MAGNETIC MOMENT OF IRON-NICKEL INVAR
ALLOYS BETWEEN 4 and 80 K

by R. W. Cochrane ©

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to rosemary
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ABSTRACT

The magnetic moment of several ferromagnetic f.c.c. iron-nickel alloys in the invar region has been investigated at low temperatures as a function of both the magnetic field and the temperature. A vibrating sample magnetometer has been constructed for these measurements with a relative sensitivity of three parts in $10^5$. Such data resolution has permitted a detailed analysis of the temperature dependence of the measurements resulting from contributions at constant volume from spin wave and single particle excitations together with a term describing the effects of volume change on the magnetization. Because of the very large and negative thermal expansion of commercial invar (Meincke and Graham, 1963), this latter contribution is very significant. When the single particle and volume terms are considered in conjunction with other thermodynamic data, they suggest that the invar alloys can be interpreted on a rigid band model. Consequently, this model has been analyzed with the result that the static magnetoelastic anomalies can be understood on the basis of an approach to instability of the ferromagnetic state occasioned by the shape of the density of states.
CHAPTER I
Introduction

(A) Introduction

This thesis is a report of low temperature magnetic moment studies of several iron-nickel alloys above 30 at.% Ni with a particular emphasis on a commercial grade invar (34 at.% Ni) manufactured by the Carpenter Steel Company. The experiments were performed on a vibrating sample magnetometer built by the author from the design published by Foner (1959). The apparatus is described in chapter two with great attention to the factors relevant to the optimum design and performance of the magnetometer. In undertaking this project, the large, negative thermal expansion coefficient of the commercial alloy has provided motivation because this anomaly was believed to be due to the volume dependent magnetic forces within the sample. Anticipating the results of later chapters, the magnetic moment was found to contain a very large contribution due to the contraction of the lattice at low temperatures in confirmation of the above assumption that the thermal expansion behaviour is controlled by the magnetic interactions. Correlation of the thermodynamic data from various sources points to an understanding of these alloys on the basis of a rigid band theory. The implications and conclusions of this model have been examined in detail in the final chapter,
and appear to be borne out by experiment to a high degree, especially in view of the rather simple nature of the model.

(B) The Invar Problem

It was in 1897 that Guillaume first alloyed 35 at.% Ni with iron and found a thermal expansion coefficient at room temperature which was an order of magnitude smaller than other metals. In obvious reference to this fact, he coined the name "invar" for the alloy. It is somewhat ironic, then, that the central characteristic of the face centred cubic iron-nickel alloys is an unusually large coupling between the lattice and spin systems which increase monotonically as more than 50 at.% iron is added to nickel. For this reason, the term invar will be used to describe the range of f.c.c. alloys from 50 at.% Ni down to below 30 at.% Ni. Invar properties have also been found in other alloy systems such as Fe-Pd and Fe-Pt so that much of the present analysis should be applicable to other than just the Fe-Ni alloys.

In spite of the long history of invar alloys, the reasons for their many unusual properties have been debated extensively, and as yet, no consensus has been reached. Detailed first principle calculations are not available so that most discussions are phenomonological, based on quite general considerations. Although the rigid band theory presented in this thesis hardly falls into the former category, it is founded on a wide variety of thermodynamic
FIGURE 1.1  PRACTICAL DIAGRAM FOR Fe-Ni ALLOYS
data. In this respect it should provide a reasonable guide to such calculations when they are performed.

Nickel crystallizes in an f.c.c. lattice structure; as iron is added, a continuous range of solid solutions is formed with the f.c.c. structure down to nickel concentrations below 30 at.% For lower nickel concentrations, the crystal symmetry is body centred cubic (b.c.c.), the low temperature \((T < 1183 \text{ K})\) phase for pure iron. Both sets of alloys exhibit ferromagnetism. Since the invar properties pertain only to the f.c.c. alloys, it is unfortunate that the transition region between the phases occurs right in the range of the invar anomalies. Such phase mixture tends to mask those properties particular to either one. Figure 1,1 represents a part of the effective phase diagram taken from Bozorth (1951) indicating the area over which the two forms may coexist. In fact f.c.c. alloys (with less than 32 at.% Ni) at room temperature are known to transform martensitically to the b.c.c. phase upon cooling to liquid nitrogen or helium temperatures. For more than 32 at.% Ni, a reasonably rapid cooling rate from the \(\gamma\) (f.c.c.) region down to room temperature is sufficient to insure that no \(\alpha\) (b.c.c.) phase is formed. Extensive temperature cycling between 4,2 K and 300 K of a 34 at.% Ni commercially available invar has shown no evidence of transformation indicating the \(\gamma\) phase is retained in metastable equilibrium even down to liquid helium temperature.
ATOMIC FOR FE-NI ALLOYS
MAGNETIC MOMENT PER

Figure 1.2

Kondorskii & Fedotov (1952)
Cranfell & Hallam (1963)
FCC
BCC
The spontaneous magnetization at $T = 0$ K plays a key role in the discussion of the invar problem. Central to most of the phenomenological theories proposed for these alloys is an explanation of this property. Figure 1.2, taken from the paper of Crangle and Hallam (1963) shows the average magnetic moment per atom (in units of the Bohr magneton, $\mu_B$) as a function of nickel concentration for both the f.c.c. and b.c.c. alloys. As the iron concentration in the f.c.c. alloys is increased, the magnetic moment rises linearly at a rate approximately corresponding to one Bohr magneton per hole added, indicating that the extra holes are all being aligned as they are added. However, in the neighbourhood of 50 at.\% Fe the moment deviates from linearity and above 60 at.\% Fe falls rapidly towards zero. On the other hand, the b.c.c. alloys exhibit only a gradual composition variation of the magnetic moment which is much larger than the f.c.c. moment throughout the region where the two phases can coexist. Figure 1.2 serves to underscore the nature of the invar alloys: as iron, which is itself magnetic, is added to the ferromagnetic 50-50 iron-nickel alloy, there is a sudden and dramatic disappearance of the ferromagnetism.

It is significant that the f.c.c. to b.c.c. transition region occurs just at the point where the f.c.c. alloys become nonferromagnetic. Since the b.c.c. phase has a large magnetic moment ($\sim 2\mu_B$ per atom), it is undoubtedly the
extra magnetic energy available in the b.c.c. phase which is responsible for the change. This hypothesis is supported by the following simple consideration. Above its Curie point when it is paramagnetic, iron does transform from b.c.c. to f.c.c. at 910°C. This indicates that the two non-magnetic lattices must still be close in energy at 0 K, i.e. a difference of approximately

\[ kT_{b.c.c.-f.c.c.} \sim 0.2 \text{ eV/atom} \quad (1.1) \]

Then it is only necessary to realize that the net exchange energy is of order 0.1 to 1.0 eV/atom, so that the magnetic energy appears sufficient to make up the deficit between the two phases.

(C) Survey of Invar Properties

Before discussing the various models which have been advanced for the invars, it is advantageous to examine some of their properties to provide a background upon which a critique of these theories may be founded. The following is by no means an exhaustive list, but certainly serves to characterize the alloys. The experiments divide into two categories which have been arbitrarily labelled, thermodynamic and heterogeneous.

(i) Thermodynamic Properties

A detailed description of the thermodynamics of a commercial polycrystalline invar (34 at.% Ni) has been given
by Graham and Cochrane (1969); the approach of this section
is similar to the outline of that paper.

Investigations of the magnetization of iron-nickel
alloys have been carried out by Crangle and Hallam (1963),
Kondorskii and Fedotov (1952), and by Rode, Gerrmann and
Mikhailova (1966). The former groups have stressed the
behaviour over the entire temperature range up the
Curie point. Extrapolation of the lower temperature points
to \( T = 0 \) yields the curve illustrated in figure 1.2. The
data of Kondorskii and Fedotov indicate little preference
between a \( T^2 \) or \( T^{3/2} \) dependence of the magnetization above
20 K; nevertheless, Crangle and Hallam have used the \( T^{3/2} \)
form exclusively. In a manner similar to the present work,
Rode, et al., have made a detailed study of the magnetization
behaviour of several iron-nickel alloys in the invar area.
However, their analysis can be faulted on two important
points. First of all, they have completely neglected the
magnetization change with volume which is undoubtedly of the
same order of magnitude as the corrections they do consider.
Secondly, the deviation term they have employed is applicable
only in the case where all the spins at \( T = 0 \) are aligned
("strong" ferromagnetism) which is certainly not the case
for the alloys with less than 50 at.% Ni.

The linear thermal expansion coefficient of iron-nickel
invars has been investigated recently by Meincke and Graham
(1963), White (1965), and by Zakharov and Fedotov (1967).
For the alloys with approximately 35 at.% Ni, the room temperature thermal expansion is indeed low, but the values show quite a wide variation between different samples. Nevertheless, the low temperature values agree remarkably well among all three. In this range the expansion is negative and much larger in magnitude than other metals and alloys. Below 10 K all the results are linear in temperature with a coefficient of order $-10^{-7}K^{-2}$. These findings are consistent with the viewpoint that the total expansion is a competition between a lattice contribution, which is small at low temperatures, and a magnetic one which dominates that interval. Hence, at low temperatures the small deviations between various experiments are not grossly apparent, whereas near room temperature when the two large contributions nearly cancel, their difference does fluctuate to a much larger extent. Finally, White's results on several other alloys with higher nickel concentrations indicate that the magnetic part decreases in size until above 50 at.% Ni the total expansion coefficient remains positive at all temperatures.

Implicit in assigning a large role in the thermal expansion to the magnetic forces is the assumption of a significant coupling between the lattice and the electrons responsible for the magnetism. Such an assumption is verified directly by the data of Kondorskii and Sedov (1958b, 1960a) and Kouvel and Wilson (1960) on the pressure...
induced change in the magnetization. The former authors, working at 4.2 K, have essentially shown that the $T = 0$ magnetization is a tremendously sensitive function of the pressure and hence of the volume. Part of the emphasis of this thesis has been to correlate the temperature changes of the magnetization and volume of these alloys to illuc—date further the effect of volume changes directly on the magnetization.

The thermodynamic Maxwell relation,

$$\frac{1}{V} \left( \frac{\partial V}{\partial H} \right)_{T,P} = -\left( \frac{\partial M}{\partial P} \right)_{T,H} \quad \text{(1.2)}$$

connects the volume magnetostriction to the pressure work referred to above. Vittoratos, Schlosser and Meincke (1969) have measured the linear magnetostriction of commercial invar. Assuming that this represents an isotropic dilation, and preliminary indications are that it does, they record a value which is 50 percent smaller than that of Kondorskii and Sedov for the comparable nickel concentration. If these results are accurate it would indicate that equilibrium thermodynamics may not be entirely applicable to this system. Further measurements by Schlosser, et al. (1969) indicate that at 4.2 K the magnetostriction is undergoing a slow relaxation towards larger values. This may help to reduce the difference, although it is still uncertain whether the discrepancy will be resolved.
Burford and Graham (1965) have measured the specific heat of the same commercial invar from 1 to 20 K. Their findings reveal a linear temperature dependence below 7 K with a coefficient of $1.2 \times 10^{-3} \text{J K}^{-2} \text{ mole}^{-1}$. The deviations from linearity are compatible with a lattice contribution for which the Debye temperature is 341 K.

(ii) Effects of Heterogeneity

Not only has crystal phase mixture been a problem in sorting out the iron-nickel anomalies, but even within the f.c.c. phase there are definite indications of magnetic heterogeneity due to the normal composition fluctuations inherent in a random alloy. Nowhere are these more evident than in the Mössbauer experiments of Nakamura, Shiga and Shikazono (1964, 1968). These authors have examined fine iron-nickel particles of submicron size for which the b.c.c. phase transition is suppressed down to at least 29 at.% Ni. For these alloys the Mössbauer spectrum shows both a ferromagnetic pattern and a paramagnetic one, or at least a magnetic one for which the internal field is not sufficiently strong to resolve the details. At any rate, the Mössbauer spectra point out the magnetic inhomogeneities whatever the exact nature of the magnetic states.

Another significant indication of the effects of composition fluctuations is the work of Siderov and Doroshenko (1964, 1965), in which they calculate the variation
of \( M(0) \) with composition for the \( fcc \), alloys. This is done by assuming that nearest neighbour iron atoms interact antiferromagnetically and then averaging the total effect over the local concentration. The excellent agreement they obtain with the results of Crangle and Hallam (1963) and Kondorskii and Fedotov (1952) seem to indicate that their consideration of the composition fluctuations is essentially correct.

(D) **Invar Models**

As pointed out in the introductory section, the interpretation of the invar properties has proceeded more or less phenomenologically. Consequently, there has arisen a variety of models attempting to explain one or more of the invar peculiarities. Several such suggestions will now be reviewed using the results just quoted to help form a critique of each.

(i) **Volume Sensitive Exchange Forces**

For many years the invars were described by assuming that the exchange forces responsible for the ferromagnetism changed radically under the extension or compression of the crystalline lattice. It was believed that the point corresponding to the mean exchange integral for invar was on the steep positive portion of the Bethe-Slater curve, a plot of exchange energy \( I \) as a function of interatomic spacing. Hence, the strong volume dependences of the
magnetic properties were explained simply by large values of $(\partial I/\partial V)$.

There are several objections to this approach. The Bethe-Slater curve itself can hardly be considered quantitative. It is based on speculations derived from a model of localized electronic spins interacting via an interatomic exchange mechanism between nearest neighbours. As neither of these assumptions is thought to apply to the 3-d transition metals, the Bethe-Slater scheme may not even have qualitative significance. Furthermore, there is the question as to why $(\partial I/\partial V)$ should be so large in the invar region and not so for the two constituents, iron and nickel.

