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MAGNETIC PROPERTIES OF CRYSTALLINE MAGNESIUM
: MANGANESE.

THE OHIO STATE UNIVERSITY, PH.D., 1978

MAGNETIC PROPERTIES OF CRYSTALLINE Mg:Mn

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Richard Wesley Garvin, B.S., M.S.

* * * * *

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1978

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Dedicated to my parents, Richard H. and Ina Garvin, and to Debbie,
my wife.

ACKNOWLEDGMENTS

I want to thank my adviser, Professor Philip E. Wigen, who has been a source of great help and enormous encouragement. I would also like to thank Dr. Thomas Stakelon for his help in growing the single crystal used in this research, and for his many helpful suggestions. Many others have also given greatly appreciated help. Among them are Dr. Anthony Gerhardstein, who I would like to thank for his help with computer analysis, and for many fruitful discussions, and Professors Jan Korringa and David Stroud, for their enlightening discussions concerning the general theory of the magnetic properties of dilute alloys. Ms. Phyllis Ford quickly and efficiently typed both the initial and final drafts. The support of a University Fellowship during the year 1971-1972 is gratefully acknowledged, as is the guidance provided during that time by Professor James R. Gaines. The work was also supported in part by the National Science Foundation.

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I. INTRODUCTION

The phenomenon of magnetism is closely related to the purely quantum mechanical idea of the exchange, or overlap of electron wave functions. The electrons which govern the magnetic behavior of most materials are the inner 3d shell electrons in the transition elements, and the 4f shell electrons in the rare earths. Intra-atomic exchange results in the empirical Hund's rules, but when aggregates of magnetic atoms are formed, longer range interatomic exchange can result in cooperative magnetic behavior, such as ferri-, ferro- and antiferromagnetic behavior. Further, the exchange can be mediated by intervening nonmagnetic atoms in ionic compounds, such as oxygen in MnO (superexchange), or the conduction electrons in a metal (indirect exchange via the RKKY interaction).

In an effort to better understand the behavior of a single magnetic ion in a metallic environment, dilute¹ magnetic alloys have been studied. Among the interesting effects observed in dilute magnetic alloys are the Kondo effect, specific heat anomalies, and spin glass behavior.

The first observation of electron spin resonance (ESR) in dilute alloys was reported in 1956 by Owen, Browne, Knight and Kittel,² for Mn in Cu, and later³ for Mn in Ag and Mg hosts. The results contradicted the predictions of existing theories. The expected fine- and

hyperfine structure of Mn, which is common in ionic hosts, was absent in the resonance spectrum. Also, the expected large positive g shift (analogous to the nuclear Knight shift), proportional to the Mn susceptibility, was not found. Instead, a small temperature independent g shift was observed.

In 1959, Hasegawa⁴ presented a comprehensive treatment of the resonance in dilute magnetic alloys. It was demonstrated that the response of the system in an applied field could not be treated as the sum of the responses of the two independent systems of the conduction electrons and the magnetic impurities. The strong exchange coupling between the conduction and localized electrons was treated in a molecular field approximation, and a pair of coupled Bloch equations for the two magnetizations was hypothesized to obtain the dynamic transverse response.

The result of the strong coupling between the conduction and localized electron magnetizations is the appearance of a "relaxation bottleneck."⁴ Bottlenecking occurs whenever the cross transfer of energy from the magnetic impurity to the conduction electrons, and vice versa, is faster than the transfer of energy from the conduction electrons to the lattice. (The direct transfer of magnetization from the magnetic impurity to the lattice is very small for an S state ($L=0$) impurity (Mn^{2+} , Gd^{3+} , Fe^{3+}), due to the absence of spin-orbit ($\vec{L} \cdot \vec{S}$) coupling.) Under such circumstances, the g value and linewidth of the coupled system are determined by the susceptibility weighted

averages of the impurity and conduction electron g value and linewidth. A systematic study of the bottleneck carried out by Gossard, Heeger and Wernick⁵ verified Hasegawa's theory.

After the initial study on Mn in Cu, Ag, and Mg, further investigations were begun using other transition metals and rare earths in a wide variety of host metals. Friedel⁶ was the first to formulate a theory to predict whether a transition metal or rare earth impurity would retain its local character in metal hosts. The "Friedel sum rule" was only partially successful in explaining why some impurities are magnetic in some hosts but not in others, and also why some host metals cause magnetic behavior for some impurities but not for other impurities. Anderson⁷ was the first to propose a quantitative theory for the transition to a magnetic state. The Hamiltonian used in the "Anderson model" is still widely used as a starting point for many calculations involving properties of dilute alloys.

As a better understanding of the general properties of dilute alloys was gained, concern grew whether a magnetic ion could be considered as an isolated impurity. Susceptibility studies were made to determine the effects of impurity-impurity interactions, which result in a departure of the susceptibility from a Curie or Curie-Weiss law. Quite often a broad maximum in $\chi(T)$ appeared.

Evidence of a possible phase transition was first obtained from Mössbauer experiments, and later from the observation of the decay of implanted muons as they precessed about the total (external plus internal) field. The most dramatic evidence of impurity-impurity

interactions was the observation in 1971 by Cannella, Mydosh and Budnick⁸ of a cusp in the low field (≤ 10 G) low frequency (~ 155 Hz.) susceptibility of a series of Au:Fe alloys. The cusp occurred at a temperature T_0 which depended on concentration. However, neutron diffraction studies showed no long range magnetic order below T_0 .

The interpretation of this behavior is that in the absence of an applied field the impurity spins collectively freeze into random directions at a single temperature due to the competition between ferromagnetic and antiferromagnetic exchange. Systems exhibiting this behavior were labeled spin glasses, in analogy with the freezing of ordinary glasses.

