with uncompensated electron spins. Heisenberg (1928) showed on his theory of "exchange forces" of electrons in atoms that ferromagnetism would or would not exist depending on the ratio of the distance D between neighbouring atoms to the radius r of the energy shell in which the electron spins are uncompensated. Slater (1930) concluded that for ferromagnetism to exist, the ratio D/r must be greater than 3.0, but not much greater. Now, if atoms that exhibit ferromagnetism in their pure state are in solution in a solvent in small concentrations, the ratio D/r will be much greater than 3.0. Thus we do not expect ferrous impurities in solution to behave ferromagnetically, but to exhibit a Langevin paramagnetism as outlined in Chapter II.

2. Ferrous Impurities Forming an Intermetallic Compound

The electron spins of the ferrous atoms are generally compensated in the formation of the chemical bond and we do not expect compounds to exhibit ferromagnetism.

3. Ferrous Impurities Precipitated in Particles

Bean (1955) has discussed the magnetic behaviour of small ferromagnetic particles. Their characteristic properties depend upon their size. If the particles are small enough, the direction

of their magnetization fluctuates thermally as first pointed out by Néel (1949). They have no remanence and no coercive force, and possess the temperature dependent magnetization curve of a paramagnetic substance with a very large moment. Bean calls this "super paramagnetism". There is no way of detecting this behaviour from the ordinary behaviour of the solvent, and hence no way of estimating the force due to the ferromagnetic particles. However, if the particles are large enough to behave ferromagnetically, we will show how it is possible to evaluate their contribution to the magnetic force.

We have stated that the force on a ferromagnetic is proportional to the intensity of magnetization $M(H)$ in a field H times the field gradient. $M(H)$ is field dependent and is known to saturate with increasing field. It will obey an equation similar to

$$M_H = M_S (1 - e^{-\alpha H}) \quad \ldots\ldots\ldots \quad (IV - 1)$$

where M_S is the saturation intensity of magnetization,

α is a constant for a given ferromagnetic,

H is the field acting on the ferromagnetic.

The way in which a ferromagnetic saturates will depend on the size of its domains and the field H acting on it will depend on its shape. Now the ferromagnetic impurity may be distributed throughout the sample with different shapes and domain sizes and may not all be satisfactorily described by one saturation equation. A discussion of the assumptions used in applying such an equation will now be given.

The field acting on the group of ferromagnetic atoms forming a "specimen" will depend upon its shape. When an external magnetic field H_{ext} is applied, free poles at the ends of the specimen will produce a demagnetizing effect which is assumed equal to $D\,M$ where D is a constant known as the demagnetization factor. The effective field acting on the specimen is $H_{ext} - D\,M_H$. The value of D can vary from $\sim 10^{-4}$ for a long narrow specimen to ~ 1 for a spherical specimen. The saturation of a ferromagnetic depends on the domain size, being much slower for small domains. If one saturation equation is used to describe the ferromagnetic, then M_S is assumed to be the average saturation intensity of magnetization of the ferromagnetic.

Keeping these considerations in mind, we will now outline the method used in the present investigation to correct for the force due to ferromagnetic impurities.

As described in Chapter III, the Gouy method was used to determine the magnetic force on a sample : the sample had a uniform cross section A and was placed in a field such that the fields at the ends of the sample were H_{max} and H_{min} , $(H_{max} \gg H_{min})$.

The force on the ferromagnetic of mass dm is

$$d F_x = dm\, M(H) \frac{\partial H}{\partial x}$$

The eliminate the dependence of $d F$ on $d x$, let us replace dm by $A \rho\, d x$.

Where A = area of the specimen which is constant,

ρ = gram of impurity per c.c. of specimen,

$d x$ = element of length

$$d F_x = A\rho \, d x \, M(H) \frac{\partial H}{\partial x}$$

Let us assume the saturation curve given by (IV - 1). This saturation equation was suggested by Dr. B. Coles and is used by Dr. W. Pugh in a method to correct for ferromagnetic impurities. The force d F is then

$$d F_x = A\rho \, d x \, M_S (1 - e^{-\alpha H}) \frac{\partial H}{\partial x}$$

We must integrate this to obtain the total ferromagnetic force on the sample. If we assume that the fields acting on the ferromagnetic are very nearly equal to the external fields applied, or in other words that $D M \ll H_{ext}$, then

$$F = A\rho \int_{H_{min}}^{H_{max}} M_S (1 - e^{-\alpha H}) \, d H$$

$$F = A\rho M_S \left[(H_{max} - H_{min}) + \frac{1}{\alpha} (e^{-\alpha H_{max}} - e^{-\alpha H_{min}}) \right] \quad \ldots (IV - 2)$$

where H_{max} et H_{min} are the external fields at the ends of the sample , M_S is the average saturation intensity of magnetization of the ferromagnetic.

As stated before, the total force F_T measured on a sample is equal to the sum of the non ferrous force $F_{n.f.}$ plus the ferromagnetic force F_f :

$$F_T = F_{n.f.} + F_f$$

Knowing F_f , we can find $F_{n.f.}$.

F_f can be estimated from equation (IV - 2) for any given field if we know the constants $A\rho M_S$ and α . We shall see how it is possible to determine these from the experimental data.

The susceptibility of the non ferrous part of the sample investigated is a constant and relative to Ge is given by

$$\chi = C \times \frac{F_{n,f.}}{F\ Ge} \quad \ldots\ldots \quad (IV - 3)$$

where C is a constant (see equation (III - 4)

or

$$\chi = C \left[\frac{F_T - F_f}{F\ Ge} \right]$$

To obtain the order of magnitude of F_f , we can assume that at high fields $d\ F_f \ll d\ F_{n\ f}$

$$\frac{d\ F_T}{d\ F\ Ge} = \frac{d\ F_{n\ f} + d\ F_f}{d\ F\ Ge} \cong \frac{d\ F_{nf}}{d\ F\ Ge}$$

or

$$\frac{d\ F_T}{d\ F\ Ge} \text{ high fields} \cong \frac{F_T - F_f}{F\ ge}$$

From this expression it is possible to estimage F_f for any given field. Knowing F_f it is then possible to substitute a value of α into equation (IV - 2) and to solve for $A \rho M_S$ at different fields. The best value of α will be the one that makes $A \rho M_S$ most constant at all fields. Substituting these rough values of $A \rho M_S$ and α into equation (IV - 2) a value for $d\ F_f$ at high fields can be calculated. Hence from the expression

$$\frac{F_T - F_f}{F\ Ge} \cong \left[\frac{d\ F_T - d\ F_f}{d\ F\ Ge} \right] \text{ high fields}$$

a better estimate of F_f can be made and hence of the constants $A\rho M_S$ and α. This procedure is repeated until $A\rho M_S$ obtained from solving equation (IV - 2) is constant within the required limit of accuracy at all fields. The value of F_f calculated from (IV - 2) is then assumed to be the true force on the ferromagnetic.

The accuracy in the determination of F_f depends on the accuracy with which $A\rho M_S$ and α can be found from the experimental data. The required degree of accuracy for α depends on the relative importance of the two terms, $(H_{max} - H_{min})$ and $\frac{1}{\alpha}(e^{-\alpha H_{max}} - e^{-\alpha H_{min}})$ in equation (IV -2). An idea of the order of magnitude of α can be obtained by assuming that the ferromagnetic is saturated to within 1 % at a field H_S. Then

$$\frac{M_H}{M_S} = (1 - e^{-\alpha H_S}) = .990$$

if H_S = 1000 gauss, $\alpha \cong 5 \times 10^{-3}$ gauss^{-1}

H_S = 10000 gauss, $\alpha \cong 5 \times 10^{-4}$ gauss^{-1}

TABLE I

I	H_{max}	H_{min}	$H_{max} - H_{min}$	$\frac{1}{\alpha}(e^{-\alpha H_{max}} - e^{-\alpha H_{min}})$		
				$\alpha = 5\times10^{-3}$	$\alpha = 10^{-3}$	$\alpha = 5\times10^{-4}$
Amps	gauss	gauss	gauss		gauss^{-1}	
4.60_o	10 150	2 170	7 980	0	- 115	- 670
3.475	8 840	1 895	6 945	0	- 150	- 750
2.320	6 650	1 420	5 230	0	- 240	- 920
1.180	3 540	770	2 770	-4	- 430	- 1020
0.61_o	1 790	400	1 390	-27	- 500	- 820

The table shows that a 200 % change in α causes only 10 % change in F_f at high fields. The value chosen for α is therefore not overly critical. If the constant $A\rho M_S$ can be determined by the above procedure to within 1 % for example, then it is assumed that F_f is also determined with an accuracy of 1 %.

Example : see Chapter V .

From $A\rho M_S$ it is possible to estimate the concentration of ferromagnetic in the sample. Let the experimental value of $A\rho M_S$ be x.

Then $$x = \frac{A\,m}{V} M_S = \frac{m\,M_S}{l}$$

or $$m = \frac{l\,x}{M_S} \quad \ldots\ldots\ldots \quad (IV - 4)$$

where m = mass of impurity

V = volume of sample

l = length of sample

The concentration c of ferromagnetic is equal to $\frac{m}{M}$

where M is the mass of the sample.

Therefore, from (IV - 4)

$$c = \frac{m}{M} = \frac{l\,x}{M\,M_S} \quad \ldots\ldots\ldots \quad (IV - 5)$$

l, m and x are known, and it is possible to assume a value of M_S, that corresponding to free iron, for example.

CHAPTER V

EXPERIMENTAL RESULTS

The susceptibility is calculated from Equation (III - 4). F_x and F_{Ge} are determined for various fields and $(\frac{Fl}{g\,m})_x$ is plotted against $(\frac{F\,l}{g\,m})_{Ge}$. The slope of this graph is equal to $\frac{\chi_x}{\chi_{Ge}}$ and will be constant at all fields for a dia- or paramagnetic substance. A non linear graph relationship indicates a field dependent susceptibility and hence the presence of ferromagnetic impurities. If such is the case, the susceptibility of the non ferromagnetic part of the substance can be calculated from

$$\chi_{x(n.f.)} = C \times \frac{\Delta F_{nf}}{\Delta F_{Ge}} = C \times \frac{\Delta F_x - \Delta F_f}{\Delta F_{Ge}}$$ (see equation IV-3).

Since the ferromagnetic tends to saturate at high fields, the term $\frac{\Delta F_f}{\Delta F_x}$ becomes smaller, requiring less accuracy in the determination of ΔF_f. Hence the changes in force ΔF used to calculate $\chi_{x(n.f.)}$ are those corresponding to high field values.

Mg Mn Alloys

These alloys were prepared by the Dow Chemical Company (Michigan) from chill cast ingots formed in graphite moulds. The concentration of Mn varied from 0 to .05 % (Table 2).

TABLE II

SPECTROSCOPIC ANALYSES

	Alloy 728	Alloy 87812	Alloy 87813	Alloy 87814	Alloy 87815
Wt% Al	< .001	< .002	< .003	< .003	< .005
" Ca	< .01	< .01	< .01	< .01	< .01
" Cu	< .001	< .001	< .001	< .001	< .001
" Fe	< .001	< .001	< .001	< .001	< .001
" Mn	< .001	.005	.019	.038	.046
" Ni	< .0005	< .0005	< .0005	< .0005	< .0005
" Pb	< .001	< .001	< .001	< .001	< .001
" Si	< .001	< .007	< .009	< .010	< .014
" Sn	< .01	< .01	< .01	< .01	< .01
" Zn	< .001	< .004	< .006	< .003	< .002

The length and mass of the samples are given on Table III and the equivalent force $\frac{F}{g}$ in milligrams for different magnet currents is given in Table IV.

The plots of $(\frac{F}{g}\frac{1}{m})$ (Figures 14, 15) show deviation from linearity at low fields indicating necessity for ferromagnetic correction.