(ii) Latent Antiferromagnetism

All the other models which have been advanced in the last ten years have concentrated on a discussion of the magnetization-composition relation, as shown in figure 1.2, and then focused on other anomalies. Undoubtedly, the most popular of these is the suggestion of "latent antiferromagnetism" made by Kondorskii (1959) and Kondorskii and Sedov (1960b). By this is meant that in the f.c.c. phase the exchange coupling between nearest neighbours iron atoms is antiferromagnetic whereas those between nickel atoms or iron and nickel atoms are ferromagnetic. Beginning at pure nickel, there is little effect upon the magnetic moment until the number of iron-iron nearest neighbour
pairs becomes significantly large. At this point, the moment starts to deviate from linearity and subsequently falls dramatically towards zero as the iron concentration is increased towards the critical composition where presumably the mean exchange energy vanishes. Presented in this way, the model essentially constructs a Bethe-Slater curve, but replaces the lattice parameter with iron concentration.

This theory has several supporting features which make it plausible. There exists some evidence, among them high temperature susceptibility measurements on f.c.c. iron-nickel alloys (Chechernikov, 1962) and low temperature measurements on an iron rich antiferromagnetic f.c.c. alloy (Kondorskii and Sedov, 1958a), which suggests that the iron rich f.c.c. alloys are indeed antiferromagnetic. Also Siderov and Doroschenko's calculation of the $T = 0$ magnetic moment as a function of composition originated from Kondorskii's idea although they do not make explicit use of it. Finally, sensitivity of the magnetization to volume changes is incorporated because of the fact that the magnetization of all the invar alloys depends critically on the actual concentration at which the mean exchange energy vanishes. By assuming that this critical concentration has a moderate volume dependence, through the exchange integrals, a large volume derivative of the magnetic moment results.

Since the qualitative predictions of Kondorskii's
model are in reasonable agreement with experiment, a critique is best aimed at the implicit assumptions. A prerequisite of this theory is that the magnetic moment of the 3d electrons is localized about their respective ionic sites. It is a fact that much of the difficulty in a coherent treatment of the 3-d transition metals has been due to the lack of a clear distinction between purely itinerant and localized effects. However, recent experimental studies on Fe and Ni (reviewed by Herring, 1966) would indicate that both the 3d and 4s electrons can be interpreted as itinerant in character. The extrapolation into the alloy system is certainly not trivial but it is difficult to imagine the alloying process changing the itinerant nature of the 3-d electrons. Moreover, Herring (1966) has reviewed the arguments for the localization of the electrons and concludes that "...evidence seems to add up to a fairly clear preference for a localized model for at least most of the rare earth metals, and an itinerant model for metals with incomplete d shells."

On a more direct level, the existence of antiferromagnetic regions which is suggested experimentally, at least indirectly, does not support this model exclusively, since a change in magnetic phase is inherent in all the theoretical approaches.

(iii) Weiss Model

R. J. Weiss (1963) proposed that the invar effect was due to the existence of two low lying electronic states
for iron in a face-centred cubic lattice—a low volume, low magnetic moment (0.5 μₜ/atom) structure stable at T = 0 which was antiferromagnetic, and a higher volume, high moment (2.8 μₜ/atom) one which was ferromagnetic. These two configurations were separated by some 0.036 eV, and were derived from one another by essentially an electron transfer from a spin up to spin down state or vice versa. By assuming that the addition of nickel to f.c.c. iron would reverse the order of these levels at 30 at.% Ni, he was able to account for the magnetic transition from non-ferromagnetic to ferromagnetic in the f.c.c. alloys. Also, the fact that the configurations have different volumes at least qualitatively recognizes the peculiar volume properties. The weakness of the Weiss model is in the temperature dependences which it predicts: the low temperature thermodynamics should be dominated by exponential terms in the specific heat, thermal expansion and magnetization which are not observed. The disagreement in low temperature behaviour is not entirely surprising since the basic idea was deduced from high temperature specific heat measurements on iron (Kaufman, Clougherty and Weiss, 1963).

(iv) Spin Wave Instability

In recent years investigations have been initiated (see Katsuki and Wohlfarth, 1966) into the relative stability of the various magnetic phases in metals. It turns out that one of the more revealing criteria for ferromagnetic
stability is the behaviour of the spin wave dispersion coefficient, \( D \), defined by

\[
E_k = k \omega_k = Dk^2 \tag{1.3}
\]

where \( E_k \) is the spin wave energy for frequency \( \omega_k \) and wave number \( k \). Although these calculations are in a quite primitive stage, the dispersion coefficient is undoubtedly a sensitive function of the band structure. This observation has led Katsuki (1967) to speculate that the invar anomaly is a result of \( D \) changing sign near 30 at.% Ni. Such an effect would destroy the ferromagnetism as the system would be unstable against the excitation of spin waves even at \( T = 0 \). The spin wave dispersion measurements of Hatherly, et al., (1964) indicate that \( D \) does decrease monotonically from pure nickel to 36 at.% Ni and below 50 at.% \( D \) falls toward zero linearly with the Curie temperature, \( T_c \).

However, with the decrease in spin wave excitation energy, one might expect a contribution to be evident in the specific heat but such is not seen. It is interesting to note that there is a parallel between this result and the band theory to be discussed in the next section. Doniach and Wohlfarth (1965) have deduced that the zero in \( D \) for a weak itinerant ferromagnet coincides with the Stoner criterion for instability of the ferromagnetic state. In view of the interpretation of this thesis that advocates just such a Stoner instability in the invars, the decrease in the spin wave dispersion coefficient may just be a
consequence of this more fundamental property,

(v) **Band Theory**

Considerations of the itinerant character of the electrons leads to the Stoner model for the ferromagnetism of metals and alloys. The description of the invar alloys in these terms is actually quite straightforward and is given in the appendix in some detail. The emphasis there is placed on the so-called weak ferromagnet for which the significant parameter at $T = 0$ is $\left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0}$ where $U$ is the total internal energy and $\sigma$ is proportional to the total magnetic moment. As $\left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0} \rightarrow 0^+$ the system goes over to a nonferromagnetic state in a continuous manner, i.e., $\sigma_0 \rightarrow 0$. The condition for this is determined by a detailed balance between the band (kinetic) energy and the exchange energy.

Shimizu (1964, 1965) has shown that the band model will support ferromagnetism even when the "Stoner Criterion" (see appendix) is itself invalid. This is accomplished by rather special band shapes in the neighbourhood of a peak in the density of states. Shimizu and Hirooka (1968) and Mizoguchi (1968) have applied simple band theory to the invars. These authors have emphasized Shimizu's extended condition for ferromagnetism due to the fact that the density of states function which they derive from specific heat data does not satisfy the Stoner criterion below 50 at.\% Ni. A consequence of this theory is that the magnetic transition
is first order and they estimate it should occur below 20 at.% Ni. Such first-order transitions have not been found in the invars, so their analysis can be faulted on this ground. Presumably, the large volume derivatives arise through sample inhomogeneities so that compression or expansion of the lattice permits some regions to transform without affecting the rest of the sample. Concentration fluctuations are undoubtedly important in certain measurements, but it is felt that they contribute because of the invar property, but are not a prerequisite for observing the thermodynamic anomalies.

The invars have been analysed in terms of the approach to the Stoner criterion by Graham and Cochrane (1969), Mathon and Wohlfarth (1968) and Wohlfarth (1969). Graham and Cochrane have applied the band model to a discussion of the thermodynamics of a commercial invar alloy. Their approach will be followed in detail in the final chapter. It will suffice here to mention that such a model naturally encompasses the observed linear temperature dependences in the thermodynamic properties as well as the significant volume anomalies which were discussed earlier. Mathon and Wohlfarth have shown that the linear relation between $T_c^2$ and concentration for Fe-Ni alloys from 25 to 50 at.% Ni (Bolling, Arrott and Richman, 1968) is a definite prediction of this theory of very weak itinerant ferromagnetism.
CHAPTER II

Vibrating Sample Magnetometer

(A) Introduction

The measurement of magnetic moments or magnetization has long been a fundamental tool in the investigation of many diversified areas of physics: ferromagnetism, antiferromagnetism, superconductivity, fermi surface topology, and others. However, it is only recently (Foner and Thompson, 1959; Argyle, Charap and Pugh, 1963) that the technology of these measurements has advanced to the point of allowing definitive measurements on the finer details of the magnetic structure in these studies, such as the spin wave magnetization of iron and nickel metals. Generally, magnetization experiments can be arranged into one of three categories, the force or torque method, induction techniques or the several ways of determining internal magnetic fields, such as NMR or Mössbauer spectroscopy.

The earliest form of the induction technique was the sample extraction method in which a magnetized sample was removed from a coil thereby generating a deflection in a ballistic galvanometer connected in series with the coil. The vibrating sample magnetometer (hereafter abbreviated VSM) was developed about ten years ago by Foner at M.I.T. and is in many ways just an extension of that original
FIGURE 2.1 GENERAL SCHEMATIC
experiment. A schematic of the VSM is shown in figure 2.1. As the name implies the sample is oscillated mechanically with a small amplitude at some low frequency; the relative motion between the sample and the pickup coils induces a voltage in the latter proportional to the product of the total magnetic moment and the relative velocity. The connection with the earlier method is obvious; the advantage lies in the fact that the operation is performed not just once, but continuously, many times a second. The periodic motion allows synchronous detection to lock into extremely small voltages even in the presence of large noise signals.

In describing the present apparatus, the main references are to the paper by Foner (1959) mentioned previously, and to a set of three papers by Feldman and Hunt (1964a, b, 1965). Necessarily, the system described here is identical in principle to these prototypes, although it does differ in many of the actual details.

The basic mechanics of the VSM are quite simple, as illustrated in figure 2.1. Motion of the sample in the vertical, z, direction is provided by direct connection of it to a loudspeaker. The time varying field of the sample is sensed by the pickup coils. If it is assumed that the sample acts as a point magnetic dipole located at its centre, then Faraday's equation implies that the voltage, V, is given by
\[ V = -\frac{d\phi}{dt} = -\frac{\partial \phi}{\partial z} \frac{dz}{dt} \]

\[ = z_0 \omega \sin \omega t \int_{\text{coil}} \frac{\partial \mathbf{B}}{\partial z} \cdot \mathbf{n} \, dA \quad , \tag{2.1} \]

where the sample motion is defined as

\[ z = z_0 \cos \omega t \quad , \tag{2.2} \]

and \( \mathbf{B} \) is the flux density of the sample. The standard form for the flux density of a point magnetic dipole of moment \( m \) pointing in the x-direction, the direction of the applied field, is

\[ \mathbf{B}(x,y,z) = \frac{\mu_0 m}{4\pi} \left[ -i \left( \frac{1}{r^3} - \frac{3x^2}{r^5} \right) + \frac{xy}{r^5} \mathbf{j} + \frac{xz}{r^5} \mathbf{k} \right] . \tag{2.3} \]

The particular component of \( \mathbf{B} \) involved in equation (2.1) depends on the axis, \( \mathbf{n} \), of the pickup coils. For example, if the coil axis is parallel to the magnetic field equation (2.1) becomes,

\[ V = z_0 \omega \sin \omega t \int_{\text{coil}} dA \left[ \frac{3\mu_0 m}{4\pi} \left( \frac{z}{r^5} - \frac{5x^2 z}{r^7} \right) \right] . \tag{2.4} \]

This result is valid for small amplitudes of vibration, since only a first-order expansion has been made about the mean sample position. Typically, amplitudes are the order of 0.1 mm which is indeed small compared with all other dimensions of importance.

Other effects may also contribute to the flux in the coil. For ferromagnetic and other samples of high moments, magnetic image effects in the highly permeable pole faces...
may be important as will the shape effects due to non-uniform and demagnetizing fields inside the sample.

Since the output voltage is directly proportional to the sample magnetic moment, this voltage can be used directly as a measure of the moment. For detailed studies of the sample magnetization a null technique is employed to increase the sensitivity and to eliminate the velocity dependence. A second control signal which also varies as the sample velocity is derived and then mixed with the sample signal to obtain a null. In his apparatus, Foner made use of a small permanent magnet fastened to the drive rod and a second set of coils situated nearby. The version produced by the Princeton Applied Research Corporation employs a vibrating capacitor assembly with one plate fixed and a second plate attached to the drive rod. In the latter arrangement, the reference voltage is a product of the velocity of the motion and the d.c. voltage applied across the capacitor. The latter type of reference signal was chosen for the present system since it can be so readily adjusted by controlling the applied voltage. Another advantage arises from the fact that the magnetometer is easily automated to provide a continuous null balance even though the sample moment may be changing due to field or temperature perturbations. When the sample signal has been offset by the reference voltage, the magnetic moment is given directly by the d.c. voltage applied to the capacitor, independently of the velocity of motion.
Details of the Vibrating Sample Magnetometer

(i) Mechanical Drive System

Central to the mechanical system is the transducer. Throughout the development of the VSM several electro-mechanical transducers have been used, but most of the experiments were carried out with a 40 watt public address loudspeaker driver manufactured by University Loudspeakers. This unit was modified to allow direct access to the hemispherical apex which forms part of the voice coil support. A teflon extension piece was epoxied directly to the apex and supported a lucite collet for direct coupling to the drive rod. This unit has proven exceptionally rugged in operation and has required no special attention in handling. Because the low frequency response cuts off below 80 Hz, the normal operating frequency was chosen to be 96 Hz, which is far enough away from 60 Hz to reduce any contamination by the a.c. line frequency or its harmonics. Some work has been done with a 30 watt high fidelity woofer from Lafayette Radio Electronics. In this case, a similar clamping arrangement was glued to the apex of the speaker cone with the result that the two drivers were completely interchangeable. The woofer has a much lower cut off frequency, but the suspension is necessarily more flexible so that this unit is more susceptible to spurious vibrations. For this reason the University P.A.
driver has been used almost exclusively. Nonetheless, it would be very interesting to study the fine structure of the magnetization curves as a function of frequency to ascertain the effects of eddy currents, image effects, etc.