Observation of crystalline fine structure and its magnitude are related to the fundamental question of the magnetic state of an impurity in a metallic host. Electron spin resonance is a suitable method for investigation of the crystal field splitting of S state ions. In insulating crystals the ESR spectra consists of several separated resonance lines with a marked angular dependence. The spectra can be described by an appropriate spin Hamiltonian which reflects the symmetry of the crystal lattice, and which contains certain fitting parameters. In spite of the growing amount of experimental data, the understanding of the mechanism of crystal field splitting is not developed so far as to permit a quantitative interpretation of spin Hamiltonian parameters.

In dilute alloys or in intermetallic compounds, the conduction electrons influence the crystal field splitting. For this reason

there is considerable interest in the crystal field splitting of localized magnetic moments in metals. In contrast to the ionic crystals, it is difficult, and in many cases impossible to resolve the fine structure in the ESR spectra of S-state ions in metallic hosts. The exchange interaction between the localized spins and the conduction electrons leads to a relaxation between the two systems and gives rise to the "Korringa" linewidth which increases linearly with temperature. The exchange interaction also causes narrowing effects between the different crystal field split transitions. Therefore, the expected resolved structure may be partly or totally narrowed into a single resonance line. The exchange narrowing caused by correlated hopping between the crystal field split Zeeman levels in the presence of varying bottleneck strengths has been recognized and calculated.^{9,10} These results have been used in the limit of an extreme bottleneck to analyze the crystal field splitting.

The work reported here is an extension of earlier work done in this laboratory by F. Kleinhans.¹¹ He investigated the ESR in three polycrystalline Mg:Mn alloys with Mn concentrations of 0.02, 0.11, and 0.49 at.%, at frequencies of 9.4 and 23.5 GHz. and at temperatures as low as 2.1 K. At temperatures below 10 K, a downfield shift of the resonance field, and an increase in the linewidth, were interpreted as being due to a transition to the antiferromagnetic (AFM) state. One source of the requisite internal anisotropy field was conjectured to be the crystal field. The investigation of a single crystal Mg:Mn

alloy was therefore intended to measure the strength of the crystal field interaction.

In the work reported here, the angular dependence of the ESR resonance field of a Mg:Mn single crystal (0.35 atomic percent Mn) was used to find the crystal field parameter D , and the linewidth was used to determine the exchange parameter J , in light of a theory⁹ concerning the exchange narrowing of a bottlenecked system. The static susceptibility was measured from 2 K to room temperature in order to identify any magnetic phase transitions. The absence of an AFM transition in the susceptibility ruled out the interpretation of the downfield shift as being due to coherent long-range magnetic order. The downfield shift has been interpreted in terms of a recent theory¹² based on columnar inhomogeneities, and the results for the downfield shift are in qualitative agreement with the theory.

The dissertation proceeds in the following manner. Chapter II outlines the theories for the formation of a local moment in a metal, ESR in dilute alloys, including discussions of crystal field splitting and spin glass behavior, and a theory for the source of internal fields which cause a rapid decrease in the resonance field at low temperatures. Chapter III contains the description of the apparatus used to grow the crystalline sample, and a discussion of the determination of the solid solution concentration of Mn. A discussion of the experimental procedures appears in Chapter IV, and the results with discussion are presented in Chapter V.

II. THEORY FOR THE MAGNETIC PROPERTIES IN DILUTE METAL ALLOYS

The earliest study of nonmagnetic metals containing dilute amounts of magnetic atoms was done in 1956-7 by Owen, et al.,^{2,3} who carried out magnetic susceptibility and electron spin resonance on Mn in Cu, Ag and Mg. Using the theory of paramagnetism for ionic crystals, the susceptibility results seemed to indicate a reduction in the magnetic moment per magnetic atom from that expected for Mn^{2+} . Also, the ESR g shift was smaller than that expected using a molecular field theory similar to that used in the analysis of the Knight shift of nuclear resonance lines.

Because of these and later developments in dilute magnetic alloys it became obvious that new theories had to be developed. This chapter outlines the theoretical work describing the behavior of atoms with unfilled inner electron shells (transition or rare earth metals) when dissolved in a nonmagnetic metal. Theories which attempt to explain the formation of a local moment in a metal are first outlined. The virtual bound state model and Anderson model are discussed, followed by the s-d model and an ionic model. These theories attempt to explain why some impurity ions are paramagnetic in one host and nonmagnetic in another, and also why some host metals cause magnetic behavior for some impurity ions but not for other impurities.

Using the local moment formulation, the Curie and Curie-Weiss laws for the static susceptibility are derived, including the effects of interactions, as well as the effects of magnetic ordering, the onset of which gives rise to spin glass behavior.

The next section is concerned with the spin resonance of dilute alloys. It is sometimes possible to observe the resonance due to conduction electrons, and in other cases, it is possible to observe the electronic resonance of the localized moments, when they exist. The properties of the local moment resonance are somewhat similar to the properties of nuclear magnetic resonance in a metal,¹³ although there are some very important differences. The perturbation of the conduction electron system caused by the local moment is large, and the form of the interaction with the conduction electrons is not easy to establish. Because the g factors of the local moment and the conduction electrons are usually quite similar, the resonance frequencies of the two systems are very close, complicating the interpretation of the observed shifts. This coupling of the conduction and localized electrons is the fundamental difference between electron spin resonance in insulators and in metals.

The coupling between conduction and localized electrons is assumed to be a direct exchange

$$H_{sd} = -J \vec{S} \cdot \vec{s}$$

where $\vec{S}$ is the spin of the local moment, $\vec{s}$ is the conduction electron spin and J is the value of exchange integral. Other contributions to J are considered in detail. The above interaction is analogous to the nuclear hyperfine contact coupling and has similar effects on the electronic resonance.

Due to the near equality of the g factors of the two spin systems, the eigenfrequency of the coupled system is a function not only of the two individual resonance frequencies and the coupling constant J , but also of the relaxation times of the two systems. When the conduction electrons relax rapidly to the lattice, a g shift Δg for the local moment resonance is found which is proportional to the average molecular field produced by the conduction electrons: $\Delta g \propto \chi_e J$, where χ_e is the static susceptibility of the conduction electron system. This allows the sign of J to be determined. Also, the relaxation rate is proportional to $J^2 kT$, which allows the value of the exchange integral J to be determined by measuring the temperature dependence of the linewidth.