TABLE III

Sample	Ge	Mg Mn				
		728	87812	87813	87814	87815
length cms	6.630	6.560	6.580	6.533	6.581	6.512
mass gms.	10.6803	2.0147	1.9851	1.6170	2.1656	1.9209

T A B L E IV

I Amps	F/g mgms	Temperature °C				
	Ge	Mg Mn				
		728	87812	87813	87814	87815
		27°	28°	26°	27°	27°
0.00_0	0.000	0.000	0.000	0.000	0.000	0.000
0.61_0	-0.295	0.274	0.303	o.268	0.404	0.372
1.18_0	-1.093	1.026	1.094	0.938	1.390	1.290
1.75_0	-2.311	2.158	2.275	1.942	2.830	2.666
2.32_0	-3.793	3.536	3.697	3.152	4.556	4.314
2.61_0	-4.582	4.264	4.446	3.791	5.460	5.184
2.89_5	-5.347	4.967	5.177	4.410	6.340	6.030
3.18_0	-6.050	5.618	5.846	4.980	7.144	6.804
3.47_5	-6.698	6.216	6.466	5.508	7.890	7.512
3.76_0	-7.292	6.771	7.036	5.988	8.578	8.166
4.03_5	-7.856	7.286	7.569	6.438	9.218	8.780
4.32_5	-8.367	7.764	8.054	6.854	9.804	9.340
4.60_0	-8.837	8.196	8.498	7.236	10.344	9.852

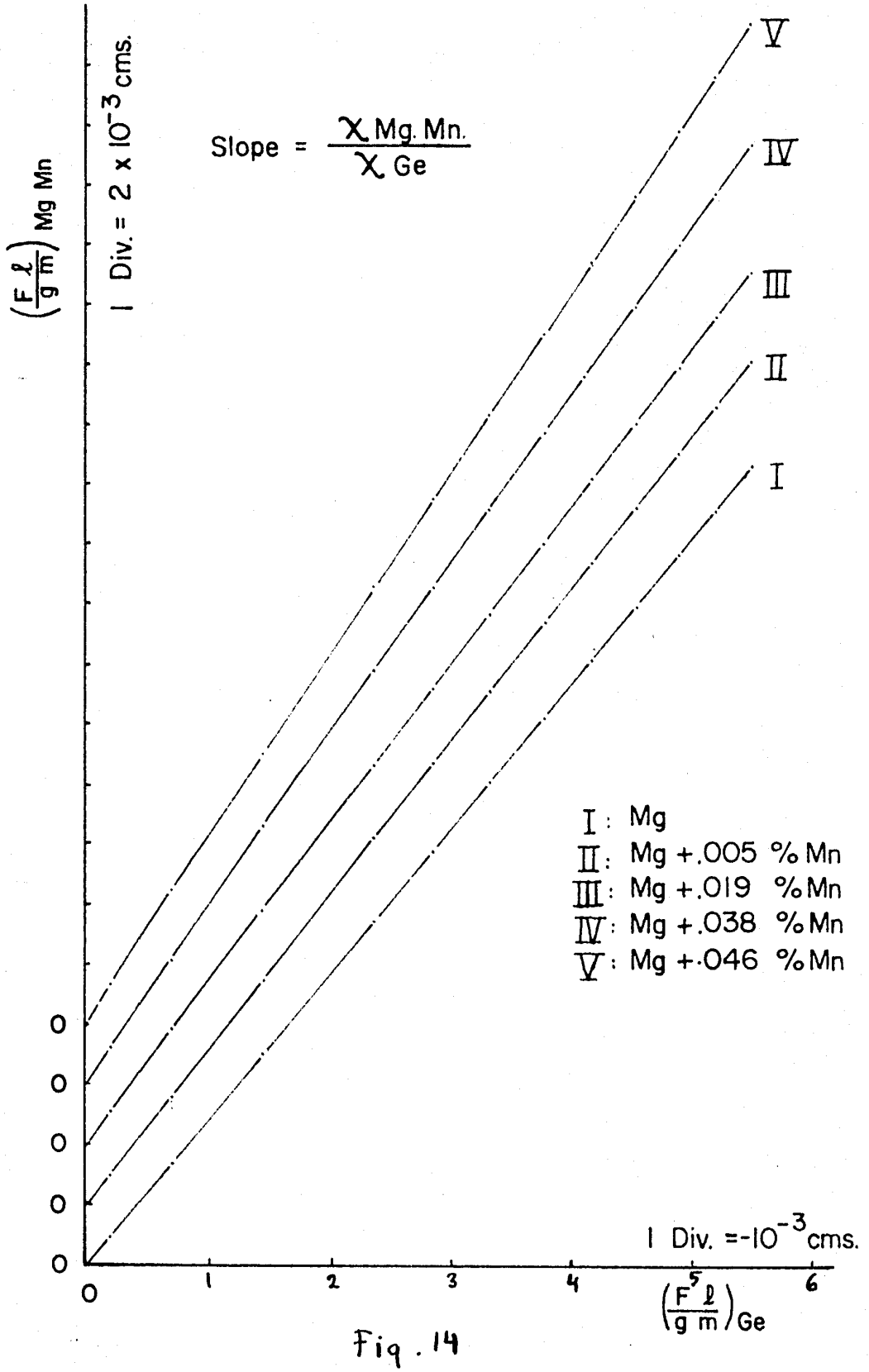

$\left(\frac{F\,l}{g\,m}\right)$ Mg Mn
1 Div. = 2×10^{-3} cms.
Slope = $\frac{\chi\,Mg.\,Mn.}{\chi\,Ge}$
V
IV
III
II
I
I : Mg
II : Mg +.005 % Mn
III : Mg +.019 % Mn
IV : Mg +.038 % Mn
V : Mg +.046 % Mn
0
0
0
0
0
1
2
3
4
6
1 Div. = 10^{-3} cms.
$\left(\frac{F^5\,l}{g\,m}\right)_{Ge}$

Fig. 14

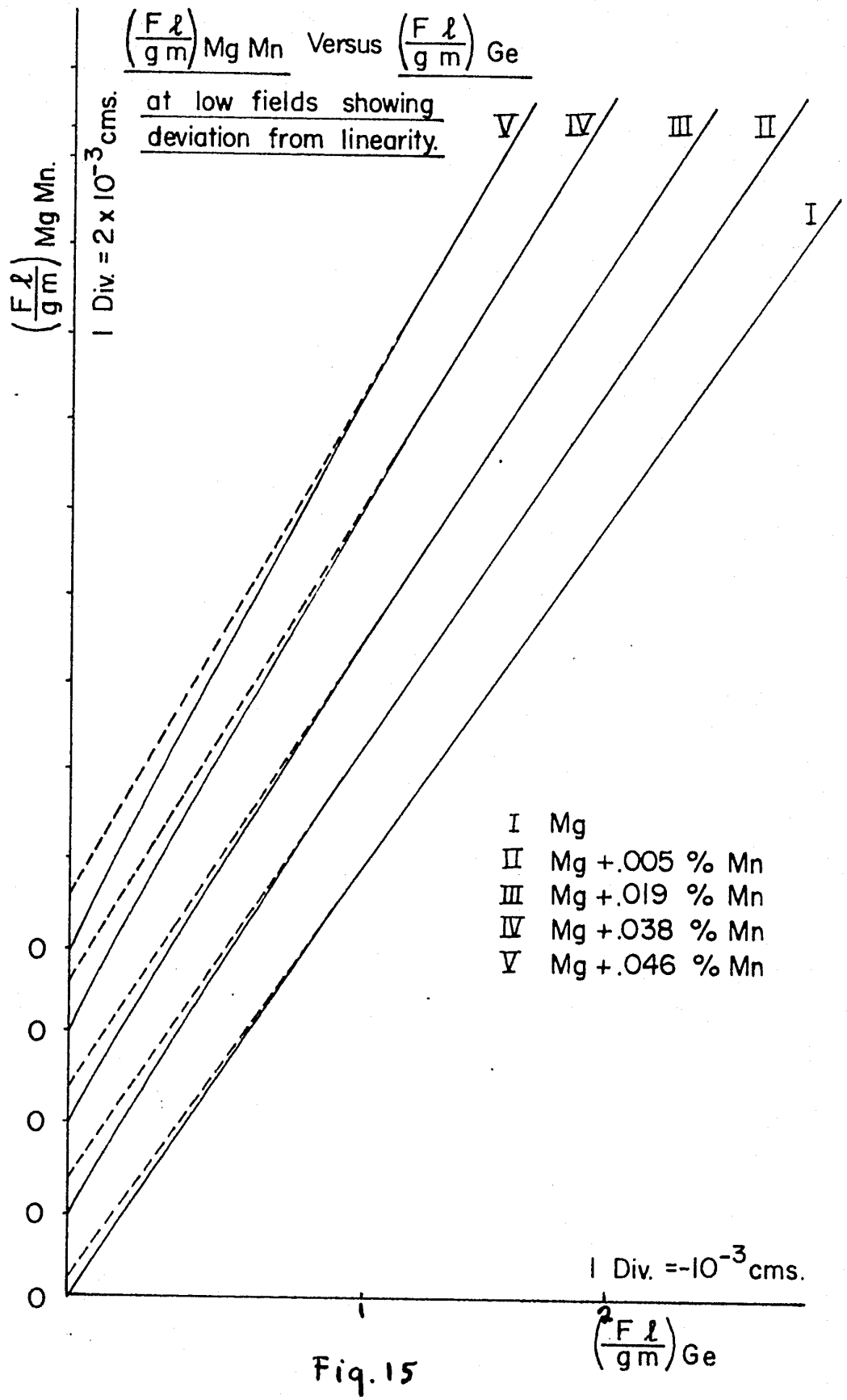

$\left(\frac{F\,l}{g\,m}\right)$ Mg Mn Versus $\left(\frac{F\,l}{g\,m}\right)$ Ge
at low fields showing deviation from linearity.
$\left(\frac{F\,l}{g\,m}\right)$ Mg Mn.
1 Div. = 2×10^{-3} cms.
V
IV
III
II
I
I Mg
II Mg +.005 % Mn
III Mg +.019 % Mn
IV Mg +.038 % Mn
V Mg +.046 % Mn
0
0
0
0
0
1 Div. = 10^{-3} cms.
1
2
$\left(\frac{F\,l}{g\,m}\right)$ Ge

Fig. 15

Sample calculation of corrected for ferromagnetic impurities for the Mg Mn alloy 87812.

To a first approximation the susceptibility is given by (ref. Chapter IV)

$$\chi_{x(n.f.)} = C \times \left(\frac{\Delta F_x}{\Delta F_{Ge}}\right)_{\text{high fields}} = C \times .947$$

From the expression

$$\frac{F_x - F_f}{F_{Ge}} = \left(\frac{\Delta F_x}{\Delta F_{Ge}}\right)_{\text{high fields}} = .947$$

F_f was calculated at various fields (Table V Column 2). And assuming $\alpha = 5 \times 10^{-3}$, equation (IV - 2) was solved for $A\rho M_s$ (column 3).

TABLE V

I Amps	$\chi = C \times .947$ $\alpha = 5 \times 10^{-3}$ gauss^{-1}		$\chi = C \times .940$ $\alpha = 5 \times 10^{-3}$ gauss^{-1}	
	F_f mgms	$A\rho M_s$ $\frac{\text{mgms}}{\text{gauss}} \times 10^5$	F_f mgms	$A\rho M_s$ $\frac{\text{mgms}}{\text{gauss}} \times 10^5$
1.18_0	.059	2.1	.067	2.4
1.75_0	.087	2.1	.103	2.5
2.32_0	.105	2.0	.132	2.5
2.61_0	.107	1.9	.139	2.4
2.89_5	.113	1.8	.151	2.4
3.18_0	.117	1.8	.159	2.4
3.47_5	.123	1.8	.170	2.4
		$A\rho M_s = 2.1 \times 10^{-5}$		$A\rho M_s = 2.5 \times 10^{-5}$

To a second approximation

$$\chi_{x(n.f.)} = C \times \left(\frac{\Delta F_x - \Delta F_f}{\Delta F_{Ge}}\right)_{\text{high fields}} = C \times .922$$

where ΔF_f was calculated from equation (IV - 2) using values of $\alpha = 5.\times 10^{-3}$ and $A\rho M_s = 2.1 \times 10^{-5}$.

Values of F_f and $A\rho M_s$ were re-estimated (column 4 and 5) giving $A\rho M_s = 2.5 \times 10^{-5} \pm 4$ %.

Since the percentage contribution of ΔF_f to ΔF_x is ~ 1 % (Table VI), F_f and hence $A\rho M_s$ need only be determined with an accuracy of 10 % to ensure a .1 % accuracy in $(\Delta F_x - \Delta F_f)$. $A\rho M_s$ is therefore within the required limit of accuracy.