The drive system is powered by a high fidelity, low hum power amplifier fed from a Marconi Instruments Limited, Model TF 2100 A.F. oscillator. The oscillator has been selected for its very high frequency and amplitude stability to insure maximum regulation of the velocity. Although the balance between the sample and reference signals is independent of the velocity, the different characteristics of the two circuits result in different transient responses to velocity changes. It is for this reason that care has been exercised to control the velocity wave. In addition, an electronic feedback network has been considered to further control the motion of the drive rod, but velocity changes do not constitute the limiting factor in the sensitivity of the present system so this alteration has not been pursued.

The drive rod was constructed from pyrex glass tubing 8 mm. in diameter at the top but only 4 mm. diameter for the lower 12 in. For low temperature application glass offered the advantages of very high thermal and electrical resistivities together with a very low thermal expansion coefficient. The two glass pieces were fused together forming a hollow tube about 80 cm. long through which the thermocouple and heater
FIGURE 2.2 DETAILS OF DRIVE ROD

- brass nuts
- brass rod
- a.c. leads
- d.c. leads
- insulating washers
- aluminum table
- heater
- thermocouple
- pyrex tubing
- 80 cm.
- copper post
- sample
leads were passed. In this manner, the sample region was accessible to the electrical leads without interference to the mechanical motion of the rod. At the sample end, a high purity copper rod, 15 mm. long, 5 mm. diameter, was glued onto the pyrex tube, forming a extension to it. Formvar coated manganin wire was bifilarly wound on this copper post as a heater and a thermocouple junction soldered to it with indium metal. To permit quick mounting of the specimens, the free end of the copper was cut into a 4-32 screw. The samples were epoxied with ecolobond cement onto a threaded copper holder which mated with the screw and insured good thermal contact between the sample, thermocouple and heater. Two small holes were made in the pyrex tube above the copper post for the leads and a teflon centring washer press fitted to the tube. At the head of the drive rod a slotted brass fitting, threaded at the top, provided coupling to the driver. Figure 2.2 shows the drive rod and the sample connection.

The reference capacitor system consists of three parallel plates two of which are rigidly fixed to the cryostat while the centre one is bolted to, but insulated from the threaded brass rod which connects the driver to the glass drive rod. The capacitor plates have been cut from 0.063 in. brass sheet and are oval in shape with a width of approximately 3 in. To avoid problems with stray charges trapped by the insulating oxide layer the plates
FIGURE 2.3 REFERENCE CIRCUIT

PHILBRICK
PR-30
C -15 ±15

10 M.

47k

40 M.

5 μf.

AD0-26

10 M.

15k

20k

0.5 μf.

TO DETECTOR

PHASE SHIFTER

DIVIDER

REFERENCE AMPLIFIER
were covered by a gold film by immersion in Atomex Gold Immersion Solution. When so plated, there was a noticeable reduction in the drift of the capacitor signal. A high input impedance difference amplifier shown in figure 2.3 is coupled across the stationary plates; the d.c. source voltage is applied to the moving plate. By using a differential connection, the reference voltage can be made independent of small changes in the relative position of the fixed and moving plates, eliminating in first order the result of undesired vibrations of the magnetometer.

(ii) **Pickup Coils**

Integration of equation (2.4) depends on the exact geometry of the sample and pickup coils, but inspection of this equation indicates that the output voltage is an odd function of $z$ (vibration axis) and an even function of both $y$ and $x$ (field axis). Such considerations are essential in designing the coils. For this experiment the coil configuration has been chosen as four pancake shaped coils with axes parallel to the magnetic field. As shown in figure 2.4 these coils are connected with the top pair in series opposition to the bottom pair so as to satisfy the above symmetry relations. Because of the series opposing orientation of the coils, this arrangement is insensitive, to first order, in the background noise due to magnetic field instabilities even though individual coils do sense these fluctuations. Furthermore, this coil configuration
Figure 2.4  COIL VOLTAGE OUTPUT
maximizes the available working space between the pole faces of the magnet, an important feature for low temperature measurements for which dewars must also be mounted in the gap. Within this coil geometry, equation (2.4) can be used to indicate the maximum signal by noting that the contribution to the flux through the coils changes sign with the factor

\[
\left( \frac{z}{r^5} - \frac{5x^2z}{r^7} \right) .
\]

Evidently the maximum signal is obtained when the coil subtends an angle $\theta$ at the sample centre given by

\[5 \cos^2 \theta - 1 = 0 \quad (2.5)\]

which is about 63 degrees.

Seven hundred turns of number 38 enamelled copper wire were wound in four layers on lucite forms, 1.5 in. in diameter and 0.25 in. thick, to a resistance of 165 ohms apiece. To support the coils rigidly, they were glued in pairs to thin lucite sheets so that they could be strapped flush against the magnet pole faces. Since the distance from the sample centre to the plane of the coils is 1.13 in., the angle subtended by each coil is nearly 53 degrees. Hence, the sample signal could be increased by making slightly larger coils or better still, by moving the present coils a little closer to the sample as this has the additional effect of reducing the $r^5$ factor.
Most important in determining the signal gain is the mean sample position relative to the coils. Figure 2.4(a) shows a rough sketch of the output as a function of sample position in the x-z plane. A detailed examination of the peak about the coil centre is given in figure 2.4(b) as measured on one of the invar samples at room temperature. This latter plot clearly reveals the necessity for reasonably precise positioning of the sample. In addition, such adjustment of the sample into the saddle point region minimizes the signal’s dependence on spurious motion of the sample or the detection coils.

For room temperature measurements other coil configurations might prove more convenient, as for example, coils with axes along the vibration direction. It is worth noting that this arrangement requires coil geometry for which the output is an even function of y and z but odd in x. In this case, the optimum angle subtended by the coil in just twice the complement of the angle for the field oriented coils, that is, 54 degrees. The factor of two comes about because the sample is centred along the coil length to satisfy the symmetry requirement in this direction. The reader is referred to the original paper by Foner (1959) for a complete study of the relative output as a function of sample position for this coil geometry.

(iii) Magnet and Power Supply

A model L-158 Harvey Wells electromagnet provides
the necessary magnetic field to magnetize the samples.
The pole faces are 12 in. diameter, while the gap is 2.62 in., allowing sufficient space for detection coils and the conventional double dewar system. Most experiments utilized a model DCR 40-125 Sorenson power supply which unfortunately suffered the limitations of poor regulation and long term current drift. These problems were remedied in the later experiments with a Harvey Wells model H.S. 1050A precision magnet power supply which has parts in $10^5$ regulation and long term stability. As both of these units generate only five kilowatts of power, the maximum field was slightly in excess of 13 kOe. A Magnion 20 kilowatt precision supply, model H.S. 10200, has just been installed and extends the available field to over 20 kOe.

(iv) **Electronic Detection System**

As described earlier, the function of the detector system is to mix and null the signals from the reference capacitor and the pick up coils and to read out the d.c. capacitor voltage which is then a direct measure of the sample magnetic moment. Basically all that is required is the application of the correct voltage to the vibrating capacitor plate producing zero output from the detector. It is apparent, however, that the signal to noise ratio of the reference voltage is proportional to the applied d.c. voltage, if it is not too large, with the result that it becomes advantageous to maintain this voltage as large
as possible. For large moment samples, the applied voltage is kept between 100 and 200 volts by tapping from a battery source of 220 volts supplied by five "B" batteries in series. The capacitor signal is fed to the reference amplifier shown in figure 2.3. Because of the high source impedance of the capacitor, this amplifier is inserted as an impedance matching device reducing the output impedance to a convenient level to power the phase shifter. Gain of the amplifier is set about 4 or 5 generating a maximum signal of nearly 200 millivolts amplitude at the detector input. This is at least a factor of two greater than the signal produced by any sample yet investigated.

The remainder of the reference input circuit is shown with the amplifier schematic. Although theoretically both signals are in phase with the velocity, the phase shifter is required to compensate any phase differences which arise in the actual coupling to these signals. Also, there may be some mechanical lag due to flexing of the drive rod. The phase shifter is quite simple, being just a phase splitter transformer followed by a capacitor and variable resistance. The advantage of this design is that the output amplitude is essentially independent of the phase angle which is important when the phase must be altered during an experiment for any reason. Correct phase adjustment is maintained by monitoring on an oscilloscope the a.c. difference signal in the detector before it is rectified. The attenuator consists of a resistive divider network of approximately 100 kΩ resistance, decreasing the maximum...
signal at the detector by a factor of 1000 in ten steps. The attenuator sets the range of the magnetometer. By selecting the proper range and a corresponding value of the detector gain, the magnetometer is conveniently adjusted to measure magnetic moments of any magnitude from the smallest to the large moments of ferromagnetic materials.

The detection coil voltage is itself amplified by a factor of fifty by means of a model 0-14 transformer manufactured by United Transformer Corporation. In using the transformer, large voltages are obtained at the detector input while the pickup coils themselves remain physically small for maximum gap space in the magnet. Although this procedure does not affect the noise characteristics for high signal levels, there is a degradation of performance for very small signals. This can be understood as follows. The transformer steps up the thermal noise voltage generated in the coil as well as the induced signal from the sample. On the other hand, if the coils were wound with a much greater turns density, the induced signal and the coil resistance would increase linearity with the number of turns. However, the thermal noise varies only as the square root of the coil resistance and so will not increase as fast as the induced signal. In this way the signal to noise ratio for small moments could be increased. In the present work, very strongly ferromagnetic metals have
FIGURE 2.5  SCHEMATIC CIRCUIT

- DRIVER
- POWER AMPLIFIER
- OSCILLATOR
- BIAS
- BATTERY
- BUCK OUT BATTERY
- P.A.R. HR 8
- 3 µf
- 10 M.
- KINTEL III AF
- MEDISTOR A-75A
- STRIP CHART RECORDER
been examined for which the thermal noise is about an order of magnitude below the limiting sensitivity. It was only when attempting to grade the magnetometer performance by using a small copper coil as a dummy magnetic moment that this effect was noticeable.

Phase sensitive detection is provided by a Princeton Applied Research Corporation model HR-8 Lock-in-Amplifier with a type A preamplifier which has an input impedance of 10 MΩ. Since the preamplifier has a difference input channel, it has been used as the mixing element in the circuit. Continuous automatic null balancing at the detector input is accomplished by electronic feedback from the detector output—a d.c. voltage—through an integrating amplifier to the vibrating capacitor plate. The feedback voltage is in series with the battery bias and adds algebraically to it. The integrating amplifier, a model 111AF Kintel d.c. amplifier, has been modified for resistive input and capacitive feedback impedances in the usual operational integrator configuration. The available output from the integrating amplifier is about ± 70 volts.

Finally, the feedback voltage is determined by a potentiometric arrangement shown in the figure 2.5. The voltage is divided down to a convenient level, bucked out from a stable supply so that the difference signal can be amplified and applied to one pen of a two pen strip chart recorder. The standard voltage supply is a 4 volt mercury battery bank feeding a precision voltage divider, model 60 A/C.
FIGURE 2.6 THE CRYOSTAT
from John Fluke Manufacturing Company, Incorporated. In practice the divisions on this attenuator are used as arbitrary units for measuring the sample magnetization. Absolute calibration requires additional procedures which are described in section (E).

(C) The Cryostat

As illustrated in figure 2.6, the cryostat and magnetometer have been integrated into a single unit. The main support plate is a 16 in. diameter, 0.25 in. thick brass disc which has a matching aluminum hat, 11 in. high to allow for evacuation of the working space. Support for the various drivers is provided by a 2 in. wide, 13 in. diameter aluminum ring held by four brass legs soldered to the cryostat floor. A padding of foam rubber over the ring mechanically isolates the driver from the rest of the apparatus. Whereas the woofer can sit directly on the supporting ring the much smaller P.A. driver is threaded into a brass plate which in turn rests on the aluminum ring. Not only does this arrangement shock mount the driver unit but the freedom of movement also allows for optimum alignment of the drive rod when connected.

The stationary capacitor plates are enclosed in a copper shielding box which mounts on a small aluminum table bolted to the cryostat plate. Lead wires are brought out through a seven pin connector screwed to the copper shield.
Electrical access to the system is furnished by three vacuum tight seals: separate continuous fusite seals for the thermocouple and the transducer wires and a demountable multi-pin Cannon connector for the other leads.

A 28 in. long appendix has been soldered into a hole cut in the cryostat floor and forms the sample chamber housing the drive rod. This tube is constructed of 0.75 in. German silver thin walled tubing at the top which telescopes to 0.375 in. tubing in the bottom 12 in. below a demountable flange with an indium O-ring seal. Alignment of the drive rod and the appendix is crucial for maximum signal resolution, since any unnecessary friction degrades the velocity and introduces unwanted synchronous vibrations to the entire apparatus. Contact should occur only at the teflon centring washer above the sample in such a manner as to minimize the oscillation of the tail section.