The values for the g shift and linewidth are altered when the relaxation rate of the conduction electrons to the lattice is less than the relaxation rate to the local moment system. This condition is referred to as a "relaxation bottleneck" and correctly characterizes the Mg:Mn system studied in this work.

Several reviews on the theory of,¹⁴⁻¹⁷ and experiments on^{15,17} dilute metal alloys can be found in the literature. The outline presented in this chapter follows the review by M. Peter, R. Orbach

and D. Shaltiel.¹⁵ Phenomenological coupled Bloch equations, and their solutions in various limits, are discussed. Sources for the various relaxation rates are outlined. Finally, a conjecture for the source for the internal field required to explain the rapid decrease in the resonance field at low temperatures is presented.

A. Local Moment Theories

When an atom with a partially filled electron shell is dissolved in dilute quantities in nonmetallic hosts, or when formed into non-metallic compounds or molecules, quite frequently a definite ionic valence state is assumed and a magnetic moment in accordance with Hund's rules is formed. In the case of a metallic host the presence of the broad conduction band is responsible for complex phenomena, one of the most important of which is the possibility of the loss of the local magnetic moment.

Early experimental work¹⁸ indicated that the presence of a magnetic impurity gave rise to anomalous properties of magnetic alloys, such as temperature dependent resistivity, antiferromagnetism and giant thermopower. The data indicated that when a resistance minimum was found, invariably some evidence of a local moment was also found, and inversely, when localized moments were revealed from some measurement, a resistivity minimum was observed.

The earliest theories simply attempted to predict whether a transition metal impurity would retain its local character in noble metal hosts. Later, these models were extended to explain the anomalous

transport properties, leading eventually to the Kondo effect which quantitatively explained the resistance minimum. In addition, Kondo formulated a characteristic temperature, T_K , below which the local moment becomes unstable and the alloy becomes nonmagnetic.

Outlines of the theoretical models which attempt to solve the problem of the formation of a local moment can be found in several review articles.¹⁹⁻²³ These models include Friedel's virtual bound state (vbs) scattering formulation,⁶ Anderson's⁷ mixing model, and the s-d exchange model, which was first proposed by Zener.²⁴ These basic theories are outlined in some detail below. A feature common to these theories is the reduction of the problem to the interaction of the conduction electrons with a single atom in the host metal. A potential is introduced which represents the addition of the impurity and a one-electron Schrödinger equation is solved. The drawback to this one-electron approach is that it has been found²⁵⁻²⁷ that the scattering of a conduction electron from a magnetic impurity cannot be considered as a one-electron problem, but must be treated as a many-body problem. The effects of other electrons (the exclusion principle, Hund's correlations, crystal fields and spin-orbit effects) must be described in terms of many-electron configuration energies.²⁸

1. Virtual Bound State Model

A phenomenological explanation for the formation of a local moment was first given by Friedel⁶ using the concept of a "virtual bound state" (vbs): the d orbitals of a transition metal atom dissolved in a simple

metal retain much of their localized character although the orbitals are embedded in the host metal conduction band. The vbs model is essentially a one electron scattering problem with all of the valence (s and d) electrons of the impurity first placed into the conduction band. The excess charge Ze of the impurity is screened by the conduction electrons to produce a one electron (spin-independent) potential which is assumed spherically symmetric. Friedel's sum rule results from a phase shift analysis which requires that the total screening charge be equal to the excess nuclear charge of the impurity. The effect of the resonant d-wave portion of the scattering amplitude of the conduction electrons is to produce a d-orbital which is broadened and shifted from the unperturbed state. To explain the net magnetization on a qualitative basis, Friedel pointed out that the exchange and spin correlation effects responsible for Hund's rules would operate to separate the energy of the vbs for spin-up electrons from that for spin-down electrons. When the virtual level is narrow enough for this to occur, a net moment results if the number of spin-up levels exceeds the number of spin-down levels for energies less than the Fermi energy, E_F . Blandin and Friedel²⁹ were able to derive a condition for the stability of the magnetic moment, and construct a table for the occurrence of a magnetic or nonmagnetic state for transition metal impurities in various hosts.

2. The Anderson Model

Anderson⁷ was the first to make quantitative the transition to the

magnetic state. His model Hamiltonian consists of four terms

$$H = H_{of} + H_{od} + H_{corr} + H_{sd} . \quad II-1$$

The first term H_{of} is the unperturbed energy of the free-electron system, and the second term H_{od} represents the unperturbed energy of the d states on the impurity atom. In second quantized notation,

$$H_{of} = \sum_{\vec{k}, \sigma} \epsilon_{\vec{k}} n_{\vec{k}\sigma} \quad II-2$$

$$H_{od} = E_d (n_{d+} + n_{d-}) \quad II-3$$

where $\epsilon_{\vec{k}}$ is the energy of a free electron of wavevector $\vec{k}$, $n_{\vec{k}\sigma}$ is the number operator for conduction electrons of wavevector $\vec{k}$ and spin index σ , and n_{d+} is the number operator for d electrons with spin up (+).