Four values of the ratio $\frac{\Delta F_{nf}}{\Delta F_{Ge}}$ are given in Table VI. The differences in current ΔI correspond to the two field values at which the differences in force ΔF were calculated. ΔF_x and ΔF_{Ge} are found from Table IV. ΔF_f is calculated from equation (IV - 2) and the susceptibility is given by $\chi_{x(n.f.)} = C \times \frac{\Delta F_{nf}}{\Delta F_{Ge}} = \chi_{Ge} \left(\frac{m}{1}\right)_{Ge} \left(\frac{1}{m}\right)_x \frac{\Delta F_{nf}}{\Delta F_{Ge}} = .5170 \times 10^{-6}$.

TABLE VI

Calculation of $\frac{\Delta F_{n.f.}}{\Delta F_{Ge}} = \frac{\Delta F_x - \Delta F_f}{\Delta F_{Ge}}$

ΔI Amps	ΔF_x mgms	ΔF_f mgms	$\Delta F_{n.f.}$ mgms	ΔF_{Ge} mgms	$\frac{\Delta F_{n.f.}}{\Delta F_{Ge}}$
$4.60_0 - 3.47_5$	2.032	.026	2.006	2.139	$.937_8$
$4.32_5 - 3.18_0$	2.208	.029	2.179	2.317	$.940_4$
$4.03_5 - 2.89_5$	2.392	.033	2.359	2.509	$.940_2$
$3.76_0 - 2.61_0$	2.590	.038	2.552	2.710	$.941_6$

The errors involved in the calculation of χ are :

- $\frac{\Delta F_{nf}}{\Delta F_{Ge}} = .940_o \pm .1\ \%$
- $\chi_{Ge} = -.103 \times 10^{-6} \pm .5\ \%$
- m and l are determined with an accuracy better than .05 %,
- giving χ absolutely to within .6 % and relatively to Ge to within .1 %.

This value of χ is that corresponding to the temperature at which the alloy was measured. To obtain the susceptibilities of all the alloys at the same temperature for purposes of comparison, it is assumed that $(\chi_{Mg\ Mn} - \chi_{Mg}) = c\,\chi_{ion^+\ Mn}$ is directly proportional to $\frac{1}{T}$. Since χ_{Mg} is temperature independent, it is possible to calculate from this relation what effect a few degress change in T will have on $\chi_{Mg\ Mn}$.

If we assume the ferromagnetic impurity to be in the form of free iron, then $M_s \simeq 200$ and the concentration of ferromagnetic (C_{Fe}) can be found from equation (IV - 5) giving

$$C_{Fe} = 4 \times 10^{-5}\ \text{Wt. \%}.$$

The summary of results for the Mg Mn alloys is given in Table VII.

T A B L E VII

Sample	α gauss^{-1} x 10^3	$A\rho M_s$ mgms / gauss x 10^5	C_{Fe} Wt% x 10^5 (M_s=200)	Contribution of ΔF_f to ΔF_x at high fields	χ x 10^6 (at 27°c) (estimated error relative to Ge)
728	5	.65	1.5	5 %	$.497_9 \pm .1$ %
87812	5	2.5	4	1 %	$.516_7 \pm .1$ %
87813	5	2.4	5	2 %	$.533_6 \pm .1$ %
87814	5	5.9	9	3 %	$.564_2 \pm .1$ %
87815	5	4.1	7	2 %	$.601_6 \pm .1$ %

Al - Mn Alloys

These alloys were prepared by the Aluminum Laboratories Limited of Canada. The concentration of Mn varied from 0 to 1 % (Table VIII).

T A B LE VIII

Spectroscopic Analyses

	% Mn Expected	Wt % Cu	Wt % Fe	Wt % Mg	Wt % Mn	Wt % Si
GKP	< .001	< .002	< .002	< .002	< .001	< .001
GKM	.01	< .002	< .003	< .002	.011	< .001
GKN	.05	< .002	< .004	< .002	.053	< .001
GKO	.10	< .002	< .003	< .002	.092	< .001

The results of preliminary measurements on these alloys is given in Tables IX to XI and in figures 16 to 19. The ferromagnetic force ΔF_f was found to be up to 30 % of ΔF_x at high fields. The estimated concentration of ferromagnetic iron was much greater than that found for the Mg Mn alloys. In such cases considerable error may arise in χ due to the difficulty to correct accurately for such large ferromagnetic forces. The susceptibility was by no means found to increase linearly with concentration of Mn.

It was therefore found necessary to heat treat these alloys. The samples were sealed off in evacuated tubes and quenched from 600° C to 0° C after several days of annealing at 600° C. In so doing, it was hoped to put the Fe in solution, thus rendering it non ferromagnetic and also to put the Mn in solution, that according to the phase diagram (Fig. 25, Chapter V) might be in the form Al_6 Mn.

The results of the measurements on these alloys after quenching are given in Tables XII to XIV and in figures 16 to 19.

The ferromagnetic force has decreased sufficiently to permit calculations of χ to $\pm$ .1 %.

TABLE IX

Sample	Ge	Al - Mn			
		GKP	GKM	GKN	GKO
length cms	6.630	6.638	6.636	6.649	6.620
mass gms	10.6803	3.346	3.351	3.356	3.345

T A B L E X

I Amps.	F_x/g (before quenching) mgms - Temp °C				
	Ge	Al - Mn			
		GKP	GKM	GKN	GKO
		30°	28°	35°	32°
0.00_0	0.000	.000	.000	.000	.000
0.61_0	-0.295	.950	2.020	1.390	1.290
1.18_0	-1.093	3.030	5.830	4.370	3.970
1.75_0	-2.311	5.890	10.550	8.315	7.540
2.32_0	-3.793	9.180	15.645	12.730	11.530
2.61_0	-4.582	10.870	18.170	14.925	13.570
2.89_5	-5.347	12.485	20.545	17.045	15.480
3.18_0	-6.050	13.975	22.685	18.940	17.220
3.47_5	-6.698	15.325	24.600	20.660	18.810
3.76_0	-7.292	16.585	26.360	22.225	20.250
4.03_5	-7.856	17.725	27.970	23.660	21.600
4.32_5	-8.367	18.785	29.460	24.985	22.825
4.60_0	-8.837	19.755	30.790	26.195	23.940

T A B L E XI

Sample	α $\text{gauss}^{-1} \times 10^3$	$A\rho M_s$ mgms / gauss $\times 10^5$	C Fe Wt % $\times 10^5$ (M_s=200)	Contribution of ΔF_f to ΔF_x at high fields	$\chi \times 10^6$ (estimated error relative to Ge)
GKP	1	42.5	40	10 %	$.61_1 \pm 1$ %
GKM	1	150	150	30 %	$.70_4 \pm 2$ %
GKN	1	92	90	20 %	$.70_0 \pm 2$ %
GKO	1	75	75	15 %	$.66_6 \pm 2$ %

T A B L E XII

Sample	Ge	Al - Mn (after quenching)			
		GKP	GKM	GKN	GKO
length cms	6.630	6.638	6.636	6.649	6.620
mass gms	10.6803	3.404	3.3400	3.3482	3.3371

T A B L E XIII

I Amps	F_x/g (after quenching) mgms				Temp ° C
	Ge	Al - Mn			
		GKP	GKM	GKN	GKO
		32°	30°	34°	37°
0.000	0.000	.000	.000	.000	.000
0.61_0	-0.295	.595	.600	.580	.620
1.18_0	-1.093	2.130	2.150	2.120	2.240
1.75_0	-2.311	4.430	4.480	4.430	4.645
2.32_0	-3.793	7.210	7.270	7.230	7.540
2.61_0	-4.582	8.675	8.745	8.705	9.060
2.89_5	-5.347	10.090	10.180	10.140	10.535
3.18_0	-6.050	11.400	11.495	11.460	11.895
3.47_5	-6.698	12.595	12.700	12.670	13.145
3.76_0	-7.292	13.710	13.805	13.795	14.305
4.03_5	-7.856	14.735	14.845	14.835	15.370
4.32_5	-8.367	15.690	15.800	15.700	16.355
4.60_0	-8.837	16.560	16.685	16.685	17.260

T A B L E XIV

Sample	α gauss^{-1} x 10^3	AρM_S $\frac{\text{mgms}}{\text{gauss}}$ x 10^5	C Fe Wt % x 10^5 (M_S=200)	Contribution of ΔF_f to ΔF_x at high fields	χ x 10^6 (32° C) (estimated error relative to Ge)
GKP	5	5.0 ± 2 %	5	1.5 %	$.602_7$ ± .1 %
GKM	5	5.5 ± 2 %	5.5	1.5 %	$.604_3$ ± .1 %
GKN	5	3.2 ± 3 %	3	1 %	$.612_2$ ± .1 %
GKO	5	6.2 ± 2 %	6	2 %	$.623_8$ ± .1 %

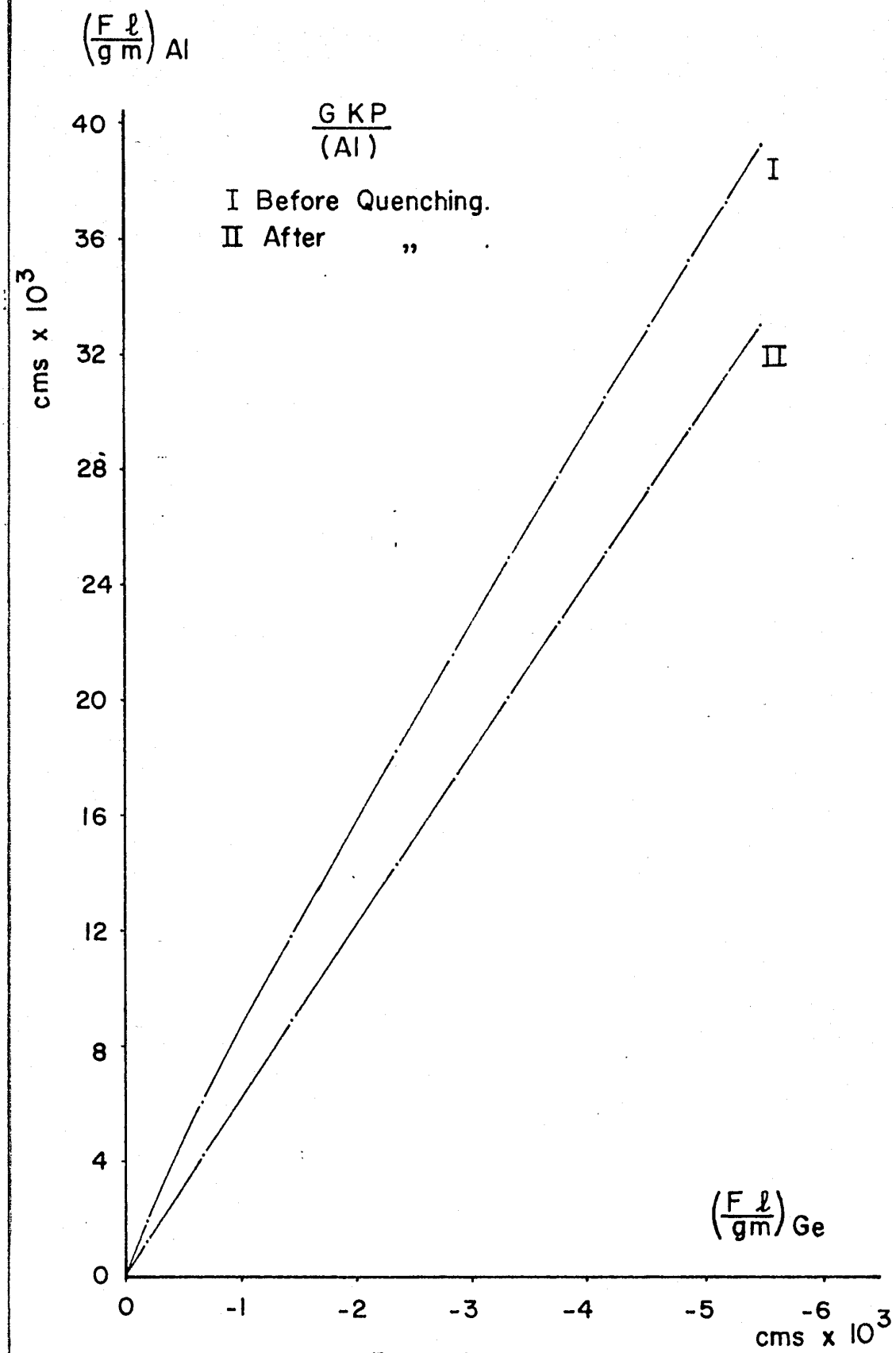

$\left(\frac{F\ \ell}{g\ m}\right)$ Al
$\frac{G\ K\ P}{(Al)}$
I Before Quenching.
II After ,,
I
II
cms x 10^3
40
36
32
28
24
20
16
12
8
4
0
0
-1
-2
-3
-4
-5
-6
cms x 10^3
$\left(\frac{F\ \ell}{gm}\right)$ Ge