Double walled glass dewars are used to store the nitrogen and helium refrigerants for experiments at low temperatures. Operation in the magnet gap forces both dewars to have narrow tail sections; the inner helium dewar has a working diameter of nearly 0.60 in. and an outer diameter of 1.0 in.; the nitrogen dewar has corresponding tail dimensions of 1.25 and 1.75 in. respectively. Soldered to the underside of the cryostat floor is a brass collar with a flange to which the helium dewar is bolted while the nitrogen dewar is suspended from the flange in a wire cage.
The inside of the magnetometer chamber is completely separate from the dewar space. The helium liquid transfer tube and the gas return line have been brazed directly into the brass collar.

In operation, the entire unit is supported on the magnet by two slotted brass panels which slide on four brass nuts threaded onto 3/4 in. brass bolts. Vertical adjustment of the cryostat and hence of the sample position is carried out by setting the height of the brass nuts. The bolts ride in the slotted holes for positioning the apparatus horizontally. This method locates the sample adequately, if somewhat crudely.

(D) Thermometry

All temperature measurements were made with a 30 gauge copper-constantin thermocouple soldered directly to the sample or to the copper sample holder. The reference junction was maintained in a water triple point cell. Although more sensitive thermocouples are available for the liquid helium temperature region, the magnetometer sensitivity did not warrant such a change, and the accessibility and ruggedness of the copper-constantin wire were definite advantages. The thermoelectric voltages were reduced on a Medistor model A-75A potentiometric microvoltmeter and recorded on the second pen of the chart recorder. Interpolation of this trace allowed voltage differences of 0.1
TABLE 2.1

Coefficients in least square fitting of copper constantin thermocouple voltage,

\[ E = \sum_{n=0}^{6} A_n T^n \]

<table>
<thead>
<tr>
<th>n</th>
<th>( A_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( 0.62472 \times 10^4 )</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>(-0.1704)</td>
</tr>
<tr>
<td>3</td>
<td>( 0.8568 \times 10^{-3} )</td>
</tr>
<tr>
<td>4</td>
<td>(-0.3714 \times 10^{-5} )</td>
</tr>
<tr>
<td>5</td>
<td>( 0.8482 \times 10^{-8} )</td>
</tr>
<tr>
<td>6</td>
<td>(-0.7742 \times 10^{-11} )</td>
</tr>
</tbody>
</table>

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to 0.2 μv to be resolved.

The thermocouple was calibrated by comparison with a platinum resistance thermometer in the region from 12 K to 300 K. A least squares fit was performed on this data in the form

\[ E = \sum_{n=0}^{6} A_n T^n, \quad (2.6) \]

where \( T \) is the absolute temperature. To take into account that

\[ \left( \frac{dE}{dT} \right)_{T=0} \equiv 0 \quad (2.7) \]

the coefficient \( A_1 \) was set identically zero so that equation (2.6) involves only six coefficients \( A_n \). Table 2.1 lists these coefficients. Equation (2.7) represented one calibration point below 12 K; a second point was the normal boiling point of liquid helium as determined from the vapour pressure. Near 4.2 K the values calculated from formula 2.6 agree with the measurements to within 0.2 K. As the temperature and hence the thermocouple sensitivity increase, this difference decreases being 0.04 K at 100 K. For this reason, the temperature was determined by inverting equation (2.6).

Extensive calibration tables for copper constantin thermocouples have been prepared by Powell, Caywood and Bunch (1962). Comparing their results to those of equation (2.6) nowhere gives deviations greater than those quoted above. This excellent agreement reinforces our confidence in...
this procedure.

Because the thermocouple was referenced to the triple point of water, the thermal voltage generated when the sample was at 4.2 K was about 6245 μV. Run to run variations in this value were about one or two microvolts. As well, drifts of the same order were observed during any one run due probably to inhomogeneities in the wire which experience varying temperature gradients as the helium and nitrogen boiled away. Compensation for these effects was made by taking the helium bath reading as the zero point and then measuring the voltage changes with respect to it. In this way a continuous calibration at the liquid helium boiling point is maintained.

(E) Operation and Calibration

The operation of the VSM involves two steps, the positioning of the magnetometer and the adjustment of the electronics. After the mechanical system has been connected the driver is shifted about to give the smoothest possible motion to the sample and a minimum of vibration to the magnetometer frame. Care at this stage can increase the ultimate sensitivity by as much as an order of magnitude. The sample space is evacuated and a small pressure of helium exchange gas introduced for thermal contact with the bath. After the dewars are mounted, the entire cryostat is centred on the magnet. Final positioning is performed
FIGURE 2.7 RECORER TRACING

\[ \Delta T = 1 \mu \text{V} \]

\[ T = 6244.2 \text{ uv} = 4.2 \text{ K} \]

\[ \frac{\Delta M}{M} = 4 \times 10^{-4} \]
by moving the sample while watching the output voltage for
the saddle point region defined by figure 2.4. It is
imperative that, upon adjusting the cryostat, the dewars
not contact the pickup coils since this dramatically
increases the noise in the sample signal.

The magnetometer has been used to measure the magnetic
moments of a number of invar alloys as a function of
temperature and applied field. Figure 2.7 shows a recorder
trace for a sample cooled to liquid helium temperatures.

Short term sensitivity in $\Delta M/M$ is seen to be several parts
in $10^5$ obtained by correlating the magnetization and tem­
perature pulses. Also evident on this trace is a monotonic
background drift whose origins are both mechanical and
electrical as discussed in the final section of this chapter.

These invar samples are ferromagnetic with magnetic moments
in the neighbourhood of 200 emu. The VSM stability allows
detection of changes of about $5 \times 10^{-3}$ emu. To investigate
the limit of detection for the apparatus a small current
carrying copper coil was mounted in place of the sample.
In this way the ultimate sensitivity was found to be of
order $10^{-4}$ emu.

When the magnetic field range was extended to 20 kOe,
it revealed a fault in the apparatus above 13 kOe. In
this region the apparent magnetic moment actually decreased
with increasing magnetic field for all samples. That this
result was spurious was independently ascertained by a
measurement of the dynamic susceptibility at 1000 Hz of
the commercial invar in the de Haas van Alphen apparatus
of R. H. Hum. This experiment revealed a susceptibility
above technical saturation which was constant to better
than a part in $10^5$ per oersted in all fields up to 30 kOe.
Two possible explanations have been proposed for this
behaviour. As the magnetic field increases there is a
considerable force on the sample which may result in a
change in its position or velocity. A second source arises
from magnetic image effects in the magnet pole faces. At
low fields the pole pieces have a high permeability so the
eddy currents induced by the varying field of the moving
sample will produce a signal in the coils. At high fields
the permeability decreases as the magnet begins to saturate
producing a corresponding change in the coil voltage. Quite
possibly the behaviour is a combination of all these effects.

Absolute calibration of the VSM is carried out in
either one or both of two methods. The obvious way is a
direct comparison of the output signals for the unknown
sample with a calibration standard of known magnetic moment,
usually taken as nickel metal. However, this requires that
both samples be positioned reasonably accurately with
respect to the pickup coils. Because of the rough
positioning facilities for this apparatus, absolute values
could be obtained to only a few percent by the comparison
method. For ferromagnets of high initial permeability, $\mu$,
Case and Harrington (1966) have reported a second calibration procedure based on the initial slope of the magnetization-field curve. For small values of the applied magnetic field, $H_a$, the internal magnetic field, $H_i$, is essentially zero; that is to say, the demagnetizing field just cancels the external field,

$$H_i = H_a - 4\pi N M \approx 0,$$

(2.8)

where $N$ is the demagnetizing factor which, for the spherical samples studied, is just 1/3. Moreover, the magnetization,

$$M = \frac{\mu - 1}{4\pi} H_i,$$

(2.9)

can be expressed as a function of the external field by combining equations (2.8) and (2.9) into

$$4\pi M = \frac{H_a}{\frac{1}{\mu - 1} + N}.$$

(2.10)

The output voltage of the magnetometer is proportional to the total magnetic moment, $MV$, where $V$ is the volume of the sample. Hence, the output voltage, $E_o$, is given by

$$E_o = KV 4\pi M = KV \frac{H_a}{\frac{1}{\mu - 1} + N}.$$

(2.11)

If the permeability is large, its contribution to equation (2.11) can be ignored so that the calibration factor, $KV$, is given in terms of the initial slope of the output voltage-field curve by

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Critique of the Apparatus

The experience accumulated over the past two years has indicated the relative strengths and weaknesses of the present system. Undoubtedly the primary feature of the VSM is the straightforward measurement of the entire spectrum of magnetic moments without recourse to intermediate operations such as voltage integration. There is, however, no doubt that quite a high degree of electronic sophistication must be attained to extract the finer details of the magnetic moment. It is felt that this requirement has been achieved with the present electronic system. On the other hand, the mechanical construction of the magnetometer could be profitably improved.

It has already been noted that the vibrating capacitor assembly tends to pick up stray charges constituting a source of output drift. Depositing a gold film on the plates reduces the drift significantly, but the subsequent performance slowly deteriorates with the result that they should be replated periodically.

Integration of the mechanical and cryogenic systems at the main support plate has proven to be the most serious limitation. Boiling refrigerants, particularly the liquid nitrogen, are a source of constant vibration, but their effect would be reduced somewhat by a separation of the
magnetometer and the dewars. Moreover, the positioning adjustment is quite crude, in part because of the intimate coupling of the various units. Decoupling of the magnetometer from the cryostat would permit the sample to be changed much more conveniently and quickly without reinitiating the entire setup procedure or without even boiling off the refrigerants. It is also felt that a positioning table with micrometer adjustment should be added. Such a device could be fitted with a rotation facility, a feature not found in the present apparatus, but very useful for examining magnetic anisotropy. In line with these alterations it would be worthwhile to combine the nitrogen and helium dewars into a single unit employing only a nitrogen cooled shield in the appendix around the sample. Such a dewar would eliminate noise caused by the nitrogen dewar bouncing against the inner helium dewar and would remove liquid nitrogen from the immediate region of the sample and the coils. This would be important for weakly magnetic samples, as nitrogen readily dissolves oxygen which is quite strongly paramagnetic.

With the present system flexure of the main cryostat plate has been a great headache. At a thickness of 0.25 in., it is not sufficiently rigid to the forces exerted on it when evacuated on one side, or by the weight of dewars and liquid on the other. Since both reference and coil signals are very sensitive to cryostat position, there is
a noticeable change in the output voltage if, for example, the system is evacuated. However, it is the reference voltage which is most affected as the stationary sections are bolted directly to the cryostat plate. This effect can be remedied by increasing the thickness of this plate. In addition, drift in the sample position occurs when liquid helium is introduced around the magnetometer appendix. Apparently the orientation of this tube is dependent upon the dimensional changes when cooled as well as the direct pressure of the liquid. The thermal contraction of the drive rod also alters the sample position, although it is impossible to separate these last effects.

As an interesting post script to this section, it is evident that the magnetometer can be readily converted for automatic data acquisition since both temperature and magnetic moment signals are ultimately reduced to d.c. voltages for plotting on a chart recorder. Some progress would be necessary on the elimination of the various drift sources, but such a data reduction scheme is certainly feasible.
CHAPTER III
Experimental Results

(A) Samples

The iron-nickel specimens under study here were obtained from several sources. The first sample was taken directly from commercial grade, polycrystalline invar manufactured by the Carpenter Steel Company of Reading, Pa. An analysis for transition metals gave the following

\[
\begin{align*}
\text{Ni: } & \quad 35.32 \\
\text{Fe: } & \quad 64.63 \\
\text{Co: } & \quad 0.05
\end{align*}
\]

weight percent.

A sphere was spark cut from the as-received rod and labelled Invar 1. A second sphere was made from a later batch of invar from the same source and labelled Invar 2. Two additional iron-nickel samples were purchased from Research Crystals, Incorporated. Although these were not single crystals they contained several grains large enough so that a single crystal sphere could be cut from each. No attempt has been made to study the orientation dependence of the magnet moments of these samples, mainly because the present apparatus has no convenient or reproducible rotational facility to determine such angular effects. Finally, a nickel sphere was cut from rods of specpure nickel from Johnson Mathey and Company, Limited.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Ni Concentration (at.%)</th>
<th>Mass (gms)</th>
<th>Diameter (cm)</th>
<th>Density at 0 K (gm cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>100</td>
<td>0.473</td>
<td>0.46</td>
<td>8.95</td>
</tr>
<tr>
<td>Fe-Ni 1</td>
<td>35</td>
<td>1.220</td>
<td>0.66</td>
<td>8.15</td>
</tr>
<tr>
<td>Fe-Ni 2</td>
<td>40$^3$</td>
<td>1.118</td>
<td>0.63</td>
<td>8.16</td>
</tr>
<tr>
<td>Invar 1</td>
<td>34</td>
<td>2.060</td>
<td>0.78</td>
<td>8.16</td>
</tr>
<tr>
<td>Invar 2</td>
<td>34</td>
<td>1.054</td>
<td>0.62</td>
<td>8.16</td>
</tr>
</tbody>
</table>

1. Remainder of samples is Iron.
2. Bozorth: Ferromagnetism.
3. Independent analysis by Falconbridge Nickel Mines, Ltd., gives 41.4 ± 0.2 wt.% Ni.
Table 3.1 lists some of the pertinent physical data for these samples.

(i) **Spark Cut Spheres**

Since the magnetic moment of the invar is field dependent even in the region of technical saturation, it is important to insure that the internal magnetic field inside the samples is homogeneous; that is to say the demagnetizing field in the specimen should be homogeneous when the applied field is. This requirement is satisfied by choosing a spherical shape for the samples.