The third term, H_{corr} , in the Hamiltonian is the correlation, or repulsive energy among the d electrons

$$H_{corr} = U n_{d+} n_{d-} , \quad II-4$$

where U is the repulsive energy among the d orbitals.

$$U = \iint |\phi_d(r_1)|^2 |\phi_d(r_2)|^2 \frac{e^2}{r_1 - r_2} d\tau_1 d\tau_2 \quad II-5$$

and is formally the exchange self-energy of the state ϕ_d as well as the Coulomb integral of that state.³⁰

The fourth part of the Hamiltonian is the s-d mixing interaction, H_{sd} ,

$$H_{sd} = \sum_{\vec{k}, \sigma} V_{\vec{k}d} (c_{\vec{k}\sigma}^* c_{d\sigma} + c_{d\sigma}^* c_{\vec{k}\sigma}) \quad \text{II-6}$$

where $c_{\vec{k}\sigma}^* c_{d\sigma}$ destroys a localized electron with spin σ and creates a free electron with momentum $\vec{k}$ and spin σ , and $V_{\vec{k}d}$ is the mixing potential which allows conduction electrons to mix with the electrons in the localized level, causing that level to be broadened and shifted. Using Fermi's golden rule, the interaction H_{sd} will give rise to a finite lifetime for occupancy of the localized state, and therefore an energy width, Δ ,

$$\Delta = \pi |V_{\vec{k}d}|^2 \rho(E_F) \quad , \quad \text{II-7}$$

where $\rho(E_F)$ is the one spin conduction electron energy density of states at the Fermi energy, E_F . It should be noted that H_{sd} is a one electron interaction which connects the s and d states, and that the calculation is done at $T=0$.

The Anderson model has had some success at explaining local moment formation. The condition $\pi\Delta/U < 1$ for formation of the magnetic state depends on estimates of Δ and U . The ionization energy U depends mainly on the impurity atom, although conduction electrons of the host reduce U from the free ion value due to screening effects. The localized state width Δ increases with increasing Fermi energy. In Al ($E_F = 11.6 \text{ eV}^{31}$) no transition metals, except possibly Mn, form local moments; in the noble metals Cu, Ag and Au ($E_F = 7.0, 5.5, 5.5 \text{ eV}^{31}$) Cr, Mn and Fe are known to have moments.³² The susceptibility

of the Hartree Fock (HF) Anderson model diverges at the point of transition to the magnetic state ($\pi\Delta \sim U$) preventing the determination of the magnetic state of a borderline magnetic alloy such as Al:Mn. Problems also arise when applications of the model are extended to finite temperature, where Kondo terms must be included.

It is apparent that one of the fundamental parameters of the dilute alloy problem is the time period over which the impurity moment exists. Since the d-states are not perfectly localized, and decay into the continuum of s-states within the single particle lifetime $\hbar/\Delta$, the moment has a finite lifetime τ . While an infinite lifetime predicted by the HF Anderson model is physically inappropriate, it may be long enough for certain situations to cause measurable magnetic effects, such as a Curie-Weiss susceptibility. This idea is incorporated into the s-d exchange model.

3. The s-d Exchange Model

The s-d exchange model is based on a series of papers by Kondo,^{19, 25,33} who starts with the assumption that a moment exists (equivalent to the HF Anderson condition $\pi\Delta/U \ll 1$, the strongly magnetic case). The impurity is assigned a spin S , which interacts with the conduction electrons of spin s , through a "contact" interaction represented by a term in the Hamiltonian;³⁴

$$H_{\text{ex}} = -J \vec{S} \cdot \vec{s} \quad J < 0 \quad \text{II-8}$$

This antiferromagnetic coupling term is not really a new term: by a proper canonical transformation³⁵ of the Anderson Hamiltonian, the mixing term H_{sd} , Eqn. II-6, can be put into the above form, Eqn. II-8, if $\pi\Delta/U \ll 1$. [A more correct form of H_{ex} would include a spatial variation $f(\vec{r})$ to represent the extent of non-localization of the d state, leading to a Fourier transform $J_{\vec{k}\vec{k}}$, of $J \cdot f(\vec{r})$. The spatial variation is assumed to be an isotropic zero range delta function, so that $J_{\vec{k}\vec{k}} = J$, a constant.]³⁶ Under the transformation, the Anderson V_{kd} mixing term is removed to first order and H_{sd} can be represented by a simple attractive potential V'_{kd} , plus an exchange term, Eqn. II-8, where

$$J = |V'_{kd}|^2 [(E_d - E_F)^{-1} + (E_F - E_d - U)^{-1}] \quad \text{II-9}$$

and where both terms of Eqn. II-9 are negative. It should be noted that the value of the total exchange J_{tot} will depend upon the relative contributions from the negative covalent mixing term, Eqn. II-9, and from the direct exchange integral contained in H_{corr} , Eqn. II-4 (see footnote 30).

The physical origin of the term H_{ex} , Eqn. II-8, can be shown to arise from the consequences of the Anderson Hamiltonian term H_{sd} . The mixing term H_{sd} allows electron transfer from the (occupied) impurity state to the spin-up conduction electron Fermi surface states, as well as from the spin-down Fermi surface states to the (nearly unoccupied) impurity state. In order to maintain equilibrium, spin-up conduction electrons "flow" into spin-down conduction electron states. Since there are more spin-down conduction electrons than spin-up conduction

electrons, a polarization is created which is opposed to the impurity moment. The exchange term $-J\vec{S}\cdot\vec{S}$ represents this antiferromagnetic coupling between the localized electrons and the Fermi surface conduction electrons.

Among the consequences of the antiferromagnetic character of the exchange term are the unusual transport properties of dilute magnetic alloys (the Kondo effect), first calculated in 1964.²⁵

For almost all cases, the Hartree-Fock (HF) one electron approximation to the Anderson model gives an appropriate physical picture for both magnetic or nonmagnetic cases far from the instability point $\pi\Delta/U \sim 1$. The impurity with one electron has energy E_d , and if another electron of opposite spin is added to the impurity (addition of a parallel spin electron is forbidden by the exclusion principle), its energy is raised by U , due to Coulomb correlations (repulsion). This correlation effect can be described in terms of electrons hopping between the impurity and conduction electron states. Due to the finite width of the impurity state, it is occupied by zero, one, or two electrons for definite periods of time. For large correlation energy U the proportion of time during which the impurity state is doubly occupied becomes very small. The state appears to the experimenter to have a single d electron if the lifetime τ of the state is such that $kT < \hbar/\tau$. At lower temperatures serious deviations are expected to occur, using the Anderson model. The lifetime τ will increase with increasing U/Δ ratio, while for the s - d model, τ should increase with decreasing coupling (decreasing J , Eqn. II-8). In the s - d model,

at temperatures such that $kT < \hbar/\tau$ the impurity should appear nonmagnetic, because the lifetime of the polarization is smaller than the time required to align the spin by an external magnetic field. Since τ is always finite in the s-d model, any impurity is nonmagnetic at $T=0$. The s-d model allows the finite temperature properties of the dilute alloy to be calculated, but produces a divergence at $T=0$ due to the Kondo $\log T$ terms in the magnetic contributions of the transport properties.