Fig. 16

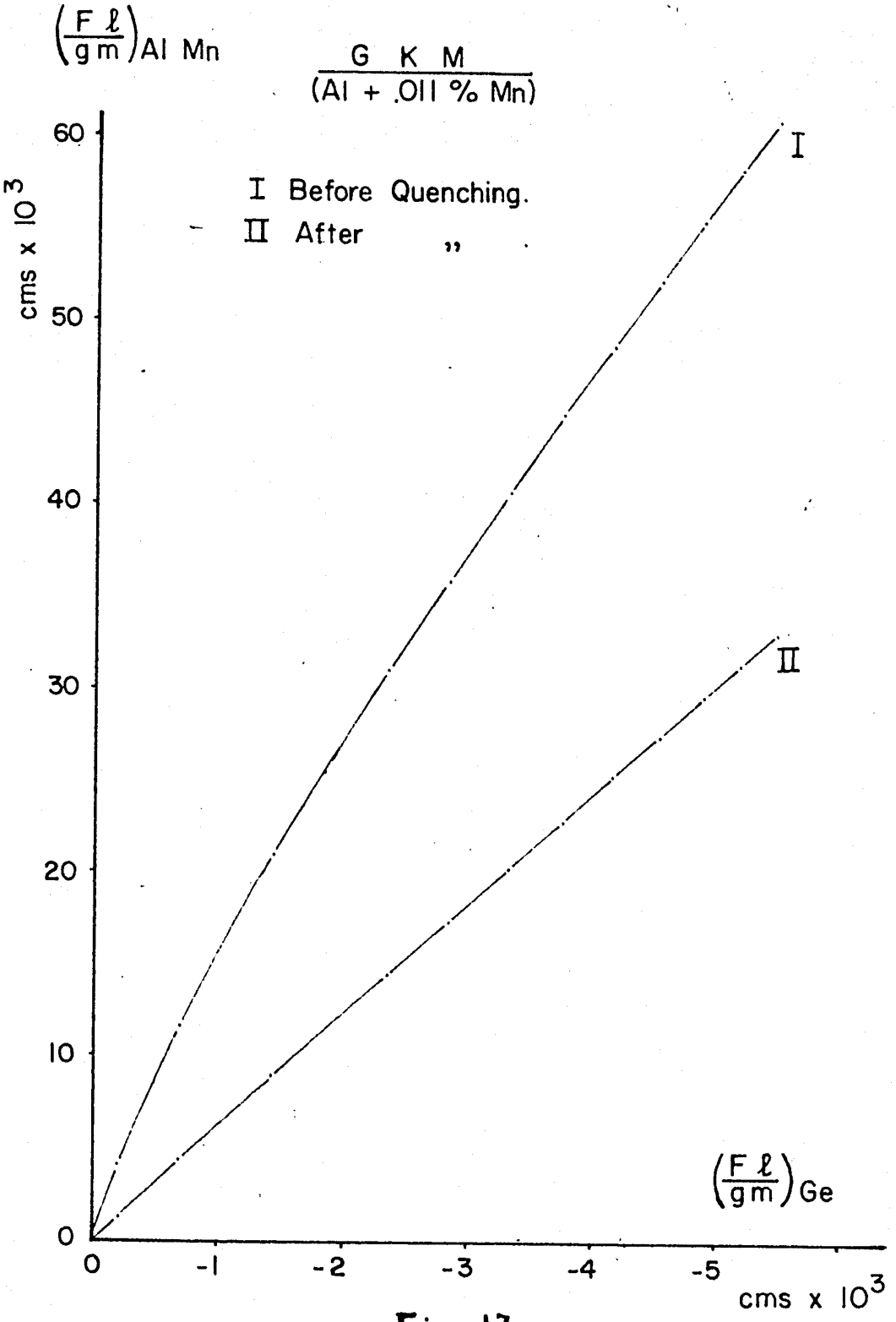

$\left(\frac{F\,\ell}{g\,m}\right)$ Al Mn
G K M
(Al + .011 % Mn)
I Before Quenching.
II After ,,
I
II
cms x 10^3
60
50
40
30
20
10
0
0
-1
-2
-3
-4
-5
$\left(\frac{F\,\ell}{g\,m}\right)$ Ge
cms x 10^3

Fig. 17

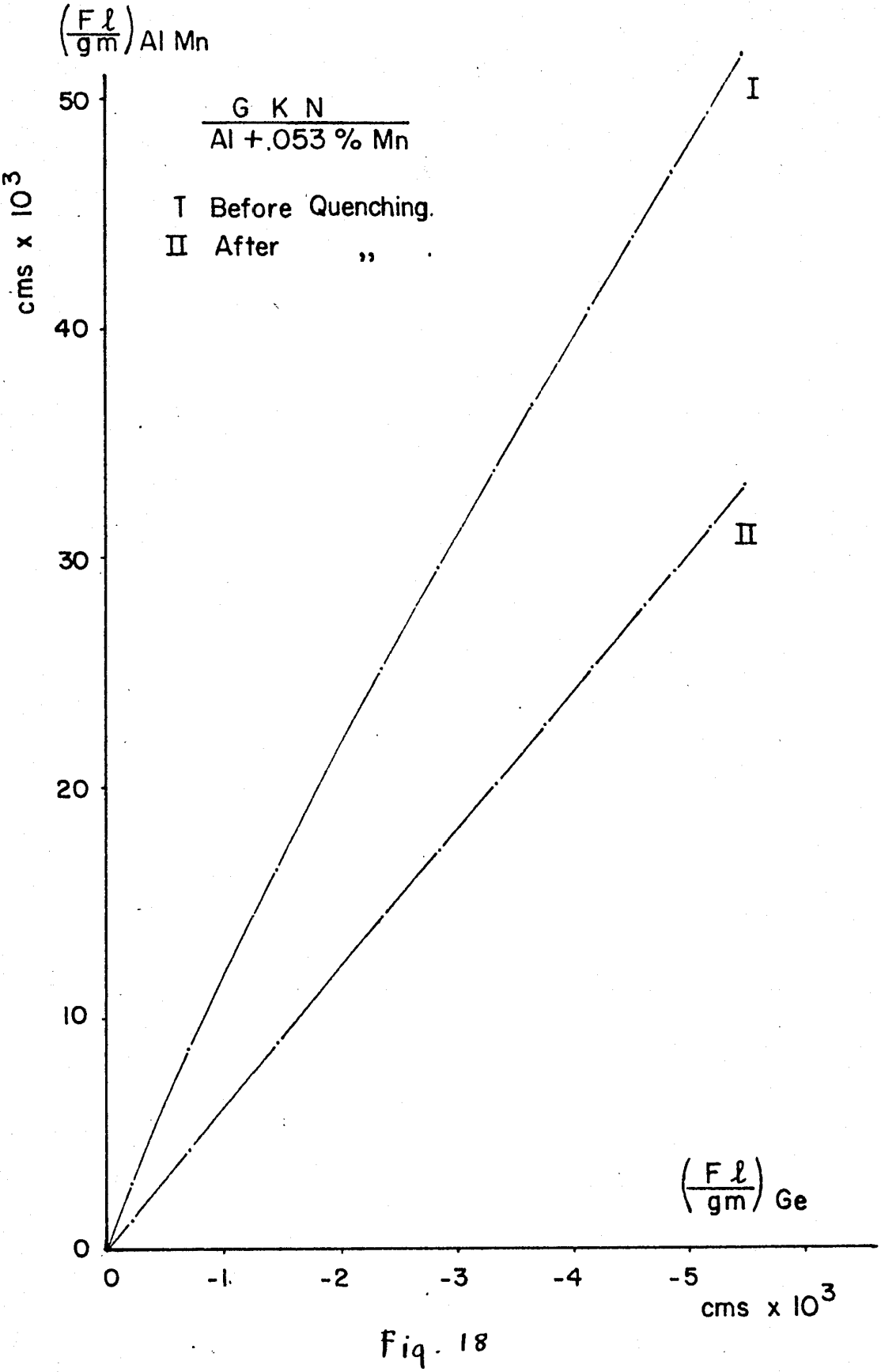

$\left(\frac{F\ell}{gm}\right)$ Al Mn
G K N
Al + .053 % Mn
I Before Quenching.
II After ,,
cms x 10^3
50
40
30
20
10
0
I
II
$\left(\frac{F\ell}{gm}\right)$ Ge
0
-1
-2
-3
-4
-5
cms x 10^3

Fig. 18

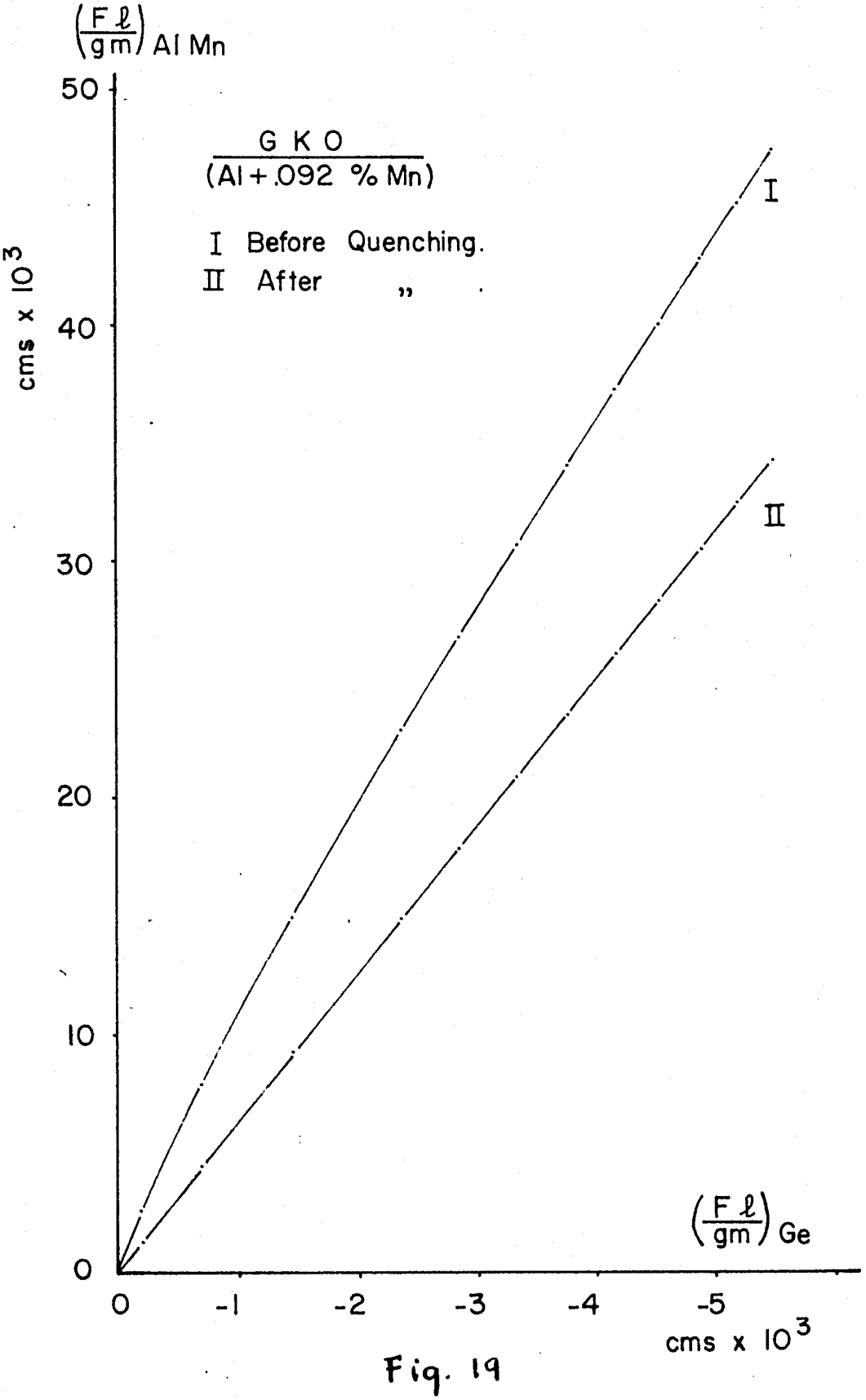

$\left(\frac{F\ell}{gm}\right)$ Al Mn
50
40
30
20
10
0
cms x 10^3
G K O
(Al + .092 % Mn)
I Before Quenching.
II After ,,
I
II
$\left(\frac{F\ell}{gm}\right)$ Ge
0
-1
-2
-3
-4
-5
cms x 10^3

Fig. 19

Al Fe Alloys

These alloys were prepared by the Aluminum Laboratories Limited of Canada. The concentration of Fe varied from .01% to .1% (Table XV).