The spheres were cut on a Servomet spark cutter by the following technique. With the unmachined rod rotating in a chuck, the tubular tool shaped the sample by spark erosion. The needle like tips which remained on both ends of the sample were subsequently smoothed out. In most cases, the tool was a rod of invar metal drilled slightly in excess of the required diameter of the finished sphere. The cut samples were spherical in appearance and micrometer measurements taken at random indicated a diameter which was constant to about one or two percent.

(ii) **Heat Treatment**

The initial measurements were undertaken on Invar 1 in the as-received condition. Over a period of months a noticeable drift occurred in the low temperature data for this sample which was thought to be due to a dimensional
FIGURE 3.1

MAGNETIZATION CURVES FOR Ni.

MAGNETIZATION (GAUSS)

MAGNETIC FIELD (kOe)

T = 4.2 K

M VS INTERNAL FIELD

M VS EXTERNAL FIELD

T = 295 K

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instability. In order to test this hypothesis, Invar 2 was cut and heat treated to examine the effect on the magnetic moment of this sample. The prescription used was: one hour at 1100°C and then quenched into water with subsequent anneals at 300°C for eight hours and finally at 100°C for forty-eight hours. The sample was treated in a helium atmosphere. Such a treatment should increase the dimensional stability of the alloy with a corresponding effect on the magnetic moment.

(B) Experimental Results

The relative stability of the magnetometer described in Chapter 2 is about 3 parts in 10^5 which is sufficient to obtain reasonably detailed behaviour of the magnetic moment of the invar samples as a function of both the applied magnetic field and the temperature. To realize the full sensitivity in the presence of the various drift sources in the apparatus, differential measurements have been taken in which the changes in the output signal are correlated with changes in external field and temperature.

(i) Magnetic Field Data

Not only does the magnetic field data provide information on the magnetization process, it can also be used to calibrate the magnetometer in situ. As pointed out in the last chapter, the initial slope of the magnetization-field curve is linear in the field, and otherwise
depends only on the demagnetizing factor of the sample and a conversion factor for the apparatus. This calibration coefficient is principally a function of the sample position and the gain of the reference loop. Assuming that the samples are spherical with demagnetizing factor, 1/3, the conversion factor is obtained directly from the initial slope.

Figure 3.1 illustrates these results for a polycrystalline Ni sphere. Several important effects are quite evident here. First of all, the linear portion of the M-H curves extends well beyond half the total magnetization, a result which was found for all of the samples investigated. Secondly, when the demagnetizing field is accounted for, the M-H curve rises very sharply at essentially zero internal field, which is a consequence of the initial assumption of the method. Also, the initial linear portion of the curve is independent of the final value of the magnetization as it must be in order to be used as a calibration tool. Finally, the effect of anisotropy manifests itself in the more gradual approach to saturation at 4.2 K than at room temperature. Even though the magnetization has decreased only slightly, the anisotropy energy has fallen at a much higher rate so that the room temperature curve exhibits quite a sharp knee at technical saturation.

A similar plot for Invar 2 is presented in figure 3.2.
FIGURE 3.3

\[ \frac{dM}{dH} : \text{INVAR 2 (UNTREATED)} \]

\( \circ \quad T = 295 \text{ K} \)
\( \times \quad T = 4.2 \text{ K} \)

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FIGURE 3.4

\[ \frac{dM}{dH} \]

INVAR 2 (HEAT TREATED)

- \( T = 295 \) K
- \( T = 79 \) K
- \( T = 4.2 \) K

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Immediately obvious is the increased percentage change in the magnetization between 4.2 K and room temperature over that for Ni. Although the anisotropy does not vary as dramatically as is the case for Ni, it none the less has a sizeable effect which is demonstrated in figure 3.3. Here the static susceptibility ($\partial M/\partial H$) above technical saturation—the so called para-process—has been determined from the data in figure 3.2 and plotted against the internal field. The fact that several thousand oersteds are required to produce a constant susceptibility is a consequence of the anisotropic and stress energies which inhibit the approach to saturation. This approach is slower at liquid helium than at room temperature. Further effects of anisotropy are displayed in the temperature behaviour and are discussed in detail in the next section.

As the knee of the magnetization curve is shaped by the mechanical state of the sample, heat treatment should make a considerable difference to this part of the graph. Figure 3.4 gives the static susceptibility of Invar 2 after being subjected to the heat treatment described earlier. Although the high field values are unaltered, the approach to saturation now occurs more sharply, indicating an improvement in the internal state of the sample. Similar data for the two single crystals has also been obtained. That these samples suffer a much smaller anisotropy is evident from the almost discontinuous change in slope at saturation.
Figure 3.5

Magnetization Curves: Fe-In 1

T = 4.2 K

T = 295 K
### TABLE 3.2
Summary of Magnetic Field Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\mathbf{M(T)} \ (\text{Gauss})$</th>
<th>Magnetic Moment $\ (\mu_B/\text{atom})$</th>
<th>$(\partial \mathbf{M}/\partial \mathbf{H}) \ (\text{Gauss/Oe.})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$4.2K$</td>
<td>$295K$</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>525</td>
<td>495</td>
<td>0.62</td>
</tr>
<tr>
<td>Invar 1</td>
<td>1310</td>
<td>960</td>
<td>1.64</td>
</tr>
<tr>
<td>Invar 2</td>
<td>1315</td>
<td>955</td>
<td>1.65</td>
</tr>
<tr>
<td>Fe-Ni 1</td>
<td>1410</td>
<td>1090</td>
<td>1.76</td>
</tr>
<tr>
<td>Fe-Ni 2</td>
<td>1420</td>
<td>1230</td>
<td>1.78</td>
</tr>
</tbody>
</table>

1. $\mathbf{M(T)}$ and $(\partial \mathbf{M}/\partial \mathbf{H})$ values are averages of several different runs. Spread in $\mathbf{M}$ is about $\pm 10$ gauss.
FIGURE 3.6  MAGNETIC MOMENT PER ATOM FOR Fe-Ni ALLOYS

MAGNETIC MOMENT ($\mu_B$)

NICKEL CONCENTRATION (at. %)

- B.C.C.
- F.C.C.  CRANGLE & HALLAM (1963)
+ KONDORSKII & FEDOTOV (1952)
A PRESENT RESULTS
from the curves for Fe-Ni in figure 3.5.

The values of the magnetic moment and susceptibility have been tabulated in Table 3.2. From the 4.2 K points the average magnetic moment per atom has been calculated and plotted in figure 3.6 along with the data of Crangle and Hallam (1963) and Kondorskii and Fedotov (1952). The agreement with these other workers substantiates the calibration procedure.

(ii) Temperature Data

In the course of setting up the magnetometer, data was obtained on Invar 1 at 6.2 kOe over a span of about six months which indicated a drift in the temperature slope of the magnetic moment for which M, normalized to its 4.2 K value, is plotted against temperature. Figure 3.7 illustrates the variation. Figure 3.8 shows that a much smaller displacement is found at higher fields. Also, as the magnetic field is increased above technical saturation, the temperature derivative of the magnetic moment should decrease in magnitude, since the thermal misalignment of the spins should be inhibited by the field. Yet figure 3.9 reveals that this requirement is violated in Invar 1, indicating that anisotropy effects are large enough to prevent a true intrinsic behaviour in fields below 10 kOe. Nor are these effects unexpected since the measurements were taken on a sample received directly from the steel company.
\[ \frac{M(T)}{M(4.2)} \]

**FIGURE 3.7**

**INVAR 1**

*(TIME STUDY AT 6.2 kOe.)*

1. MARCH 25.
2. APRIL 1, SEPT. 2, 4.
3. APRIL 17, SEPT. 13.
4. JULY 24, 29.

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Figure 3.8
Invar 1:
(Time study at 9.5 kOe.)

\[ \frac{M(T)}{M(4.2)} \]
Figure 3.9

Magnetic Moment for Invar I

\[ \frac{M(T)}{M(4.2)} \]

- \( H = 9.5 \) kOe.
- \( H = 6.4 \) kOe.
It is known that invar alloys are subject to a certain amount of dimensional instability due to the presence of stresses which vary both with time and temperature. The stresses in the sample will contribute to the anisotropy energy, and hence inhibit the onset of magnetic saturation. In this manner it is apparent why the time study exhibits more structure at 6.2 than at 10.0 kOe. The lower field value occurs in the region of the knee of the magnetization curve where the internal stresses have their most noticeable influence as far as the present experiment is concerned.

Although stress and anisotropy effects constitute a field of study in their own right, the aim of the present investigation is to determine the temperature behaviour of the intrinsic magnetic moment of the invars without the additional constraint of anisotropy. This can be accomplished in at least two ways: by using magnetic fields strong enough to overcome the anisotropy (see for example Zavaritskii and Tsarev, 1963), or by heat treating the specimen to relieve the internal stresses. In this experiment the second alternative was chosen using the heating prescription described in the last section.

The second invar sample, Invar 2, was machined from another batch of commercial grade material. Before heat treating, the magnetic moment of this sample was taken and is displayed in figure 3.10 where the overlap between different field curves is again the result of anisotropy.
FIGURE 3.10
MAGNETIC MOMENT:
INVAR 2 (UNTREATED)
FIGURE 3.11
MAGNETIC MOMENT: 
INVAR 2 (HEAT TREATED)
FIGURE 3.12

MAGNETIC MOMENT FOR FE-NI I

- $H = 10.0$ kOe.
- $H = 12.5$ kOe.

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FIGURE 3.13
MAGNETIC MOMENT FOR Fe-Ni 2

\[ \frac{M(T)}{M(4.2)} \]

- H = 8.0 kOe.
- H = 10.0 kOe.

TEMPERATURE (K)
FIGURE 3.14
MAGNETIC MOMENT CURVES AT 10.0 kOe.
There is excellent agreement between Invar 1 and 2 at comparable fields which must be considered somewhat surprising in view of the possibility of a variation in sample composition between these two samples. That the magnetic moment of Invar 2 after heat treatment behaves in a more intrinsic manner is seen from both the temperature data of figure 3.11 and the field data mentioned earlier (figure 3.4). In figure 3.11 the curves for different magnetic field values all stack in the expected way.

The next two diagrams, figures 3.12 and 3.13 give similar temperature data for the samples, Fe-Ni 1 and 2, respectively. Note that the scale of the latter is twice that for all others. Although the detailed analysis of the temperature terms has been reserved for the next chapter, there is evidently an increase in the temperature slopes as the amount of Ni is lowered. For convenience figure 3.14 illustrates this fact for four samples at a field of approximately 10 kOe. Even by compensating for the differences in the values of M(4.2) given in Table 3.2, there remains a marked increase in temperature slopes throughout the series. On the basis of higher temperature results Crangle and Hallam (1963) concluded that a law of corresponding states could not be applied to the Fe-Ni series. The detailed low temperature measurements collected in figure 3.14 certainly support their conclusion.
CHAPTER IV

Analysis of the Temperature Variation of M

It has been mentioned above that one of the objects of the present research has been to correlate the very large and negative low temperature thermal expansion coefficient with the changes in magnetic moment over the same temperature interval. The approach adopted has been thermodynamic, by considering the equation,

\[
\frac{1}{M_0} \left( \frac{dM}{dT} \right)_{P,H} = \frac{1}{M_0} \left( \frac{dM}{dT} \right)_{V,H} + \frac{V}{M_0} \left( \frac{dM}{dV} \right)_{T,H} \beta ,
\]

(4.1)

which relates the temperature slope of the magnetic moment at constant pressure to a term at constant volume together with one proportional to the volume thermal expansion coefficient, \( \beta \). Specifically, the experiment determined the total magnetic moment and not its temperature derivative; the integration of equation 4.1 gives

\[
\frac{[M(T) - M(4.2)]}{M(4.2)} = \frac{[M(T) - M(4.2)]}{M(4.2)} + \int_{T}^{T} \Gamma(T') \beta(T') \, dT' .
\]

(4.2)

Normalizing to the values at 4.2 K rather than 0 K is a matter of convenience, as \( T = 4.2 \) K has been used as the reference temperature throughout these experiments. The quantity,

\[
\Gamma(T) = \frac{V}{M(4.2)} \left( \frac{dM}{dV} \right)_{T,H} = \frac{d(\ln M)}{d(\ln V)} \left( \frac{d\ln V}{d\ln V} \right)_{T,H} ,
\]

(4.3)
is used as the measure of the volume dependence of the magnetic moment. If $\Gamma$ is assumed to be independent of temperature, equation 4.2 reduces to

$$\left[ \frac{M(T) - M(4.2)}{M(4.2)} \right]_{E_H} = \left[ \frac{M(T) - M(4.2)}{M(4.2)} \right]_{V_H} + \Gamma \left[ \frac{V(T) - V(4.2)}{V(4.2)} \right]_{E_H} \quad (4.4)$$

Since the thermal expansion coefficient exhibits a strong negative peak in the neighbourhood of 25 K, the data analyzed according to equation (4.4) will yield a value of $\Gamma$ most appropriate to this temperature.

In order to evaluate the coefficient $\Gamma$, it is necessary to separate explicitly the constant volume contributions to equation (4.4) which themselves contain valuable information concerning the invar properties. Two different terms have been considered: the collective or spin wave excitations and the single particle spin deviations of the Stoner type. These two terms are derived in the appendix and have been summarized in equation (4.5).

$$\left[ \frac{M(T) - M(4.2)}{M(4.2)} \right]_{V_H} = \left\{ \begin{array}{l} A(T^2 - (4.2)^2) \quad \text{single particle} \\
+ B \left[ \frac{3}{2} (1 + G(H, T)) - (4.2)^2 (1 + G(H, 4.2)) \right] \quad \text{spin waves}
\end{array} \right. \quad (4.5)$$

It should be noted that the single particle contribution is specifically for an unsaturated ferromagnet at $T = 0$, i.e. one...
for which the total moment is less than it would be if all spins were aligned. This is certainly the case for the invars. The factor \((1+G(H,T))\) specifies the effect of the magnetic field on the spin wave spectrum. No similar effect is included in the single particle term since no closed form for such variation is available. Moreover, for temperatures up to 70 K, it does not change significantly from the \(T = 0\) value and hence should not alter the \(T^2\) dependence on temperature.