Various schemes^{20,22} have been used to remove the Kondo divergence for $T \ll T_K$; however, for Mg:Mn, the Kondo temperature is very small, perhaps as low as $10^{-3}K$. Temperatures well below this are presently unattainable, so that for the purposes of this investigation, the consequences of the divergence will not be discussed.

4. The Ionic-type Hirst Model

An ionic model using a d-(or f-) electron configuration based approach has been proposed by Hirst.²⁸ Although this model seems to apply quite readily to rare earth impurities in metals, it is not clear that transition metal impurity moments can be explained using this model. It is included here because the model and its connection with the previously mentioned theories are straightforward, and also for reasons of completeness.

A generalized Anderson Hamiltonian is the starting point for this model,³⁷

$$H = H_{\text{ion}} + H_{\text{cond}} + H_{\text{sd}} . \quad \text{II-10}$$

The term H_{cond} represents the conduction electron system as in Eqn. II-2, H_{sd} is the one electron mixing interaction as in Eqn. II-6, and H_{ion} describes the localized interactions at the impurity site,

$$H_{\text{ion}} = -Vn + Un(n-1)/2 + H_{\text{intra}} . \quad \text{II-11}$$

Here n is the number operator for the total number of 3d (or 4f) electrons, V is the binding energy at the impurity site and U is the leading term in the d electron Coulomb interaction and yields an energy proportional to the number of 3d pairs. The term H_{intra} represents the intra-configurational splitting energies which produce spin-orbit and crystal-line electric field effects, and Hund's rule correlations.

The ionic Hamiltonian term, Eqn. II-11, describes a tendency toward the formation of ionic-type localized states, belonging to definite electron configurations, $3d^n$. The mixing interaction tends to break up the configurations and to mix 3d electrons into the conduction band. As in the Anderson model, the properties of the impurity are determined by the competition of these two tendencies.

The exact structure of the resonant nonmagnetic state and also the precise mechanism for the demagnetization remain open in the first theory, mainly because the Boltzmann statistics obeyed by the impurity states, and the Fermi statistics obeyed by the conduction electrons resist simultaneous treatment. The theory predicts that only two well-defined configurations are resonating in the nonmagnetic state,

and on a scale larger than Δ , the resonant states retain their individual Hund's rule structure fairly well. The nonmagnetic state could then be the result of invoking the uncertainty principle.

B. Static Susceptibility

In an extensive review of bulk magnetic properties, Rizzuto³² has classified dilute alloys into three categories, based on the temperature dependence of the susceptibility. Class (a) systems have a Pauli (enhanced) temperature independent susceptibility; class (b) systems follow a Curie-Weiss law, Eqn. II-14; and class (c) systems obey a free ion or Curie law, Eqn. II-13. The transition from class (a) to class (c) systems corresponds to a shift of the state of the impurity from nonmagnetic to strongly magnetic.

The first ionic model, and the HF Anderson model (in the strongly magnetic regime), both predict that the impurity will behave like an isolated ion with a Curie law susceptibility

$$\chi_{\text{imp}}(T) = C/T = N\mu_{\text{eff}}^2/3kT \quad \text{II-12}$$

where

$$\mu_{\text{eff}}^2 = g^2\mu_B^2S(S+1) \quad \text{II-13}$$

N is the number of impurities per unit volume, C is the Curie constant, and k is Boltzmann's constant, T is the absolute temperature, μ_{eff} is the effective number of Bohr magnetons per impurity, g is the spectroscopic splitting factor and μ_B is the Bohr magneton. For an ionic

impurity, the spin S should have definite values, $S=n(1/2)$, where n is an integer. A variety of systems follow a Curie-Weiss law of the form

$$\chi_{\text{imp}}(T) = N\mu_{\text{eff}}^2/3k(T + \theta) \quad \text{II-14}$$

over a wide temperature range, where θ is the Weiss temperature. The Curie-Weiss law can be reproduced using the s-d model, with the result

$$\langle S_z \rangle = \frac{g\mu_B S(S+1)H}{3kT} \left(1 + \frac{(J\rho)^2 \ln(kT/E_F)}{1 - J\rho \ln(kT/E_F)} \right) \quad \text{II-15}$$

$$\langle s_z \rangle = J\rho \langle S_z \rangle \quad \text{II-16}$$

and the total susceptibility to order $(J\rho)^2$, is

$$\chi_{\text{tot}}(T) = \frac{Ng^2\mu_B^2 S(S+1)}{3kT} \left(1 + \frac{J\rho}{1 - J\rho \ln(kT/E_F)} \right) \quad \text{II-17}$$

where J is the exchange constant defined in Eqn. II-8 and ρ is the host metal one spin density of states per atom. To within 1/2%, this can be rewritten,

$$\chi(T) = \frac{Ng^2\mu_B^2 S(S+1)}{3k(T+4.5T_K)} (0.82) . \quad \text{II-18}$$

Thus the effective moment is reduced by about 10% compared to the ionic calculation.

The (HF) Anderson model also predicts a reduction in the effective paramagnetic moment due to overlap of the two virtual bound states (for a single d electron impurity). Although the effective moment can be calculated⁷ in a selfconsistent manner quite easily for a single d

electron impurity, and although the extension to a many-electron impurity is implied, the calculation has not been carried out. Thus only a qualitative understanding of the reduction in moment is obtained from the Anderson model.

Figure 1 shows some experimental results for the effective number of Bohr magnetons per impurity for V, Cr, Mn, Fe, and Co in various hosts. The systematic reduction in moment (by $\approx 20\%$) from the free ion value (dashed line) is clear.