TABLE XV

Spectroscopic Analyses

	% Fe expected	Wt.% Cu	Wt.% Fe	Wt.% Mg	Wt.% Si
GKJ	.01	$<$.002	.01	$<$.002	$<$.001
GKK	.05	$<$.002	.05	$<$.002	$<$.001
GKL	.10	$<$.002	.11	$<$.002	$<$.001

Preliminary measurements on these alloys gave a ferromagnetic contribution to the force of $\simeq$ 80%. The alloys were then heat treated by annealing for several days at 600° C and quenching to 0° C. Since the maximum solid solubility of Fe in Al at 600° C is .025% (Fig. 27, Chapter V), it was hoped to put this amount into solution and to put the rest of the Fe in the alloys, which is as high as .1%, in the non ferromagnetic form Al_3Fe (see phase diagram Fig. 26, Chapter V). The results of measurements on these alloys after quenching are given in Tables XVI to XVIII and Fig. 20.

TABLE XVI

Sample	Ge	Al - Fe (after quenching)		
		GKJ	GKK	GKL
length cms	6.630	6.657	6.662	6.653
mass gms	10.6803	3.3271	3.2921	3.3467

TABLE XVII

I Amps.	$F_{x/g}$ (after quenching) mgms			Temp °C
	Ge	Al - Fe		
		GKJ	GKK	GKL
		30°	33°	33°
0.00_0	0.000	.000	.000	.000
0.61_0	-0.295	.575	.570	.675
1.18_0	-1.093	2.100	2.070	2.320
1.75_0	-2.311	4.365	4.315	4.740
2.32_0	-3.793	7.130	7.035	7.610
2.61_0	-4.582	8.575	8.465	9.120
2.89_5	-5.347	9.980	9.860	10.580
3.18_0	-6.050	11.280	11.140	11.915
3.47_5	-6.698	12.460	12.315	13.140
3.76_0	-7.292	13.560	13.410	14.275
4.03_5	-7.856	14.590	14.420	15.325
4.32_5	-8.367	15.535	15.360	16.300
4.60_0	-8.837	16.400	16.210	17.190

TABLE XVIII

Sample	α gauss^{-1} x 10^3	$A\rho M_s$ mgms/gauss x 10^5	C Fe Wt % x 10^5 (M_s=200)	Contribution of ΔF_{fer} to ΔF_x at high fields	χ x 10^6 (32° C) (estimated error relative to Ge)
GKJ	5	4.0 ± 2 %	4	1 %	$.603_5$ ± .1 %
GKK	5	3.5 ± 4 %	3.5	1 %	$.605_4$ ± .1 %
GKL	5	11.5 ± 4 %	11.5	3 %	$.605_2$ ± .2 %

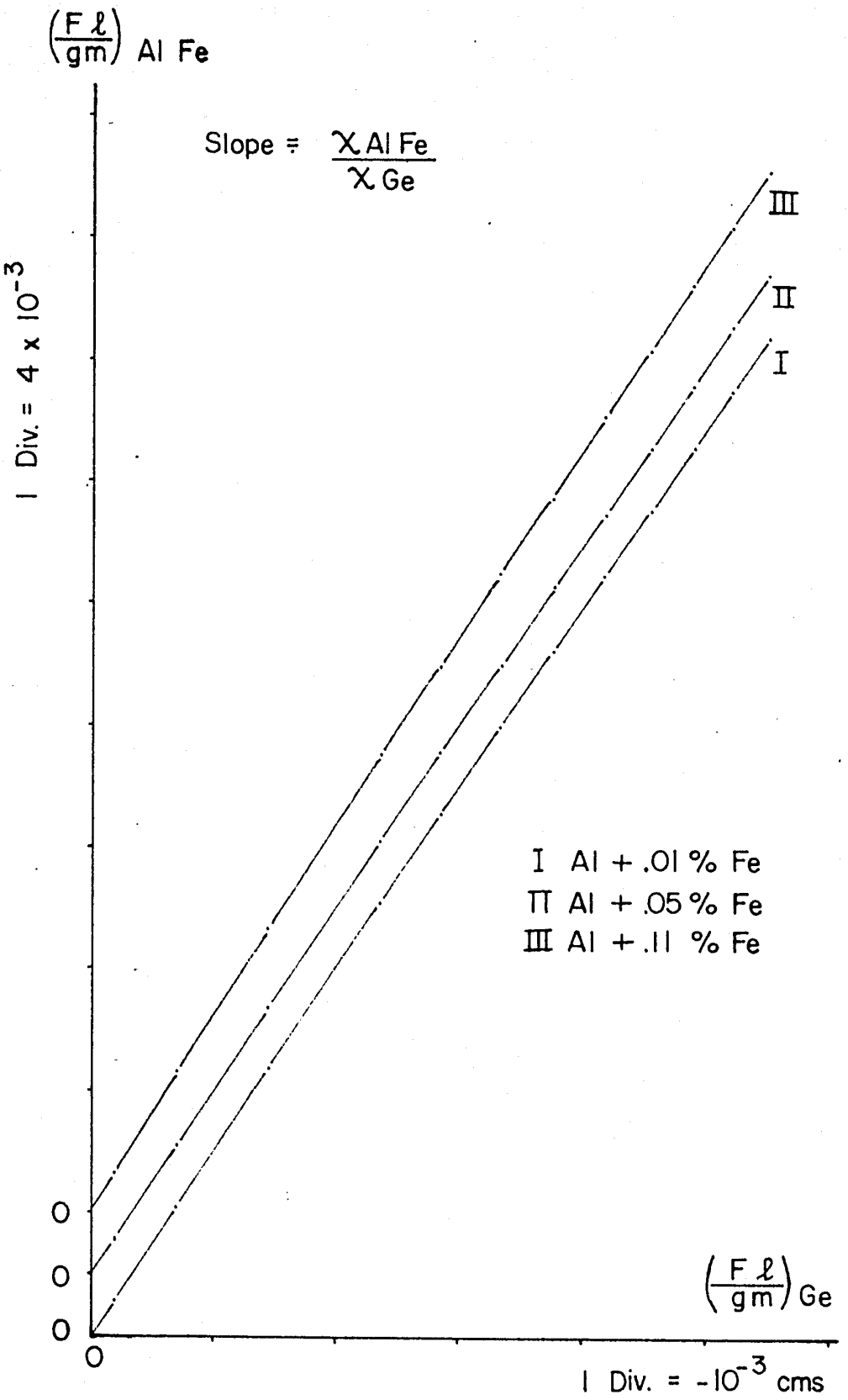

$\left(\frac{F\ell}{gm}\right)$ Al Fe
Slope = $\frac{\chi \text{ Al Fe}}{\chi \text{ Ge}}$
III
II
I
1 Div. = 4×10^{-3}
I Al + .01 % Fe
II Al + .05 % Fe
III Al + .11 % Fe
0
0
0
$\left(\frac{F\ell}{gm}\right)$ Ge
1 Div. = -10^{-3} cms

Fig. 20

Mg Fe Alloys

These alloys were prepared by the Dow Chemical Company (Michigan) from chill cast ingots formed in graphite moulds. The concentration of Fe varied from .0023 to .015 Wt% (Table XIX).

TABLE XIX

Spectroscopic Analyses

	727 - 1	727- 2	757-1	757-2
Wt% Al	< .001	< .001	< .001	< .001
" Ca	< .01	< .01	< .01	< .01
" Cu	< .001	< .001	< .001	< .001
" Fe	.0023	.0027	.015	.014
" Mn	< .001	< .001	< .001	< .001
" Ni	< .0005	< .0005	< .0012	< .0011
" Pb	< .001	< .001	< .001	< .001
" Si	< .001	< .001	< .001	< .001
" Sn	< .01	< .01	< .01	< .01
" Zn	< .001	< .001	.038	.039

Before heat treatment there was a strong ferromagnetic force on these alloys. Since the maximum solid solubility of Fe in Mg at the melting point of Mg (651°C) is .026 %, attempts were made to put more Fe in solution by annealing at 600° C and quenching to 0° C. Even after heat treatment, the ferromagnetic force on the Mg + .015% Fe was $\sim$ 10 times greater than the non ferromagnetic force, making an accurate determination of the non ferromagnetic part of the susceptibility impossible.

The Mg + .0025% Fe samples had a ferromagnetic contribution to the force of $\sim$ 20 % before and after heat treatment.

The results of measurements on these alloys are given in Tables XX to XXII and Figure 21. Unfortunately $\chi_{(n.f.)}$ is only determined to 1 and 2 % and an error of this order can swamp out the effect the small concentration of Fe in solution will have on the susceptibility.

It was therefore decided to measure these alloys using the Curie method (Chapter III). Up to now the Gouy method has been used because the magnetic force can be measured more accurately. However, the errors involved in correcting for large ferromagnetic forces removes this advantage. In such cases the Curie method provides a simpler and more accurate way of correcting for ferromagnetic impurities since the entire sample is in a field sufficient to saturate the ferromagnetic. The force on a Mg Fe sample in sufficiently high fields is given by (Chapter III)

$$F_{MgFe} = (m\chi)_{MgFe} \quad H \frac{d H}{d y} + (m M_s)_{fer} \quad \frac{d H}{d y}$$

where m_{fer} is the mass of ferromagnetic in the sample. The force on Ge is

$$F_{Ge} = (m\chi)_{Ge} \quad H \frac{d H}{d y}$$

Hence

$$\frac{(F/m)\ MgFe}{(F/m)\ Ge} = \frac{\chi\ MgFe}{\chi\ Ge} + \frac{c\ M\ s}{\chi\ Ge} \quad \frac{1}{H}$$

where c is the concentration of ferromagnetic. The value of χ MgFe may be found by plotting $\frac{(F/m)\ MgFe}{(F/m)\ Ge}$ against the corresponding values of $\frac{1}{H}$, and finding the intercept at $\frac{1}{H} = 0$.