Both these terms have been derived theoretically for metallic ferromagnets. Furthermore, reference to existing data on metallic systems provides a useful justification for such a selection. In the case of nickel metal, Pugh and Argyle (1962) and Argyle, Charap and Pugh (1963) have made definitive measurements and analysis of the magnetization and have concluded that the spin wave law is valid to a high degree of accuracy at low temperatures. In fact, they would ascribe the deviations at higher temperatures to a quartic term in the spin wave energy spectrum (which leads to a magnetization variation as \(T^{5/2}\)) rather than any single particle behaviour. The same authors have also investigated iron metal which they find to follow a spin wave law as well, but the deviations in this case are equally well described by either a single particle contribution or a higher order spin wave term.

Spin waves have been observed directly for the iron—
FIGURE 4.1 SPIN WAVE MAGNETIZATION COEFFICIENT

(NOTATION OF HATHERLY ET AL., 1964)
nickel alloy system in the neutron scattering work of Hatherly, et al. (1964) who have published values for the spin wave dispersion coefficient, D. By using these coefficients one may determine the parameter B in equation (4.5) (c.f. equation A19 of the appendix) which is plotted as a function of nickel concentration in figure 4.1. The fact that Argyle, et al., obtain excellent agreement in their measured coefficient with the value calculated in this way is a further indication that the spin wave excitations are responsible for the decrease in magnetic moment with temperature, at least for iron and nickel.

On the other hand, the itinerant electron model as first applied by Stoner (1938) leads to a $T^2$ variation of the magnetization with temperature. The success of this model in accounting for such phenomena as electronic specific heat and non-integral magneton numbers suggests that the true energy states of a ferromagnetic metal correspond to a considerable degree with this picture. Experimentally, Ogawa and Sakamoto (1967) have found such a $T^2$ magnetization dependence for ZrZn$_2$ and have described it as a weak itinerant electron ferromagnet for this reason. It can be concluded, then, that the constant volume terms described in equation (4.5) are realized experimentally as well as theoretically in various metallic ferromagnets.

The approach of the present analysis has been to fit the data by a least squares routine to the three terms.
defined by equations (4.4) and (4.5). No attempt was made to determine a $T^{5/2}$ term, such as Argyle, et al. (1963), because the degree of scatter of the data did not warrant the introduction of extra parameters, which would only obscure the fitting of the main terms. (The above authors have shown that the $T^{5/2}$ terms are still an order of magnitude smaller at 100 K than the dominant spin wave demagnetization and hence are negligible for the present purposes.) Even without higher order contributions the separation of the remaining three coefficients ($A$, $B$, and $T$) is ambiguous to a certain degree. This is because each term can be represented approximately by a temperature dependence of the form $T^n$ where $1.5 \leq n \leq 2$, and their magnitudes are all of the same order. These are limitations which Argyle, et al. (1963) did not face and which certainly hinder the determination of the coefficients. To perform a precise separation would require data over a much wider temperature range, but then the higher order terms could no longer be ignored.

As a first step, the data were fitted with the three parameters $A$, $B$, and $T$ allowed to vary independently. However, this procedure did not lead to very consistent values of the coefficients for the different runs. The $T$ values exhibited a spread of a factor of two, and the $A$ and $B$ values were distributed likewise with some of the $B$ values even being positive. In order to examine the structure of this
FIT PARAMETERS: INVAR 2

\( H = 10.0 \text{ kOe} \)

\[ A \times 10^6 \]

\[ B \times 10^6 \]

\[ S \times 10^6 \]

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procedure in greater detail, the values of $\Gamma$ were fixed in the range, $0 \leq \Gamma \leq 25$, and the data fitted to the remaining two terms. This approach generated a series of coefficients $A(\Gamma)$, $B(\Gamma)$ and the minimized sum of squares of the deviations, $S(\Gamma)$, for each fixed value of $\Gamma$. Figure 4.2 illustrates this for one run on Invar 2 at 10.0 kOe. The minimum in the curve of $S(\Gamma)$ corresponds to the value obtained in the initial fit. The broadness of the minimum is typical of all the curves. If a range in $S(\Gamma)$ of $\pm 30\%$ about the minimum value is taken as the significant region, then a broad band of acceptable values for all coefficients results.

The broadness of the fit is apparently due to a small systematic deviation below 15 K which could not be detected in the $M(T)$ versus $T$ plots. If, however, \[
\frac{M(T)-M(4.2)}{M(4.2)(T^2-4.2^2)}
\] is plotted as a function of \[
\frac{\nu(T)-\nu(4.2)}{\nu(4.2)(T^2-4.2^2)}
\], this deviation shows up as a slight turn up at the low temperature end. Figure 4.4 illustrates one such plot for Invar 2. The slope of this curve is due to contributions from $\Gamma$ and from the spin wave term. Moreover, the spin wave term should push this graph downwards at low temperatures. Extrapolation from higher temperatures reveals that the magnitude of this effect is only one part in $10^4$ of the total signal, i.e. just slightly greater than the resolution. The source of this effect has not yet been determined. One possible explanation might be the existence of time dependent relaxation phenomena,
FIGURE 4.3 VOLUME DEPENDENCE OF MAGNETIC MOMENT

KONDORSKII & SEDOV (1960)

PRESENT RESULTS

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as found in the compressibility (Fletcher, 1969) and the magnetostriction (Schlosser, et al., 1969), which would inhibit complete magnetic moment changes within the normal measuring time of two or three minutes. In any case such small time-dependent changes would be masked by the other drift sources within the apparatus. Another possibility could be the temperature dependence of \( \Gamma \). A significant increase in \( \Gamma \) above the 4.2 K value would have the observed result. To test this on the data, \( \Gamma \) was given the following temperature dependence: a linear rise by a factor of two from 4.2 K to 25 K and constant thereafter. When the data was fitted on this basis, the minima in the \( S(\Gamma) \) curves shifted to lower values of \( \Gamma \) and their shape became somewhat sharper producing a more consistent set of fit parameters. This \( \Gamma \) variation was chosen quite arbitrarily. Linear magnetostriction work by Schlosser, et al. (1969) does indicate that \( \Gamma \) increases by approximately 30% in this temperature range so that the temperature variation of \( \Gamma \) undoubtedly makes some contribution to this anomaly.

Much of the ambiguity of this fitting procedure would be removed if one of the parameters could be determined independently. The reasonable agreement between the spin wave demagnetization calculated from neutron results of Hatherly, et al. (1964) and as measured by Argyle, et al. (1963) suggests that the dispersion coefficients can be used to define the coefficient \( B \). Consequently, by selecting
### TABLE 4.1

Temperature coefficients of magnetic moment according to:

\[
\frac{\Delta M}{M(4.2)} = A\Delta(T^2) + B\Delta(T^{3/2}) + \Gamma_0 \frac{\Delta V}{V(4.2)}
\]

<table>
<thead>
<tr>
<th>Samples</th>
<th>A (x 10^6) (K^-2)</th>
<th>B (x 10^6) (K^-3/2)</th>
<th>(\Gamma_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invar 1</td>
<td>-2.3 ± .3</td>
<td>-13.0</td>
<td>14 ± 2</td>
</tr>
<tr>
<td>Invar 2 (untreated)</td>
<td>-2.3 ± .5</td>
<td>-13.0</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>(heat treated)</td>
<td>-2.3 ± .3</td>
<td>-13.0</td>
<td>11 ± 1</td>
</tr>
<tr>
<td>Fe-Ni 1 (35 at.%Ni)</td>
<td>-1.8 ± .2</td>
<td>-11.5</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>Fe-Ni 2 (40 at.%Ni)</td>
<td>-0.53 ± .05</td>
<td>-8.5</td>
<td>1.5 ± 1</td>
</tr>
</tbody>
</table>

1. The thermal expansion coefficients used here are those of Meincke and Graham (1963) for the 34 at.% Ni alloy so a small systematic error may have been introduced.

2. The thermal expansion data of White (1965) was used for this alloy.

3. The thermal expansion data of Meincke and Graham (1963) was used for this alloy.
the values of A and T consistent with the calculated B, a set of parameters is generated with a much greater internal agreement than previously. In every case, the corresponding value of S falls within 30% of the minimum value. As a result, the coefficients were chosen in this way and are listed in Table 4.1. The somewhat larger value of T for Invar 1 may indicate a slight difference in composition as it was taken from an earlier batch of stock material.

This procedure is justified independently in the work of Bower, Claridge and Tsong (1968) who have measured the elastic constants of several iron-nickel alloys at 4.2 K. These measurements permit them to calculate the lattice contribution to the specific heat. With this term fixed, they have refitted the specific heat results of Dixon, Hoare and Holden (1968) to determine both the electronic and spin-wave contributions. The spin wave part so fitted agrees quite well with the one calculated from the dispersion coefficients of Hatherly, et al. (1964). The refitted results show much better agreement than the original fit without the lattice term fixed. This qualitative behaviour was certainly found in the present analysis. Moreover, the agreement which Bower, et al. obtain with the spin wave dispersion measurements reinforces our confidence in choosing them as the basis for our fitting procedure.

As an additional test of consistency, the T values given in Table 4.1 can be compared with the measurements of
Kondorskii and Sedov (1960a) on the pressure induced change in the magnetization of iron-nickel alloys. Using a value of the compressibility of $-8.0 \times 10^{-13}$ cm$^2$ dyne$^{-1}$, the results of Kondorskii and Sedov can be converted to $\Gamma$ values and are shown in figure 4.3 along with the present results. The agreement here is quite satisfactory. It is interesting to note that these authors find no temperature variation in their values of $\Gamma$ to within experimental uncertainty of $\pm 20\%$. This was also assumed in the present analysis. On the other hand, recent experiments on the linear magnetostriction coefficient of invar by Schlosser, et al. (1969) from the same stock as Invar 2 imply a $\Gamma$ of approximately 7, i.e. some 50% smaller. The assumption is made that the linear magnetostriction represents one third of an isotropic volume change which preliminary data have verified. This seems to imply a breakdown of equilibrium thermodynamics. In fact, Schlosser has found that the linear magnetostriction increases with temperature by about 50% up to 100 K and that at 4.2 K there is a distinct relaxation with time. The details of these results are still to be explained.
CHAPTER V
Discussion of Results

(A) Summary of Data

The data presented and analyzed in the last two chapters exhibit several striking features which contribute to the present understanding of the invar problem. In the first place, there is the sudden increase in the magneto-elastic coupling for increasing iron concentration as given by the parameter \( \Gamma \). This has also been observed in other measurements such as the magnetostriction and thermal expansion. It is believed that the present result is the first for which the effect of volume change has been distinctly detected in the measurement of the magnetic moment at low temperatures. In the samples Invar 1 and 2, the \( \Gamma \) contribution represents a first-order effect which underscores the exceptionally large size of the magneto-elastic coupling. Reference to figure 3.6 shows the effect to be increasing in the composition region where the \( \Gamma = 0 \) magnetic moment begins to fall significantly.

A second feature of the data, which has not been emphasized here as strongly as the volume dependence, is the growth of the temperature contribution proportional to \( T^2 \). For the 34 at.% Ni alloys studied here, the \( T^2 \)...
term surpasses the others below 10 K, so that it represents the dominant one over essentially the entire temperature region investigated. This represents a radical departure from the situation in both iron and nickel, and for that matter in the 40 at.% Ni alloy. The breakdown of the law of corresponding states, by which the reduced magnetization versus reduced temperature curves for alloys of different compositions should be identical, reported by Crangle and Hallam (1963), could easily be due to just this effect. The shift in character from a predominantly spin-wave to single-particle behaviour will certainly invalidate such a law in this composition range.

In view of the measurements of other thermodynamic properties, the $T^2$ term in the magnetic moment assumes a greater significance. As already mentioned in the introductory chapter, both the specific heat, $C_v$, and the thermal expansion, $\beta$, of the 34 at.% Ni alloy are dominated at low temperatures by a linear temperature dependence. The magnetization derivative, $(\partial M/\partial T)_V$, of this alloy likewise has a large linear temperature term. Not only are these quantities linear in temperature, but all three possess a coefficient which is exceptionally large. From the low temperature values of $\beta$ and $C_v$, the limiting value of the Grüneisen parameter, $\gamma_0$, may be obtained through the relation

$$\gamma_0 = \frac{\beta V}{C_vH} \chi_{HT} \quad (5.1)$$
In the region where the heat capacity is linear in $T$, we may identify $C^V_H$ with $S/V$ where $S$ is the total entropy. In this approximation, the Grueneissen parameter becomes

$$\gamma_0 = \left( \frac{\partial \ln S}{\partial \ln V} \right)_{H,T}$$

(5.2)

in which form it is analogous to the magnetoelastic parameter,

$$\Gamma = \left( \frac{\partial \ln M}{\partial \ln V} \right)_{H,T}$$

(5.3)

In most materials, both $\gamma_0$ and $\Gamma$ are of order unity. For the 34 at.% Ni alloy, $\gamma_0 = -22$ and $\Gamma = +11$, both of which are extraordinarily large. However, the ratio,

$$\frac{\gamma_0}{\Gamma} = \left( \frac{\partial \ln S}{\partial \ln M} \right)_{H,T}$$

(5.4)

has a value $-2$ for this alloy. That this ratio is the same order as other ferromagnetic metals has important implications for the invar alloys. Since the entropy has only a moderate dependence on the magnetization, but both these quantities are extremely volume sensitive, it is concluded that the entropy changes with volume through the magnetization. Under this condition, the analysis of the invars is simplified as one need only treat the magnetization directly to account for the anomaly in both these properties.