1. Interactions Between Impurities

The theories which have been outlined thus far have attempted to describe the behavior of a single impurity atom in a metallic host. The application of the theories to a system which contains many impurities is valid only when each impurity behaves like an isolated atom which interacts only with the conduction electrons of the host. Thus the most obvious approach has been to study alloys where transition metal atoms are dilute impurities. The impurity concentration is made lower and lower until the bulk properties of the alloy vary only linearly with concentration. The term dilute is difficult to define; whether the transition atoms in a host can be considered dilute depends both on the type of host and the impurity, as well as the temperature range involved. For example, even one part per million (ppm) Mn in Cu is not dilute below 0.01 K^{38} while in some intermetallic compounds, e.g. Ce in Al,³² the impurities can be thought of as an assembly of isolated Ce atoms.

FIGURE 1. Typical experimental data for p_{eff} for transition metals in various hosts compared to the free ion value, dashed line. After Rizzuto.³² Error bar for Mg:Mn represents the spread in values from Table 4.

The interactions which take place between impurities in an alloy can be classified into two categories³² according to the effects caused by their presence. The first is the long-range interaction between impurity moments, caused by the spin polarization induced in the conduction electrons (the RKKY interaction). The spin polarization gives rise to internal fields, which, below some critical temperature, cause the magnetic moments to align. The effects caused by the presence of these long range interactions are called "ordering effects."

The second type of interactions between impurities does not cause long-range order, but change the character of the impurity. These interactions are called "coupling interactions," and normally are caused by clustering of impurities as the result of thermal treatment, or simply because the concentration is not dilute enough, as discussed above. The properties observed in the alloy may appear to be the result of different kinds of impurities, although the "different kinds" of impurities may simply be pairs, triplets or larger clusters of impurities.

W. M. Star³⁹ has derived an empirical criterion which must hold for an impurity to be free from interaction effects:

$$c < \theta / T_f$$

II-19

where θ is the (concentration independent) Weiss temperature, T_f is the Fermi temperature and c is the fractional impurity concentration.

Relation II-19 implies that for Mg:Mn, c must be less than about 10 ppm, assuming a Weiss temperature of about 1 K. It should be noted that it would be very difficult to make reflection microwave resonance measurements at this concentration, although transmission ESR measurements have been done⁴⁰ for a 60 ppm Mg:Mn sample. The low field dc susceptibility could also be measured in this concentration range, but only by using a SQUID magnetometer.

The effects of ordering can be easily observed in the temperature dependence of the susceptibility. The susceptibility departs from the Curie (or Curie-Weiss) law at a temperature T_0 which should depend linearly on concentration.

The effects of "coupling interactions" are more difficult to detect and to analyze. It is possible to interpret the observed susceptibility as being due to two or more overlapping Curie-Weiss laws: one Curie-Weiss contribution for single impurities with a Weiss temperature θ_1 ; a second contribution for pairs of impurities with a Weiss temperature θ_2 ; and so on for clusters of 3, 4 or more impurities. Typically then,

$$M(H) = cM_1(H) + c^2M_2(H) + \dots \quad \text{II-20}$$

where $M(H)$ is the total magnetization, $M_1(H)$ is the contribution due to single impurities, $M_2(H)$ is due to pairs of impurities and c is the concentration. Then (to order c^2) a plot of $M(H)/c$ vs. c serves to identify M_1 and M_2 . For this type of analysis to be accurate, measurements must be made over a large concentration range.

2. Effects of Spin Glass Order

Until recently, the effects of ordering on the susceptibility of dilute alloys were believed to result simply in a departure from the expected Curie or Curie-Weiss law. In several alloys with concentration $c > 0.1$ at.%, as the temperature was lowered, a broad maximum in $\chi(T)$ appeared. This was first interpreted as indicating the onset of a magnetic transition at the temperature of $\chi_{\max}$.

Mössbauer studies provided the first indication that a low temperature magnetic ordering was occurring. The Mössbauer spectra showed the onset of hyperfine splitting at a well defined temperature T_0 . The onset of a hyperfine field, assumed proportional to the atomic magnetization, has usually been associated with magnetic order. A careful analysis of the intensity ratios of the hyperfine spectra indicated, however, a random alignment of spins. In addition, neutron scattering data indicated the absence of long range magnetic order in these types of alloys.

In 1971,^S low field ($H \leq 10G$) ac susceptibility data for a series of low concentration AuFe alloys revealed a very sharp peak (cusp) at a temperature T_0 which increased with increasing concentration. This development led to increased activity, both experimental and theoretical, in the investigation of the properties of non-dilute magnetic alloys (i.e. no longer single, noninteracting impurities).

Two new terms describing these alloys arose: "spin glass" and "mictomagnet," which refer to non-dilute magnetic systems whose

impurity moments freeze into random directions at a distinct temperature. For small concentrations, the interaction responsible for the cooperative freezing is the long-range RKKY interaction. This is the spin glass regime. Mictomagnetism refers to larger concentrations where magnetic clusters form due to direct exchange between nearest and next-nearest neighbor impurities, which in turn interact with each other via the RKKY potential.

It should be emphasized that there is no sharp transition from spin glass to mictomagnetic behavior. Rather, spin glasses are collections of single impurities, each of whose moments freeze with random directions. A mictomagnet contains clusters of 20-20,000 impurities, in which short range order aligns the individual moments inside each cluster. At the freezing temperature T_0 , the total magnetic moment vector of each cluster freezes with a random orientation.

The experimental properties of spin glasses are reviewed by Mydosh,⁴¹ and a summary of the theoretical developments has been provided by Heber.⁴² The following is a brief summary of the magnetic properties of spin glasses and mictomagnets.