Gouy Method (after quenching)

T A B L E XX

Sample	Ge	Mg + .0023 % Fe (727-1)	Mg + .0027 % Fe (727-2)
length cms	6.630	6.625	6.623
mass gms	10.6803	2.3051	2.2292

T A B L E XXI

I Amps.	F/g mgms Ge	Temp. ° C Mg Fe 727-1	Mg Fe 727-2
		26°	26°
$.00_0$	0.000	.000	.000
$.61_0$	-0.295	.841	.634
1.18_0	-1.093	2.380	1.910
1.75_0	-2.311	4.346	3.608
2.32_0	-3.793	6.543	5.542
2.61_0	-4.582	7.652	6.526
2.89_5	-5.347	8.711	7.471
3.18_0	-6.050	9.667	8.328
3.47_5	-6.698	10.542	9.113
3.76_0	-7.292	11.342	9.836
4.03_5	-7.856	12.089	10.508
4.32_5	-8.367	12.768	11.115
4.60_0	-8.837	13.380	11.671

T A B L E XXII

Sample	α gauss^{-1} x 10^3	$A\rho M_s$ mgms gauss x 10^5	C Fe Wt % x 10^5 (M_s=200)	Contribution of ΔF_{fer} to ΔF_x at high fields	χ x 10^6 (26°C)
727-1	1	49	70	20 %	$.51_5$ ± 2 %
727-2	1	33	50	15 %	$.50_8$ ± 1 %

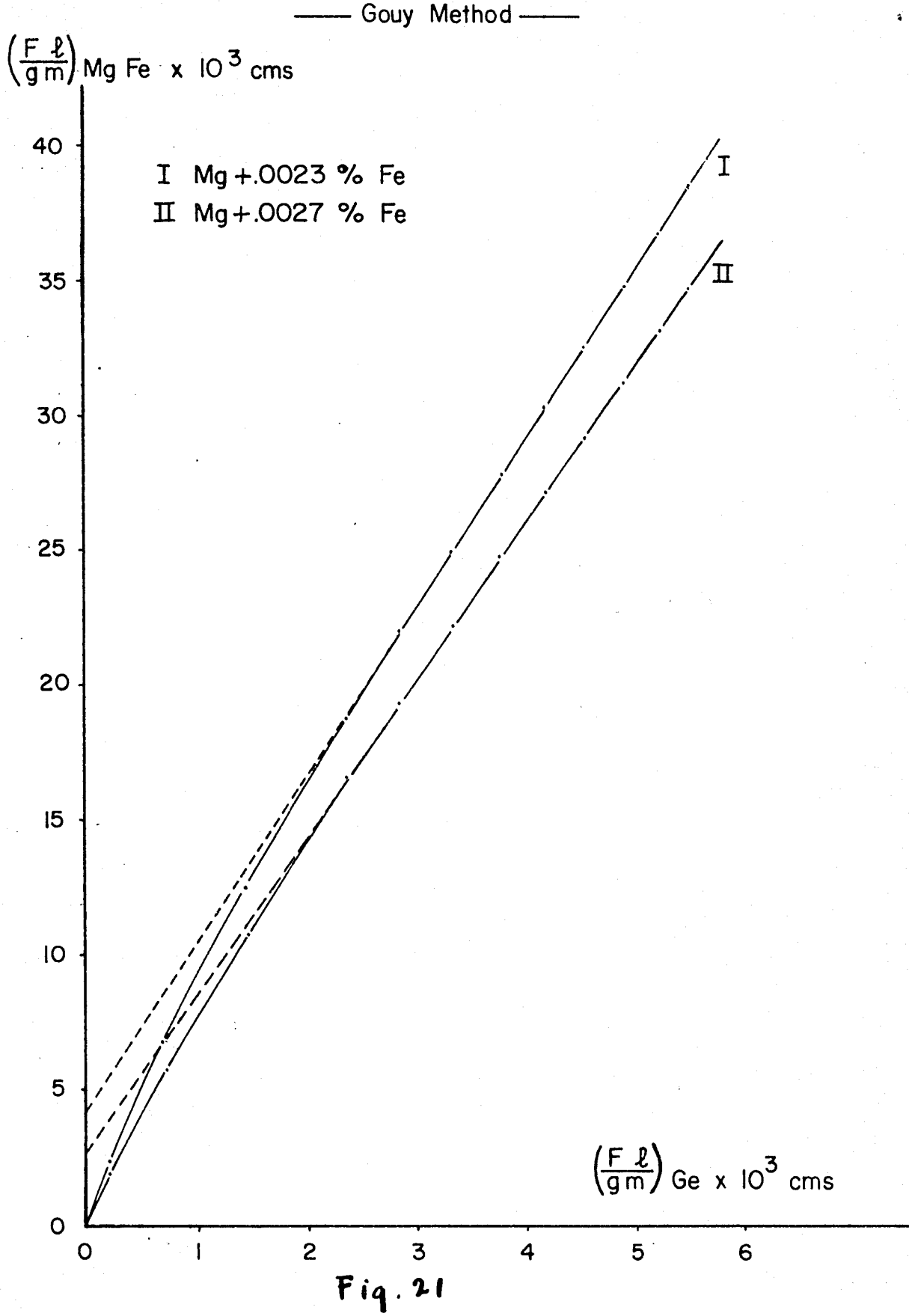

Gouy Method
$\left(\frac{F\ell}{gm}\right)$ Mg Fe x 10^3 cms
I Mg +.0023 % Fe
II Mg +.0027 % Fe
I
II
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
$\left(\frac{F\ell}{gm}\right)$ Ge x 10^3 cms

Fig. 21

From the slope it is possible to estimate the concentration of ferromagnetic by assuming a value for M_s.

The results of measurements on these alloys using the Curie method before and after quenching are given in Tables XXIII to XXV and figures 22 and 23.

Curie Method

T A B L E XXIII

Sample	Ge	Mg + .0023 % Fe (727-1)	Mg + .0027 % Fe (727-2)
		(before quenching)	
mass gms.	2.0980	.3728	.4354
		(after quenching)	
mass gms.	2.0980	.2563	.3733

T A B L E XXIV

I Amps.	F/g mgms Ge	Temp. °C Mg - Fe			
		Before quenching		After quenching	
		727-1	727-2	727-1	727-2
		22°C	22°C	24°C	24°C
0.0_0	.000	.000	.000	.000	.000
0.4_0	- .042	.062	.078	.066	.122
0.9_0	- .208	.280	.328	.239	.422
1.4_0	- .524	.603	.731	.492	.837
1.9_0	- .938	1.024	1.224	.814	1.338
2.4_0	-1.396	1.472	1.757	1.150	1.861
2.9_0	-1.864	1.893	2.265	1.467	2.342
3.4_0	-2.238	2.242	2.680	1.725	2.743
3.9_0	-2.570	2.551	3.044	1.953	3.084
4.4_0	-2.848	2.812	3.343	2.142	3.379
4.8_0	-3.038	2.984	3.548	2.266	3.572

T A B L E XXV

Sample	Before quenching		After quenching	
	C Fe Wt% x 10^5 (M_S=200)	χ x 10^6 (22°C) estimated error relative to Ge	C_{Fe} Wt% x 10^5 (M_S=200)	χ x 10^6 (24°C) estimated error relative to Ge
727-1	30	.496 $\pm$ .5 %	60	.502 $\pm$ .5 %
727-2	40	.496 $\pm$ .5 %	80	.502 $\pm$ .5 %

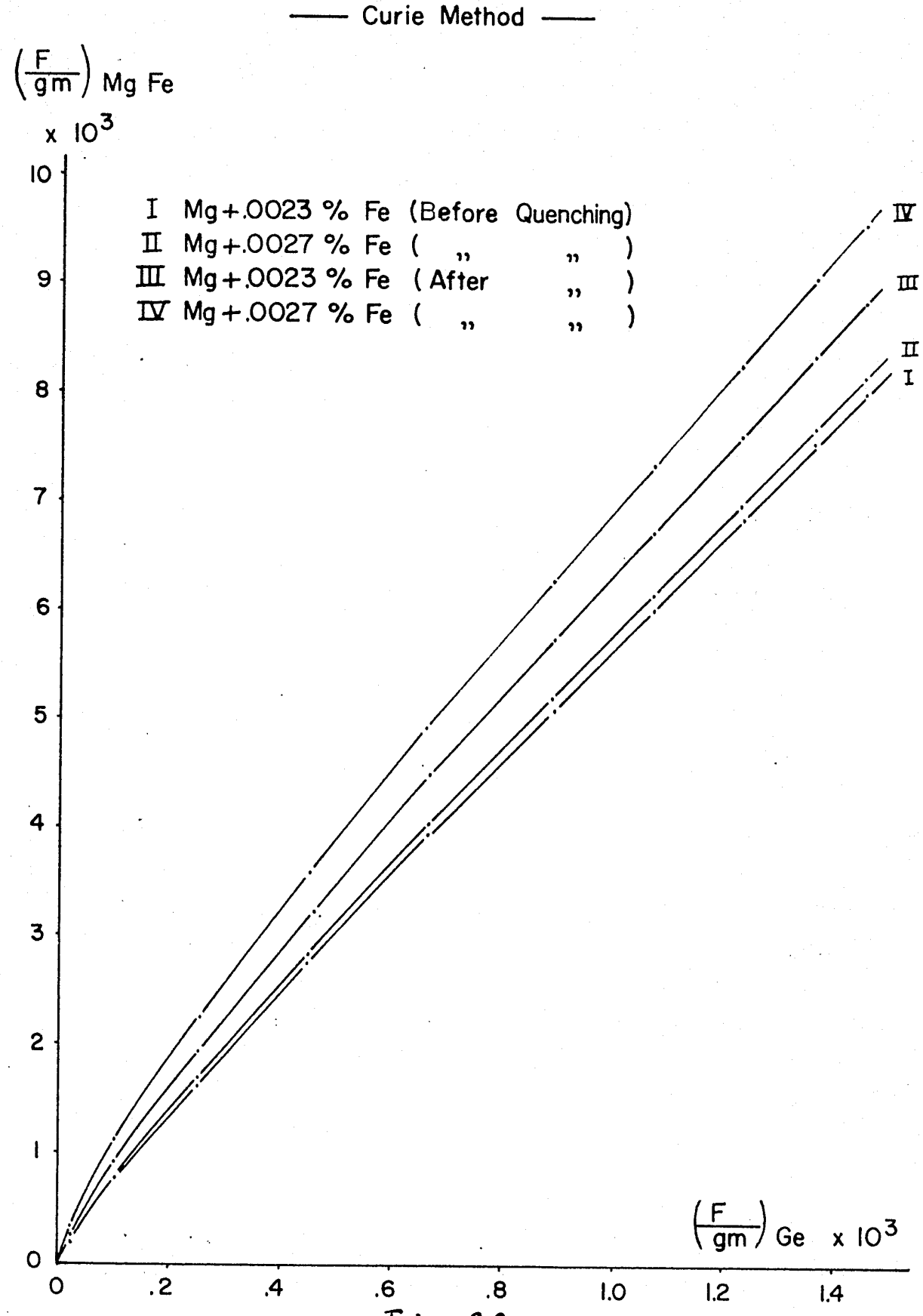

— Curie Method —
(F/gm) Mg Fe
x 10^3
I Mg+.0023 % Fe (Before Quenching)
II Mg+.0027 % Fe (" ")
III Mg+.0023 % Fe (After ")
IV Mg+.0027 % Fe (" ")
10
9
8
7
6
5
4
3
2
1
0
0
.2
.4
.6
.8
1.0
1.2
1.4
(F/gm) Ge x 10^3

Fig. 22

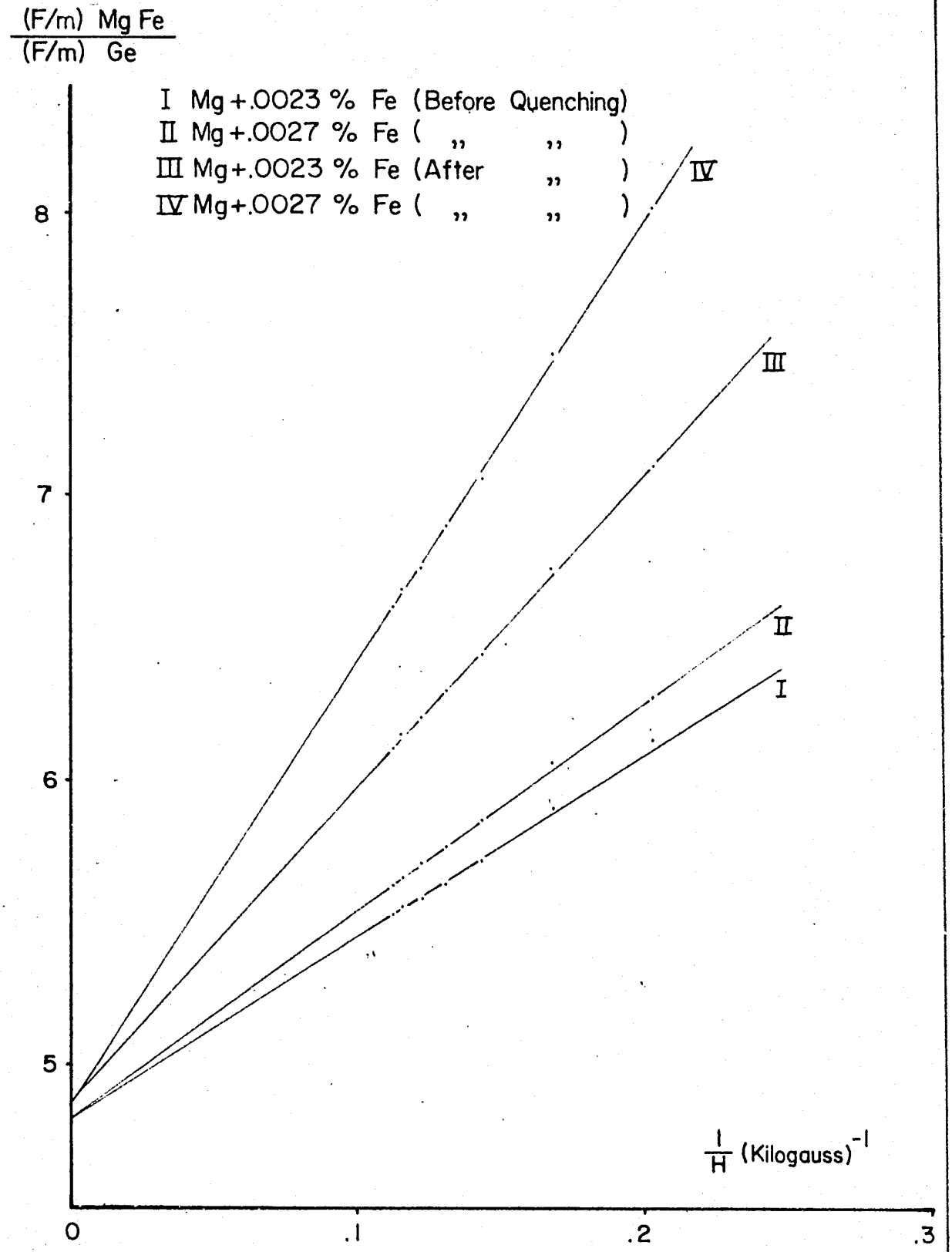

(F/m) Mg Fe
(F/m) Ge
I Mg+.0023 % Fe (Before Quenching)
II Mg+.0027 % Fe (,, ,,)
III Mg+.0023 % Fe (After ,,)
IV Mg+.0027 % Fe (,, ,,)
8
7
6
5
0
.1
.2
.3
I
II
III
IV
1/H (Kilogauss)^-1