On the other hand, the total entropy at low temperatures
cannot be directly a function of the magnetic moment. This is understood by considering the specific heat at constant magnetic moment,

\[ C_{VM} = T \left( \frac{\partial S}{\partial T} \right)_{V,M} = C_{VH} - T \left( \frac{\partial M}{\partial T} \right)_{V,H}^2 \left( \frac{\partial H}{\partial V} \right)_{V,T}^{-1} \quad (5.5) \]

The correction term is only about 20% even at 100 K indicating that the observed electronic specific heat is essentially at constant magnetic moment. That is to say, the total entropy must involve excitations which do not affect the magnetic moment directly.

(B) Rigid Band Model

Reiterating the conclusion of the last section, the low temperature thermodynamic data is characterized by three features: the temperature dependence of the derivatives, \( C_{VH}, \beta_H, \) and \( (\partial M/\partial T)_{H,T} \), is linear to a high degree; the total entropy is determined by non-magnetic excitations, whereas the entropy change with volume is directly related to the volume dependence of the magnetic moment. Taken together, these results suggest that the invars can be understood from the simple viewpoint of a rigid band model. This proposition has been made by several authors, Graham and Cochrane (1969), Mathon and Wohlfarth (1968), Shimizu and Hirooka (1968) and Mizoguchi (1968). The latter two publications differ in their details from the former by emphasizing the extended condition for ferromagnetism.
(see appendix). This approach is somewhat weakened by the fact that ordinarily the Curie point would be a first-order transition which is just not observed. Graham and Cochrane and Mathon and Wohlfarth consider the usual case of "weak" ferromagnetism, for which the latter have shown that the variation of the Curie temperature found by Bolling, Arrott and Richman (1968) is consistent with this model. The former authors have derived the volume dependence of the entropy and magnetic moment. It is this approach which is adopted here.

The suggested interpretation of the invar alloys is that they form a system of weak itinerant ferromagnets for which the shape and size of the density of states function becomes unfavourable for ferromagnetism below about 30 at.% Ni. It is shown in the appendix how this model allows for the variation of the ferromagnetic moment due to a delicate balance between the kinetic energy of the electrons and their magnetic or exchange energy. Moreover, the density of states is becoming progressively more unfavourable as the critical concentration is approached because $(\partial^2 U/\partial \sigma^2) \rightarrow 0^+$ along with $\sigma_o \rightarrow 0$. Hence, the extremum condition, equation (A4) of the appendix, is a maximum on the non-ferromagnetic side of this transition, but only a very shallow minimum on ferromagnetic side.

To facilitate the qualitative understanding of this model, the density of states function has been estimated from the electronic specific heat data of Gupta, Cheng and Beck (1964), Keesom and Kurrelmeyer (1940), and Burford.
3-d DENSITY OF STATES

Figure 5.1
and Graham (1965) on both Fe-Ni and Ni-Cu f.c.c. alloys.
The result, shown in figure 5.1, was constructed under
the following assumptions:

(i) there are approximately 0.55 electrons per
atom in a flat 4S band for all nickel concentrations;
(ii) down to 50 at.% Ni all the holes in the d-band
occur in one spin subband only;
(iii) the spin subbands are identical in shape.

There are several difficulties with this procedure which
hinder the quantitative determination of this function,
particularly at either end of the alloy system where the
ferromagnetism is disappearing. Moreover, the assumption
is made that the electronic specific heat does reflect
the density of states accurately without any additional
contributions. One such contribution might come from
exchange enhancement of the electronic mass as the
ferromagnetic instability is approached. It is of interest
to note that Bucher, et al. (1967) have reported exchange
enhancement for both ferromagnetic and paramagnetic NiRh
alloys about the critical concentration of 63 at.% Ni,
so that a similar term may be important in the NiFe system.

The curve in figure 5.1 lends qualitative support
to the present interpretation. If an average density of
states, $\bar{\nu}$, is defined by,

$$\nu_+ - \nu_- = \bar{\nu} \sigma$$  \hspace{1cm} (5.6)

where $\nu_+$ and $\nu_-$ are fermi levels for spin subbands,
then equation (A7) of the appendix gives the condition:

$$\frac{1}{\nu} < \frac{1}{2} \left[ \frac{1}{\nu(\mu_+)} + \frac{1}{\nu(\mu_-)} \right]$$

(5.7)

Moving away from the peak in the density of states will result in increasing difficulty in satisfying condition (5.7). In fact, for the 34 at.% Ni alloy, the calculated density of states has already violated this requirement. Nevertheless, the qualitative assertion, that the shape of the density of states leads to an instability of the ferromagnetic state as the nickel concentration decreases, is certainly borne out by the estimated density of states even if the quantitative details are somewhat inaccurate.

The three conclusions which begin this section are readily incorporated into the theory. The total entropy in a rigid band model is proportional at low temperatures to both the temperature and the sum, $\nu(\mu_+)+\nu(\mu_-)$, of the subband densities of state. This means that the electronic entropy is determined by the intraband transitions (conserving spin) and not the interband excitations, in agreement with the experimental requirement. The specific heat must also be linear in temperature; the large coefficient of this term is a consequence of the relatively large values of the densities of state of both subbands (see figure 5.1). As the critical invar composition is approached, one would also expect an increase in the quadratic temperature term in the magnetic moment. This
arises because of the factor \((32U/3 \sigma_r^2)\) in the denominator of equation (A13) which acts as an enhancement factor.

In the limit of very small \(\sigma_o\), Edwards and Wohlfarth (1968) have shown that:

\[
\sigma^2(H,T) = \sigma_o^2 \left\{ 1 - \left(\frac{T}{T_c}\right)^2 + \frac{2\chi_o H}{\sigma(H,T)} \right\}, \quad (5.8)
\]

or

\[
\sigma_o(T)/\sigma_o = 1 - \frac{1}{2} \left(\frac{T}{T_c}\right)^2. \quad (5.9)
\]

Since \(T_c\) is proportional to \(\sigma_o\) in this regime (Thompson, Wohlfarth and Bryan, 1964), then the coefficient of \(T^2\) in the magnetic moment dependence on temperature should continue to increase as \(\sigma_o^{-1}\), upon converging towards the critical composition.

Because the equilibrium magnetic moment is a function of both the kinetic and magnetic energies, there are two contributions to its volume derivative: the shift of the exchange energy with volume, and the change of the density of states under compression or expansion of the lattice. Since \(\Gamma\) is positive for invars, the larger, if not both, of these contributions must be positive. The quantitative analysis of these effects will in general be a complicated affair because of the behaviour of the density of states under volume dilation. If, however, it is assumed that the density of states varies linearly and uniformly when the volume is changed by a small amount, \(\Delta V\), then
Figure 5.2 Volume Dependence of Band Energy
a particularly simple expression for $\Gamma$ is obtained. Characterizing the change in the density of states by

$$\delta = \frac{1}{\nu} \left( \frac{\partial \nu}{\partial \lambda} \right), \quad (5.9)$$

it is evident that the first-order shift in the band splitting parameter is given by:

$$\Lambda(\Delta \nu) = \frac{1}{2} \left[ \mu_+ (\Delta \nu) - \mu_- (\Delta \nu) \right] = \Delta(0)/(1 + \delta \Delta \nu)$$

$$= \Delta(0) (1 - \delta \Delta \nu) \quad .$$

(5.10)

It is useful at this point to refer to the appendix for the manner in which the energy of the ferromagnetic state is derived. In particular, the equilibrium state is defined by equation (A4) for which $\Lambda = \Lambda_m$, the molecular field inside the sample. Figure 5.2 is a composite graph illustrating these two functions for two different values of the volume, $V_0$ and $V_0 + \Delta V$. Also shown are the internal energies of these states, all plotted as a function of $\sigma$. This latter diagram indicates the way the energy for the new state can be formed from the initial one: proceed from the minimum, $U_0$, at constant $V$, i.e. at constant $I$ and $\nu$, and then go at constant $\sigma$ to $V_0 + \Delta V$ from $V_0$. The energy of the new state can be written almost by inspection as

$$U(\sigma, \Delta \nu) = U_0 + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \sigma^2} \right)_0 (\Delta \sigma)^2 - \frac{1}{2} (I + \Delta I) \sigma^2 - \frac{1}{2} \delta \Delta \nu \int_0^\sigma \Delta(0) d\sigma \quad .$$

(5.11)

The new equilibrium state minimizes $U(\sigma, \Delta \nu)$.
$$\frac{\partial U}{\partial \sigma} (\sigma, \Delta V) = \left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0} \Delta \sigma - \Delta I (\sigma_0 + \Delta \sigma) - \frac{1}{2} \Delta (0) \delta \Delta V = 0 \quad (5.12)$$

Since only small volume changes are being considered equation (5.12) reduces to

$$\left( \frac{\partial \sigma}{\partial V} \right) = \frac{\sigma_0}{\left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0}} \left( \frac{\partial I}{\partial V} + I \delta \right) \quad , \quad (5.13)$$

or equivalently:

$$\Gamma = \frac{V}{\sigma_0} \left[ \frac{\partial \sigma}{\partial V} \right] = f \left( \frac{\partial \ln I}{\partial \ln V} + \frac{\partial \ln V}{\partial \ln V} \right) \quad , \quad (5.14)$$

where,

$$f = \left[ \frac{1}{I} \left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0} \right]^{-1}$$

The presence of the enhancement factor, $f$, in equation (5.14) is the key to understanding the nature of the anomalously large magnetoelastic parameter, $\Gamma$, for the invar alloys. The enhancement of $\Gamma$ can be perceived intuitively by realizing that $(\partial^2 U/\partial \sigma^2)$ represents the difference in the slopes of the curves $\Delta$ and $H_M$ plotted in figure 5.1 (and A.1). The limit $(\partial^2 U/\partial \sigma^2)_{\sigma_0} \rightarrow 0$ implies that these two functions cross at an increasingly small angle. Under this condition a small change in either curve results in a large shift in their point of intersection, which is just the enhancement effect.

The final requirement of the thermodynamic data is that the entropy depend on the volume essentially through the magnetic moment. The Grueneisen parameter, $\gamma_0$, shows an
### TABLE 5.1
Band Parameters Determined from Data

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_0$</th>
<th>$\Gamma$</th>
<th>$(\frac{\partial^2 U}{\partial \sigma^2})_{\sigma_0}$ eV-atom$^{-1}$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Invar 2 (34 at.% Ni)</td>
<td>$^{1}$-22</td>
<td>$^{1}$+11</td>
<td>$2.0 \times 10^{-2}$</td>
<td>12</td>
</tr>
<tr>
<td>Fe-Ni 1 (35 at.% Ni)</td>
<td>$^{2}$-20</td>
<td>$^{2}$+9</td>
<td>$2.3 \times 10^{-2}$</td>
<td>10</td>
</tr>
<tr>
<td>Fe-Ni 2 (40 at.% Ni)</td>
<td>$^{3}$-11</td>
<td>$^{3}$+1.5</td>
<td>$1.6 \times 10^{-1}$</td>
<td>1.4</td>
</tr>
</tbody>
</table>

1. $\gamma_0$ and $C_v$ values from Burford and Graham (1965).

2,3. $\gamma_0$ and $C_v$ values found in White (1965).
enhanced value because it is proportional to \( \Gamma \) and the ratio can be expressed in terms of the present model as:

\[
\frac{\gamma_o}{\Gamma} = \sigma \frac{\partial S}{\partial \sigma} = \frac{1}{2} \frac{\sigma}{v(\mu_+)+v(\mu_-)} \left[ \frac{v'(\mu_+)}{v(\mu_+)} - \frac{v'(\mu_-)}{v(\mu_-)} \right] .
\] (5.15)

Comparison of equation (5.15) with (A13) of the appendix permits the estimation of \((\partial^2 U/\partial \sigma^2)_{o_o}\):

\[
\left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{o_o} = \left( \frac{\partial S}{\partial \sigma} \right)_{V,T} \left/ \left( \frac{\partial \sigma}{\partial T} \right)_{o_o} \right. \sim \frac{C_V}{\sigma_o} \frac{\gamma_o}{\Gamma} / 2 \sigma_o \Delta T ,
\] (5.16)

where \(\Delta\) is the coefficient of \(T^2\) listed in table 4.1. Table 5.1 is a compilation of these calculations together with an estimation of the enhancement factor, \(f\), for the alloys investigated. In calculating \(f\), the value of \(I\) was taken to be constant at 0.23 eV-atom, the value found from the band splitting parameter \(\Delta\) given in figure 5.1. It is evident that \((\partial^2 U/\partial \sigma^2)_{o_o}\) is decreasing with the nickel concentration in agreement with the initial assumption of this discussion.