The low field susceptibility is completely reversible, and exhibits a very sharp peak at T_0 which uniquely defines the freezing temperature. At zero temperature, a finite susceptibility is found, and for concentrations below about 5 at.%, the ratio $\chi(0)/\chi(T_0)$ is nearly constant (~ 0.6). Above T_0 , a Curie-Weiss susceptibility holds, and for concentrations greater than ~ 1 at.%, the effective moment per impurity increases with concentration. This is attributed to the

growing importance of short range atomic order. The Weiss temperature θ is nearly zero when short range correlations are unimportant, but $|\theta|$ increases to small values as short range correlations and the effective moment grow. For impurity concentrations below about 10 at.%, $T_0 \propto c^m$ where c is the fractional impurity concentration and $0.75 > m > 0.55$.

When the susceptibility is measured in an applied field H_a greater than some threshold value $(H_a)_c$, the sharp peak is smeared out, and the process is no longer reversible. If the temperature is decreased below T_0 in the presence of an external field, hysteretic losses occur, and a remanent magnetization is produced, which relaxes in zero field with a characteristic time constant, $\tau(c, H_a, T)$, which can be on the order of minutes. The remanent magnetization is stronger for a micro-magnet, but neither a spin glass nor a micro-magnet displays any remanance when cooled in zero field.

In addition to the above properties, an interesting experiment has been performed⁴³ on CuMn and AuFe alloys using muons. In order to sample the local fields in the alloys, the alloy was placed in a beam of muons and subjected to an external field. The precession of the muon spin around the combined external and internal fields was measured by the oscillations in the emitted positron intensity. Since the decay positrons are emitted preferentially in the direction of the muon spin, the total intensity of the detected positrons as a function of time should show damped oscillations, the damping arising from the inhomogeneities in the total field. At temperatures above T_0 the oscillations were damped (spins dephased) rather slowly. This was attributed

to the fact that the internal fields oscillated much more rapidly than the muon spins, so that the muons responded to the external field only. At temperatures below T_0 , the oscillations of the positron signal dephased much more rapidly, indicating the presence of large inhomogeneities in the total field. This was attributed to static, local, randomly oriented, internal fields, resulting from "frozen" moments.

3. The Effect of Crystalline Anisotropy on the Susceptibility

That the crystalline anisotropy will not effect the susceptibility is shown in the following thermodynamic treatment. The argument follows the calculation of magnetic properties of a paramagnet from Abragam and Bleaney.⁴⁴

The partition function for a system of N particles per unit volume, characterized by energy levels W_i , is

$$Z = \sum_i \exp(-W_i/kT) , \quad \text{II-21}$$

and the magnetization of the system is

$$M = NkT \left(\frac{\partial}{\partial H} \ln Z \right)_T . \quad \text{II-22}$$

The spin Hamiltonian for a spin $5/2$ Mn^{2+} ion with isotropic g factor in an axial environment is

$$H = g\mu_B H S_z + 1/2 g\mu_B D(3\cos^2\theta - 1) [S_z^2 - 1/3 S(S+1)] \\ + \text{off-diagonal terms} . \quad \text{II-23}$$

The full spin Hamiltonian is treated in detail in the next section.

The energy levels W_{m_s} determined by the Hamiltonian above are, to first order,

$$W_{m_s} = g\mu_B H m_s + 1/2 g\mu_B D(3\cos^2\theta - 1)[m_s^2 - 1/3 S(S+1)] . \quad \text{II-24}$$

For temperatures such that $kT \gg W_M$, Z may be expanded in a power series in $(kT)^{-1}$ as

$$\begin{aligned} Z/n &= 1 - \langle W \rangle / kT + \langle W^2 \rangle / 2 (kT)^2 - \dots \\ &= 1 + \sum_{p=1}^{\infty} b_p T^{-p} , \end{aligned} \quad \text{II-25}$$

where $\langle W^p \rangle$ is the average of the p^{th} powers of the energy levels, whose total number is n . The series expansion for $\ln Z$ is then

$$\ln Z = \ln n - \sum_{r=1}^{\infty} a_r T^{-r} \quad \text{II-26}$$

where

$$a_r = b_r - 1/2 \sum_{p=1}^{r-1} b_{r-p} b_p + 1/3 \sum_{p=1}^{r-2} \sum_{q=2}^{r-2} b_{r-p-q} b_p b_q - \dots \quad \text{II-27}$$

From the thermodynamic equations, then

$$M = Nk \sum_{n=1}^{\infty} \left(\frac{\partial a_n}{\partial H} \right)_T T^{-(n-1)} . \quad \text{II-28}$$

If the origin of energy is chosen such that $\langle K \rangle = 0$, then

$$M/N = \frac{1}{2kT} \left(\frac{\partial \langle K^2 \rangle}{\partial H} \right)_T - \frac{1}{6(kT)^2} \left(\frac{\partial \langle K^3 \rangle}{\partial H} \right)_T + \dots, \quad \text{II-29}$$

When $\langle K^2 \rangle$ is evaluated, the only term which depends on H is the Zeeman term, the terms proportional to D being independent of H . Also, for an isotropic g factor, the terms proportional to D in $\langle K^3 \rangle$ do not contribute to M .

C. Electron Spin Resonance in Dilute Alloys

1. Hasegawa's Bloch Equations

In 1959 Hasegawa⁴ presented the first successful comprehensive treatment of the resonance of dilute magnetic alloys. He realized that the molecular field treatment used by Owen, et al.,^{2,3} which assumed that the coupling of the conduction electrons to the lattice was stronger than the coupling to d electrons (via the s - d exchange), would not necessarily be valid under the dynamical conditions of a resonance experiment. In a resonance experiment, the magnetization of the conduction electrons $\vec{M}_e$ does not remain at its thermal equilibrium value, i.e., its value in the absence of the rf field, but precesses following the localized electron magnetization $\vec{M}_s$, so that $\vec{M}_e$ is parallel to $\vec{M}_s$. Since the molecular field $\lambda \vec{M}_e$ or $\lambda \vec{M}_s$ cannot exert a torque on $\vec{M}_s$, or $\vec{M}_e$, the s - d interaction will not affect the resonance line position so much as it will affect the relaxation mechanisms.