Fig. 23

Phase Diagram
Al - Mn

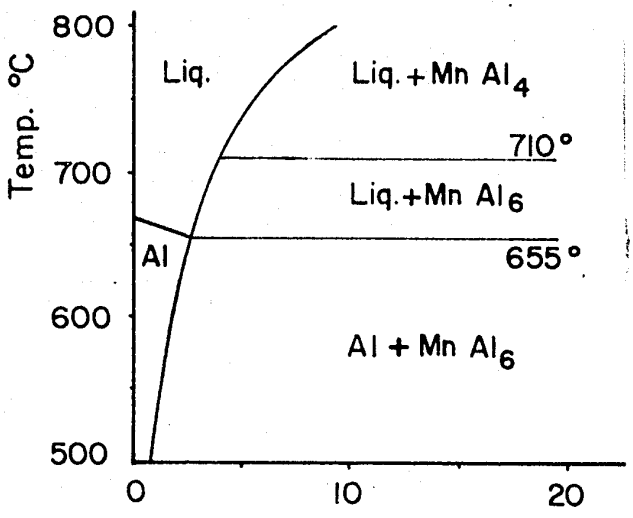


Fig. 25

Phase Diagram
Mg - Mn

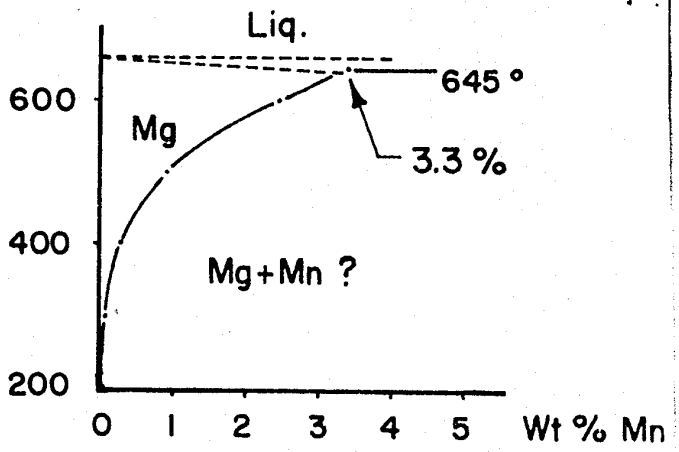


Fig. 24

Phase Diagram Al - Fe

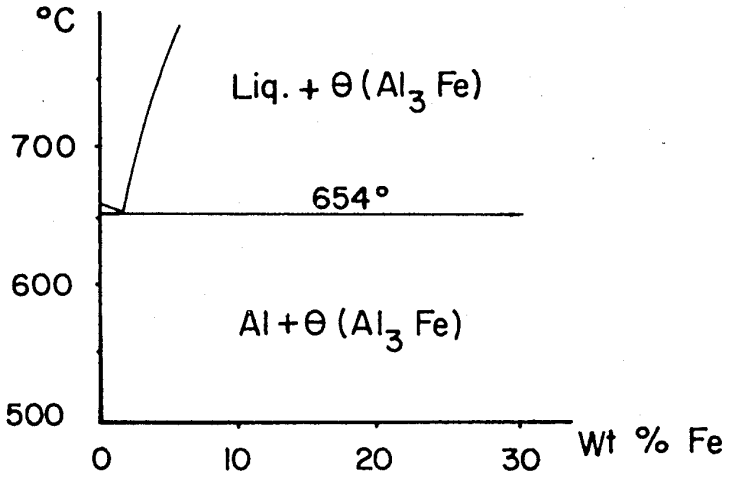


Fig. 26

Maximum Solid Solubility of Fe in Al.
(Supplied by Al. Labs. Ltd. Canada).

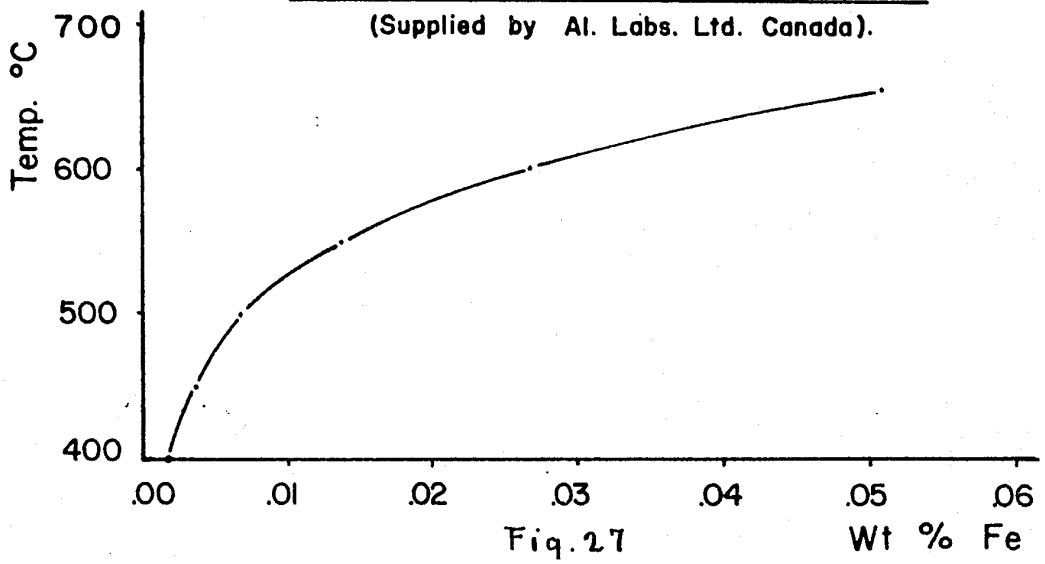


Fig. 27

Previously observed values for the absolute susceptibilities of Al and Mg are listed in Table XXVI .

TABLE XXVI

	$\chi \times 10^6$	Reference
Al	0.65	Honda (1910)
	0.58	Cheneveau (1928)
	0.645	Auer (1934)
	$0.602_7 \pm .6\%$	present thesis
Mg	0.55	Honda (1910)
	0.54	Mahn (1948)
	$0.497_9 \pm .6\%$	present thesis

The values of χ are generally found to be higher than the ones observed presently, which is believed to be due to the presence of ferromagnetic impurities.

CHAPTER VI

DISCUSSION of EXPERIMENTAL RESULTS

As discussed previously, the purpose of the present investigation is to obtain information about the electronic configuration of the transition elements Fe and Mn in solution in the non transition elements Al and Mg. At present, the behaviour of the 3d electrons of the solute atoms is not yet well established. There are two extreme pictures, that the d electrons remain localized about their respective atoms, or that they form a d band.

For dilute concentrations of the transition element, it might be expected that the d electrons are in localized states about their respective atoms and that the solute atoms retain their free ionic configuration of 5 and 6 d electrons for Mn and Fe respectively. Since in an alloy there exists a conduction band common to all atoms of the crystal, there may be a change in the population of the 3 d shell as a result of some of the d electrons entering the conduction band or some of the conduction electrons entering the 3 d shell of the solute atom. This effect will of course alter the spectroscopic state of the ion and hence the measured value of the effective magneton number.

.....

As the concentration of transition elements increases, the wave functions of the d electrons may spread out sufficiently through the crystal to form a d band. The d electrons thus begin to behave the way in which they are thought to behave in the pure transition metal. The most simple model proposed is that of Mott (1935), who regards the outermost electrons in the transition elements of the first long period as being in two bands derived from the 3d and 4s states of the free atoms. In the pure transition metal the d and s bands are not completely filled and in alloys the d band may or may not be filled depending on its position relative to the Fermi level of the conduction electrons. Such a change in population of the bands will alter the value of the density of states at the Fermi level, and thus the electronic susceptibility.

From experimental studies of magnetic susceptibilities and electron transport properties, it has been found that the localized d electron picture is adequate for dilute alloys of transition elements in non transition elements and breaks down for concentrations of transition element above 50 % where a d band is thought to form (Hume Rothery, Coles, 1954). For intermediate concentrations, overlap of the d electron wave functions takes place, but it is not certain to what extent a d band may be said to exist.

It is possible to distinguish among the above cases from magnetic susceptibility measurements :

- If the d electrons are localized, the unpaired spins will give rise to a large paramagnetic susceptibility, which is inversely proportional to the temperature. As discussed in Chapter II, the difference in susceptibilities $\Delta\chi$ between the alloy and the pure solvent metal will be directly proportional to the concentration of transition element in solution

$$\Delta\chi = c \frac{N (p_B \mu_B)^2}{3k (T - \theta)} \quad \ldots\ldots\ldots \quad (VI - 1)$$

- A change in population of the 3 d shell will introduce a corresponding change in the measured effective Bohr magneton number .

- If the wave functions of the d electrons overlap to form a band, then only those electrons at the Fermi level will contribute to the susceptibility and hence the paramagnetism will be relatively small ($\sim \frac{1}{100}^{th}$ of the paramagnetism due to localized d electrons at room temperature) and temperature independent. It is generally found that the density of states in the d band is higher than in the s band, and hence if the d band is not completely filled, the electronic susceptibility will be proportionally higher.

The dilute alloys studied were found to have a large temperature dependent paramagnetism (*). The effective Bohr magheton numbers calculated from equation (VI - 1) are listed in Table XXVII. The large p_B values found for the Mg alloys indicate that most of the 3 d electrons of the transition element remain localized. However, the small p_B values found for the Al alloys point to a significant difference with the free ionic configuration of the 3 d shell (for spin only $p_B(Fe^{+2}) = 4.9$ and $p_B(Mn^{+2}) = 5.9$). If in a given alloy system there is a change in the spectroscopic state of the ion or the formation of a d band as the concentration of transition element increases, then there will be a corresponding change in p_B which will introduce a non linear dependence of $\Delta\chi$ on c (see equation VI - 1). However, as can be seen in figures 28 and 29, for the Mg Mn and Al Mn alloys no such concentration dependence was observed and it is fair to say that the spectroscopic state of the ion does not change by more than 4 and 5 % for the Mg and Al alloys respectively.

By comparing experimental and theoretical p_B values it is possible to deduce the number of unpaired spins for the solute transition element atom (see Chapter II). However, as

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* From temperature runs on the Mg Mn alloys (F.T. Hedgcock), the Weiss constant θ was found to be approximately zero. With this in mind and from the fact that concentrations were smaller than .1 %, θ was assumed to be zero for all the alloys studied. This makes it possible to calculate p_B from room temperature values of susceptibility alone.