(C) Conclusion

It has been shown that the rigid band model is in good qualitative and semi-quantitative agreement with the thermodynamic data of the present experiment as well as that from several other sources. Moreover, these same considerations lead naturally to the prediction of large enhancement effects for the various volume derivatives and the paraprocess.
enhanced value because it is proportional to \( T \) and the ratio can be expressed in terms of the present model as:

\[
\frac{\gamma_0}{\Gamma} = a \frac{\partial S}{\partial \sigma} = \frac{1}{2} \frac{\sigma}{\nu(\mu_+)+\nu(\mu_-)} \left[ \frac{\nu'(\mu_+)}{\nu(\mu_+)} - \frac{\nu'(\mu_-)}{\nu(\mu_-)} \right] .
\]  

(5.15)

Comparison of equation (5.15) with (A13) of the appendix permits the estimation of \( (\partial^2 U/\partial \sigma^2)_{\sigma_0} \):

\[
\left( \frac{\partial^2 U}{\partial \sigma^2} \right)_{\sigma_0} = \left( \frac{\partial S}{\partial \sigma} \right)_{V,T} \frac{C_V}{\sigma_0} \cdot \frac{\gamma_0}{\Gamma} \cdot \frac{1}{2\sigma_0 AT} ,
\]  

(5.16)

where \( A \) is the coefficient of \( T^2 \) listed in Table 4.1. Table 5.1 is a compilation of these calculations together with an estimation of the enhancement factor, \( f \), for the alloys investigated. In calculating \( f \), the value of \( I \) was taken to be constant at 0.23 eV-atom, the value found from the band splitting parameter \( \Delta \) given in Figure 5.1. It is evident that \( (\partial^2 U/\partial \sigma^2)_{\sigma_0} \) is decreasing with the nickel concentration in agreement with the initial assumption of this discussion.

(C) Conclusion

It has been shown that the rigid band model is in good qualitative and semi-quantitative agreement with the thermo-dynamic data of the present experiment as well as that from several other sources. Moreover, these same considerations lead naturally to the prediction of large enhancement effects for the various volume derivatives and the paraprocess
susceptibility without recourse to further ad hoc assumptions. This is the underlying strength of the band model. That is not to say that the various models discussed in the introductory chapter are completely invalid while the band model accurately explains all the relevant data. In fact, it is helpful to compare the band model with the latent antiferromagnetism proposition of Kondorskii. The rigid band theory indicates quite clearly that the ferromagnetic state is unstable with respect to some nonferromagnetic one, without attempting to describe the nature of this latter state. On the other hand, Kondorskii attributes the loss of ferromagnetism to the appearance of antiferromagnetism, without further explanation of why the ferromagnetic state does not remain stable. His analysis is based on a localized spin picture for the 3d electrons. Beyond this point both theories provide for sensitive volume derivatives through the associated change in the magnetic moment. However, the itinerant character of the magnetic carriers and the thermodynamic properties they contribute can be treated in a more straightforward manner by the band theory, which makes it a more meaningful starting point for the discussion of the invar alloys.
APPENDIX

Ferromagnetic Theory

(A) Rigid Band Model

The description of the magnetic carriers in terms of an itinerant or band model begins with the carriers distributed in two subbands with densities of state, $v_+$ and $v_-$, for the plus and minus spins. In general, these bands are different, but for the sake of simplicity, only a rigid band model is considered here, with identical shape for both subbands. The ferromagnetic state is taken into account self-consistently by considering the exchange forces to split the bands just that amount which results in the desired magnetic moment. This approach is static in nature and does not encompass dynamic effects, such as spin waves.

At $T = 0$, the total internal energy is the sum of a kinetic or band energy, a magnetic potential energy and the field energy:

$$U(\sigma, T = 0) = \int_0^{\mu_+} E v(E) dE + \int_0^{\mu_-} E v(E) dE - \frac{1}{2} I \sigma^2 - \mu_B \sigma H$$  \hspace{1cm} (A1)

where $I$ is the exchange energy,

$$\sigma = \int_0^{\mu_+} v(E) dE - \int_0^{\mu_-} v(E) dE$$  \hspace{1cm} (A2)

is the excess number of plus spins and $\mu_+$ and $\mu_-$ are the
fermi levels of the plus and minus bands measured from the bottom of the band. The total magnetic moment is \( M = \mu_B g N \); \( \mu_B \) is the Bohr magneton, and \( N \) is the total number of atoms.

As pointed out by Shimizu (1964, 1965), the essential condition for ferromagnetism is

\[
U(\sigma) - U(0) < 0 \quad \text{for} \quad \sigma > 0 ,
\]

that is to say, the ferromagnetic state is lower in energy than the paramagnetic. It is thus possible for ferromagnetism to exist for a large \( \sigma \) even when such a state is energetically unfavourable at small values of \( \sigma \). This is the extended condition for ferromagnetism in distinction to the Stoner criterion, \( 2I\nu(\mu_0) > 1 \), for which the internal energy initially decreases with increasing \( \sigma \).

At this point it is necessary to distinguish between so called "strong" and "weak" ferromagnetism. These labels are somewhat misleading since the term "weak" does not necessarily refer to systems with small magnetic moments; more informative titles might be "saturated" and "unsaturated". In the former case, the exchange forces are strong enough to completely polarize all the spins at \( T = 0 \). The result is that the subbands are completely split so all the magnetic carriers are in one band only. Generally, the low temperature interband effects are then dominated by an energy gap, \( E_g \), between the occupied fermi level and the bottom of the empty band. In the second or weak case, the magnetic
moment is less than the maximum even at 0 K which means that at all temperatures, there are carriers in both bands. The equilibrium value of the magnetic moment minimizes the energy,

$$\frac{\partial U}{\partial \sigma} = \frac{1}{2} (\mu_+ - \mu_-) - I\sigma - \mu_B H = 0 \quad (A4)$$

where the conservation of electrons,

$$v(\mu_+)d\mu_+ = -v(\mu_-)d\mu_- = \frac{1}{2}d\sigma \quad (A5)$$

has been used to simplify equation (A4). Equation (A4) is the basis of a molecular field approximation for which the field is defined as:

$$H_M = I\sigma + \mu_B H \quad (A6)$$

To insure that the extremum condition is indeed a minimum, the additional stability criterion is imposed:

$$\frac{\partial^2 U}{\partial \sigma^2} = \frac{1}{4} \left( \frac{1}{v(\mu_+)} + \frac{1}{v(\mu_-)} \right) - I - \mu_B \left( \frac{\partial H}{\partial \sigma} \right) > 0 \quad (A7)$$

Once the density of states is known, the equilibrium magnetic moment can be determined by applying conditions (A4) and (A7). For purposes of illustration, it is helpful to plot the two terms, \( \Delta = \frac{1}{2}(\mu_+ - \mu_-) \) and \( H_M \), on the same graph as a function of \( \sigma \). Figure (A1) shows such a plot. The intersection of the two curves define solutions to equation (A4) while equation (A7) determines which ones are indeed stable. In fact, this relation requires that \( \Delta \)
FIGURE A.1  BAND FUNCTIONS

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intersect \( H_M \) from below so that point A in the figure is stable while B is not.

(B) **Low Temperature Excitations**

The low temperature excitations are of two types which can be considered independent. These are the single particle excitations in which an electron is actually transferred from one subband to the other, and the collective excitations, known as spin waves or magnons, in which the entire electronic system participates in generating quanta of spin reversal.

(a) **Single Particle Excitations**

As already noted the single particle spin flips are characterized by an energy gap in the case of a strong or saturated ferromagnet. This is true for the low temperature magnetization for which Thompson, Wohlfarth and Bryan (1964) derive,

\[
\frac{\Delta \sigma}{\sigma_0} = A I(T) \exp \left( -\frac{E_g}{kT} \right) \quad , \quad (A8)
\]

with \( I(T) \sim T^{3/2} \) for a free electron band.

In the case of the weak ferromagnet the usual procedure for obtaining the low temperature magnetization is to expand

\[
\sigma = \int_0^\infty \left[ f(\mu_+ - E) - f(\mu_- - E) \right] \nu(E) dE \quad , \quad (A9)
\]

according to the rules for the Fermi functions, \( f \). To order \( T^2 \) the result is,
\[ \frac{\Delta \sigma}{\sigma_0} = -\frac{a}{c\sigma_0} T^2 \]  \hspace{1cm} \text{(A10)}

in which,

\[ a = \frac{(\pi k_B)^2}{6} \left[ \frac{\nu'(\mu_+)}{\nu'(\mu_+)} - \frac{\nu'(\mu_-)}{\nu'(\mu_-)} \right] \]

\[ c = 2I - \frac{1}{2} \left( \frac{1}{\nu'(\mu_+)} + \frac{1}{\nu'(\mu_-)} \right) \]

and the primes refer to the derivative with respect to energy.

It provides a greater insight to rederive equation (A10) in another way. If at \( T = 0 \) the system is characterized by an internal energy, \( U_0 \), with corresponding magnetic moment, \( \sigma_0 \), then at low temperatures the free energy can be written:

\[ F(\sigma, T) = U_0 + \left( \frac{\partial U}{\partial \sigma} \right)_0 \Delta \sigma + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \sigma^2} \right)_0 (\Delta \sigma)^2 + \ldots \]

\[ + \left( \frac{\partial U}{\partial T} \right)_0 T + \frac{1}{2} \left( \frac{\partial^2 U}{\partial T^2} \right)_0 T^2 + \ldots \]  \hspace{1cm} \text{(A11)}

\[ + \frac{1}{2} \left( \frac{\partial^2 U}{\partial \sigma \partial T} \right)_0 T (\Delta \sigma) + \ldots \]

where \( S \) is the electronic entropy which is linear in \( T \) in this range and given by:

\[ S = \frac{(\pi k_B)^2}{3} (\nu(\mu_+) + \nu(\mu_-)) T \]  \hspace{1cm} \text{(A12)}

Evaluating the derivatives in equation (A11) this relation simplifies to

\[ \Delta F(T, \sigma) = \frac{1}{2} \left( \frac{\partial^2 U}{\partial \sigma^2} \right)_0 (\Delta \sigma)^2 - \frac{1}{2} TS \]
Minimizing the change in free energy with respect to \( \sigma \) at constant volume and temperature yields,

\[
\frac{\Delta \sigma}{\sigma_0} = \frac{1}{2} \left[ \frac{\partial^2 G}{\partial \sigma^2} \right]_{V,T} \int \frac{\partial^2 G}{\partial \sigma^2} \sigma_0 \]

\[
= -\left( \frac{\pi k_B}{6\sigma_0} \right)^2 T^2 \left[ \frac{\nu'(\mu_+)}{\nu(\mu_+)} - \frac{\nu'(\mu_-)}{\nu(\mu_-)} \right] \left[ 2I-\frac{1}{2} \left( \frac{1}{\nu(\mu_+)} + \frac{1}{\nu(\mu_-)} \right) \right],
\]

as given by equation (A10). The presence of the factor \( \left( \frac{\partial^2 G}{\partial \sigma^2} \right) \) in the denominator of equation (A13) assumes a great significance in the description of the behaviour of invar alloys.

(b) **Spin Wave Excitations**

Recent theoretical developments by Edwards (1962), Thompson (1963) and others have given support to the postulate by Herring and Kittel (1951) that metallic ferromagnets, as well as insulating ones, must exhibit low energy collective modes, or spin waves. Each spin wave excited reduces the \( T = 0 \) magnetic moment by one quanta, i.e. by one unit of spin excitation which has an associated magnetic moment of \( g \mu_B \).

The low temperature thermodynamics of spin waves are taken into account by considering them to be bosons which obey the dispersion relation,

\[
E_q = Dq^2 + g \mu_B H_{\text{int}},
\]  

for which \( E_q \) and \( q \) are respectively the energy and wave
vector of the spin wave and,

$$H_{\text{int}} = (H_0 - H_D + H_A + \frac{4}{3} \pi M_0)$$

is the internal magnetic field, $H_0$ is the external field, $H_D$ demagnetizing field due to the sample shape, $H_A$ the anisotropy field and $\frac{4}{3} \pi M_0$ is the Lorentz field, which accounts to first order for the smearing effects of the anisotropy energy on the spin wave spectrum (Argyle, Charap and Pugh, 1963). In general, the dispersion coefficient, $D$, is a complicated function of the band structure. Since each spin wave carries $g \mu_B$ units of magnetic moment reversal, the resultant moment is obtained by counting the number of spin waves according to the prescription:

$$\frac{\Delta \sigma}{\sigma_0} = -\frac{g \mu_B}{\sigma_0} \sum_k \langle N_k \rangle$$

$$= \frac{g \mu_B}{M_0} \frac{1}{(2\pi)^3} \int_0^\infty 4\pi q^2 dq \left[ \exp \left( \frac{E_q}{kT} \right) - 1 \right]^{-1},$$

where $M_0 = \sigma_0 / V \equiv$ magnetization at $T = 0$.

$$\frac{\Delta \sigma}{\sigma_0} = -\frac{g \mu_B}{8\pi^2 M_0} \left( \frac{k_BT}{D} \right)^{3/2} \sum_{n=1}^\infty \left( \frac{1}{n} \right)^{3/2} \exp \left( -nT_g/T \right), \quad \text{(A16)}$$

and $kT_B = g \mu_B H_{\text{int}}$.

By using the expansion derived by Robinson (1951) for $T > T_g$, equation (A16) reduces to

$$\frac{\Delta \sigma}{\sigma_0} = -BT^{3/2} \left[ 1 + G(H, T) \right], \quad \text{(A17)}$$
for which,

\[ 1 + G(H, T) = 1 - 1.36 \left( \frac{T_g}{T} \right)^{1/2} + 0.56 \left( \frac{T_g}{T} \right) , \quad (A18) \]

to at least 1%, and,

\[ B = 0.0587 \frac{E\nu_B}{M_o} \left( \frac{k_B}{D} \right)^{3/2} \quad (A19) \]

These are the results used in the text.
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