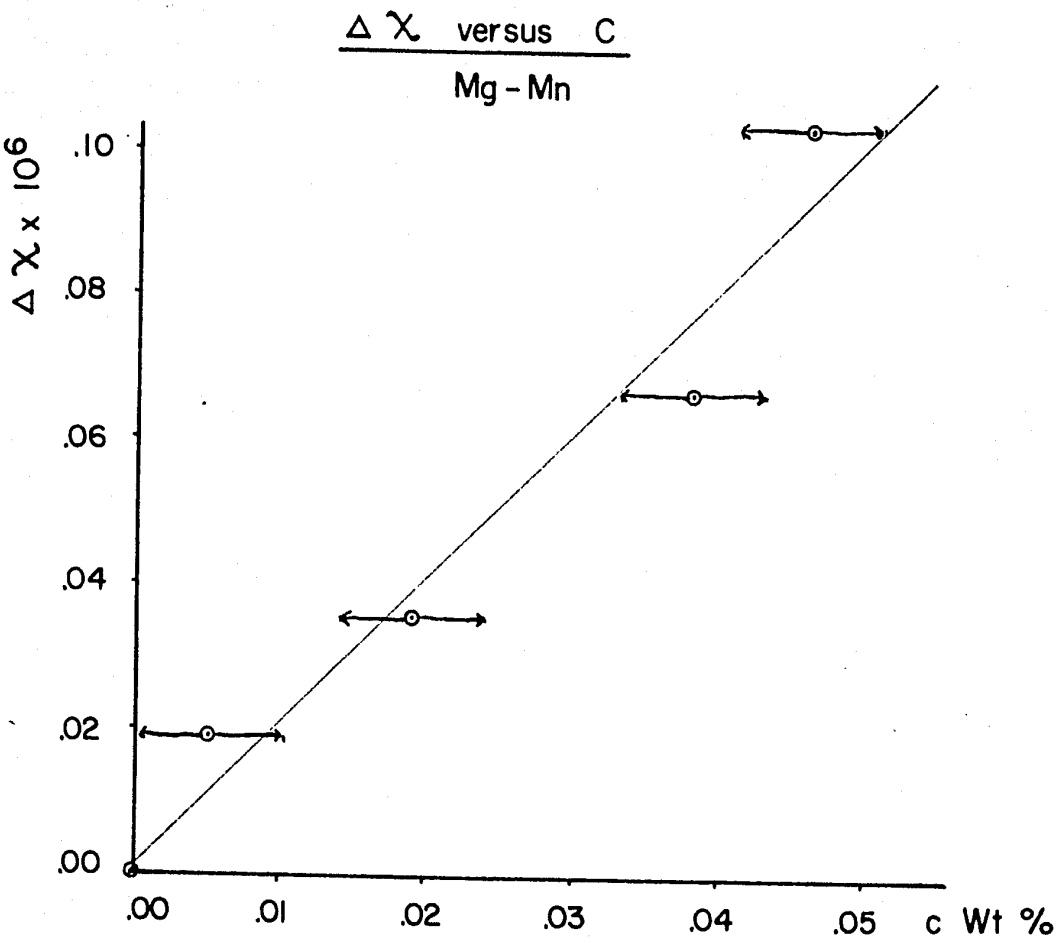
Δ χ versus C
Mg - Mn
Δ χ x 10⁶
.10
.08
.06
.04
.02
.00
.00
.01
.02
.03
.04
.05
c Wt %

Fig. 28

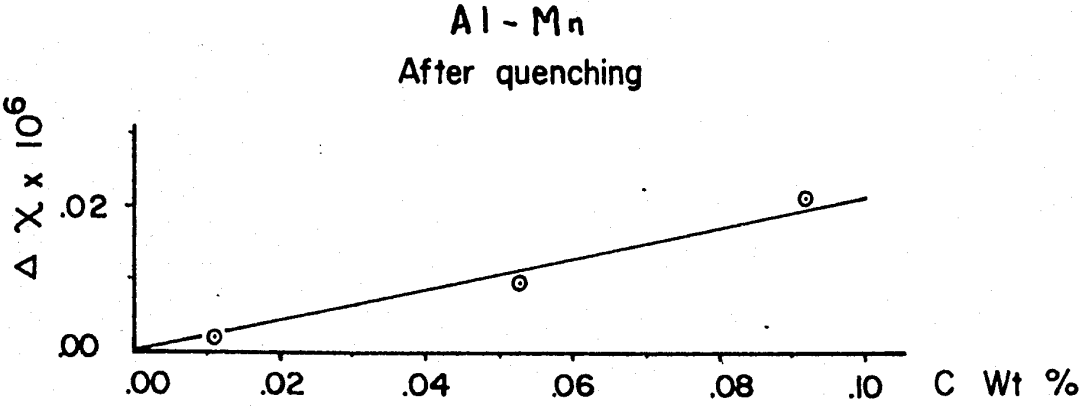
Al - Mn
After quenching
Δ χ x 10⁶
.02
.00
.00
.02
.04
.06
.08
.10
C Wt %

Fig. 29

T A B L E XXVII

Alloy	Wt % of transition element given by spectroscopic analysis	P_B expt
Mg Mn		
87812	.005	7 ± 1
87813	.019	5.0 ± .2
87814	.038	4.8 ± .1
87815	.046	5.5 ± .1
Al Mn		
G K M	.011	1.4 ± .6
G K N	.053	1.6 ± .1
G K O	.092	1.7 ± .1
Mg Fe		
727-1	.0023	) 4.7 ± 1.5
727-2	.0027	)
	Wt % given by solid solubility curve *	
Al Fe		
G K K	.025	1.2 ± .4
G K L	.025	1.2 ± .5

* The maximum solid solubility of Fe in Al at the quenching temperature of 600° C is .025 % (Fig.27). The remaining Fe must be in the form Al_3 Fe which owing to the small concentrations involved will have a negligible effect on the susceptibility.

TABLE XXVIII

Alloy	p_B expt * (average)		p_B theor. (spin only)	Number of unpaired spins	Possible electronic configurations
Mn in Mg	5.2 ± .2		5.9 4.9	5 4	5 4 or 6
Mn in Al	1.7 ± .1		1.7	1	1 or 9
Fe in Al	1.2 ± .3		1.7	1	1 or 9
Fe in Mg	4.7 ± 1.5		4.9	4	4 or 6
		Ref.			
Mn in Cu	5.0	(1)	4.9	4	4 or 6
Mn in Ag	5.5 5.8	(1) (2)	5.9	5	5
Mn in Au	5.2	(2)	5.9 4.9	5 4	5 4 or 6
Mn in Mg	3.5	(1)	3.9	3	3 or 7
Fe in Au	4.0	(3)	3.9	3	3 or 7

* The average p_B values for the Mg Mn and Al Mn alloys were calculated from the slopes of figures 28 and 29.

Ref. (1) - Owen, Browne, Arp, Kip (1956)
(2) - Kronquist, Giansoldati (1953)
(3) - Kronquist (1952)

can be seen in Table XXVIII, in most cases there are two possible electronic configurations. For example, Mn and Fe in Al have either 1 or 9 electrons, corresponding to the population or the depopulation of the conduction band. It is of interest to see whether it is possible to distinguish between the two electronic configurations by studying the effect this change in conduction electron density will have on the susceptibility. The effective Bohr magneton numbers given in Table XXVIII were obtained assuming the validity of equation (VI - 1) where the difference in electronic susceptibilities between the alloy and the pure solvent metal was considered to be negligible (see Chapter II). However, it is possible that a change in conduction electron density between the metal and the alloy will cause a significant difference between their electronic susceptibilities and thus in the calculated p_B values. For example let us consider the Al Mn alloys. Al has 3 conduction electrons and Mn has 7 electrons outside the complete 3 p shell. If, when Mn is in solution in Al , it retains 9 d electrons, then each Mn atom has deprived the conduction band of two electrons. In order to maintain the electron to atom ratio of 3, there is therefore a deficit of 5 electrons for each Mn atom. If c is the concentration of Mn, then the number of conduction electrons per atom in the alloys is $N_{alloy} = (3 - 5\,c)$. Now the highest concentration of Mn is .05 At %. Therefore $N_{alloy} = (3 - .0025)$ which is .1 % smaller than N_{Al} . Let us now see what percentage difference

this will introduce in the electronic susceptibilities. The total number of conduction electrons is equal to the area under the density of states curve below the Fermi level ξ. If the shape of the curve is known, then from the % change in conduction electron density and thus in the area under the curve, it is possible to calculate the % change in ξ and then in $g(\xi)$. From the g(E) curve for Al proposed by Matyas (1948), it was found that the estimated decrease of .1 % in N introduced a .1 % decrease in $g(\xi)$ and thus in the electronic susceptibility. This in turn would increase $\Delta\chi$ given by equation (VI - 1) by 3 % and consequently ρ_B would be 1.5 % larger than the previously calculated value. Unfortunately the experimental error in ρ_B is $\pm$ 5 % which makes it impossible to distinguish between the two possible electronic configurations for Mn in Al from the present experimental data. For the other alloys studied the concentration of transition element and/or the % change in conduction electron density are lower, making such a distinction equally impossible.

Experimental ρ_B values for Mn and Fe in various other solvents are listed in Table XXVIII. Only one Mg Mn alloy was studied by Owen et al, and they have stated that their relatively low value for Mn in Mg may be due to incomplete solution of the Mn (the concentration of Mn was approaching the solubility limit). In the Mg Mn alloys

presently investigated, the spectroscopic state of the Mn is seen to be similar to that observed for Mn in the noble metals Cu, Ag and Au ; the number of unpaired spins is between 4 and 5, 5 corresponding to the free ionic configuration Mn^{+2} . Fe in Au is seen to have 3 unpaired spins. Thus Mn and Fe in Mg and the noble metals behave differently than in Al, where only 1 unpaired spin was observed.

It is of interest to compare the observed electronic configurations of Mn and Fe in the various solvents listed in Table XXVIII to the recent predictions of Lomer and Marshall (1958). They assume :

1. In alloys whose components have roughly the same conduction electron density, each atom retains approximately the d electron configuration characteristic of the pure metal ;
2. In alloys where the conduction electron densities of the pure metals are very different, the number of d electrons on the minor component may change to decrease this difference.

Lomer and Marshall classify the pure metals Fe, Mn and Al as high conduction electron density or low d elements, and Cu as a high d element. The classification of Fe as a low d element is based on the experimental work of Weiss and De Marco (1958) who claim that the pure metal Fe has $2.3 \pm .3$ d electrons and thus 5.7 conduction electrons.

We would thus expect alloys of Mn and Fe with Al, which all have high conduction electron densities, to behave

according to hypothesis 1. Fe and Mn should retain approximately the 2 localized d electrons characteristic of the pure metal. They were found experimentally to have 1 unpaired spin and thus, according to Lomer and Marshall, 1 localized d electron rather than 9.

Alloys of Mn and Fe with Mg and the noble metals should behave according to hypothesis 2. The minor components are low d elements whereas the solvents are high d elements. In order to decrease this difference, we expect the solute atoms to have more d electrons when alloyed than in the pure metal state. They were found experimentally to have 4 to 6 localized d electrons, which is in agreement with Lomer and Marshall's predictions.

CHAPTER VII

CONCLUSION

The mass susceptibilities of the pure metals Mg and Al were found to be $0.497_9 \times 10^{-6}$ and $0.602_7 \times 10^{-6}$ respectively. A method was developed to correct for ferromagnetic impurities in the Gouy method, which enabled the susceptibilities to be determined with an accuracy of .1 % relative to Ge.

From magnetic susceptibility measurements on the dilute alloys of Mn and Fe with Al and Mg , information was obtained about the electronic configuration of the transition elements. There was no evidence that the d electron wave functions spread out sufficiently through the crystal to form a d band. Nor was any dependence of electronic configuration on concentration of transition element observed for a given alloy system.

The effective Bohr magneton numbers of 5.2 and 4.7 for the Mg Mn and Mg Fe alloys respectively indicate that 4 to 6 of the d electrons of the transition element remain localized about their respective atoms. This is in agreement with the previously observed behaviour of Mn in Cu, Ag and Au, and of Fe in Au.

In the Al alloys however, a significant difference in the spectroscopic state of Mn and Fe was found. The

measured p_B values of 1.7 and 1.2 respectively indicate that the 3d shell could have either 1 or 9 d electrons with a corresponding change in the population of the conduction band. It was hoped that this change in conduction electron density would affect the electronic susceptibility sufficiently to make it possible to distinguish between these two electronic configurations, but the consequent change in p_B was found to be smaller than the experimental error. However, by comparing the results to the recent predictions of Lomer and Marshall (1958), it is expected that Fe and Mn in Al retain 1 d electron rather than 9.

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