Hasegawa proposed two coupled phenomenological Bloch equations to describe the coupled spin system of a dilute magnetic alloy. The molecular field theory was retained and relaxation mechanisms were introduced. The molecular field constant λ was defined, using the zero-Fourier component $J(0)$ of the s-d exchange integral, i.e.

$$H = -J(0) \sum_i \vec{S}_i \cdot \vec{s}(\vec{r}) \delta(\vec{R}_i - \vec{r}) , \quad \text{II-30}$$

as

$$\lambda = J(0) / \{g_e g_s \mu_B^2 N_0\} \quad \text{II-31}$$

where N_0 is the number of atoms per unit volume, $\vec{S}_i$ is the impurity spin at site $\vec{R}_i$, and $\vec{s}(\vec{r})$ is the spin of a conduction electron at $\vec{r}$. In this notation, the subscript s refers to the localized electrons, and the subscript e refers to the conduction electrons. The rate of change of the conduction electron magnetization, $d\vec{M}_e/dt$, and the rate of change of the localized electron magnetization, $d\vec{M}_s/dt$, are given by

$$\frac{d}{dt} \vec{M}_e(t) = \gamma_e \vec{M}_e \times (\vec{H} + \lambda \vec{M}_s) - \delta_{e1} (\vec{M}_e - \vec{M}_e^0) - \delta_{es} \vec{M}_e + \delta_{se} \vec{M}_s \quad \text{II-32}$$

$$\frac{d}{dt} \vec{M}_s(t) = \gamma_s \vec{M}_s \times (\vec{H} + \lambda \vec{M}_e) - \delta_{s1} (\vec{M}_s - \vec{M}_s^0) - \delta_{se} \vec{M}_s + \delta_{es} \vec{M}_e . \quad \text{II-33}$$

$\vec{H}$ represents the vector sum of all the external fields, the static applied field $\vec{H}_a$, and the microwave field $\vec{H}_{rf}$; γ_e and γ_s are the gyro-magnetic ratios for the two spin species, $\gamma_e = g_e \mu_B / \hbar$ and $\gamma_s = g_s \mu_B / \hbar$.

The relaxation parameters δ represent: relaxation from the localized electron system to the conduction electrons (δ_{se}); relaxation from the conduction electrons to the localized electrons (δ_{es}); relaxation from the conduction electrons to the lattice (δ_{el}); and, for symmetry, the relaxation of the localized electrons directly to the lattice (δ_{sl}). The last relaxation rate, δ_{sl} , requires spin-orbit coupling, and is usually negligible compared to the other relaxation rates for an S-state ion such as Mn^{2+} .

The term $\vec{M}_e^0$ represents the equilibrium value for the conduction electron magnetization. Hasegawa presented results for the cases in which $\vec{M}_e$ relaxes to the time averaged value of the molecular field, and to the instantaneous field:

$$\text{Case A: } \vec{M}_e^0 = \chi_e (\vec{H}_a + \vec{M}_s^0) \quad \text{II-34}$$

$$\text{Case B: } \vec{M}_e^0 = \chi_e (\vec{H}_a + \vec{M}_s(t)) \quad \text{II-35}$$

where χ_e is the Pauli conduction electron susceptibility, and $\vec{M}_s^0$ is the time averaged, or equilibrium value of $\vec{M}_s(t)$. Arguments of passivity and causality,⁴⁵ and the requirement of positive energy absorption, determined case B to be correct.

The physical meaning of the terms in Eqns. II-32 and 33 is easily seen. In II-32, for example, the first term on the right is the torque exerted on the conduction electrons by the total molecular field $\vec{H} + \lambda \vec{M}_s$; the second term represents the transfer of energy to the lattice

which occurs when a spin flips back to the ground state via any mechanism other than s-d exchange; the third term represents the transfer of magnetization from the conduction electron (e) system to the localized electron (s) system; and the last term represents the transfer of magnetization from the localized (s) system to the conduction electron (e) system. The last two relaxation terms are caused by the exchange coupling of the two spin systems.

The diagram shown in Figure 2 indicates the relaxation paths for a coupled s-d electron system. The so-called "relaxation bottleneck" occurs when $\delta_{es} > \delta_{el}$, i.e. the conduction electrons relax more rapidly to the d electrons than to the lattice.

The reasons for the success of the molecular field theory in dilute alloys are not obvious. The RKKY interaction should cause a nonuniform static polarization of the conduction electrons near the impurity, which should considerably alter the molecular field sublattice configuration of the conduction electrons. As outlined in the review by Orbach, Peter and Shaltiel,¹⁵ the reason that the molecular field model seems to work is that as shown by microscopic theories,⁴⁶⁻⁵⁰ the dynamic polarization of the conduction electrons at or near resonance is a very long-range effect. The argument is as follows: if the g factors of the magnetic impurities and the conduction electrons are very close (so that the two spin systems precess at very nearly the same frequency) then only the $\vec{q} \approx 0$ conduction electron spin wave mode is resonant with the magnetic impurities. If the conduction electrons are moving at near the Fermi velocity v_F , then during the time of one

FIGURE 2. Relaxation paths for a dilute alloy in a resonance experiment. A relaxation bottleneck occurs when $\delta_{es} > \delta_{el}$.

precession at the Zeeman frequency, the conduction electrons have traveled a distance $\lambda = v_F / [\text{Zeeman frequency}]$, which is of the order of $10^8/10^{10} \sim 10^{-2} \text{ cm}$. (for microwave frequencies). The conduction electron sublattice which couples to the ions is effectively rigid over this correlation length λ , and spin wave modes with $1/q < v_F / [\text{Zeeman frequency}]$ are not resonant with the magnetic impurities.

The Bloch equations can be solved to give the following results: in the absence of a bottleneck, i.e. $\delta_{el} \gg \delta_{cs}$, the g shift is given by

$$\delta g_0 = J(0)n(E_F)/N_0 = \lambda \chi_e \gamma H \quad \text{II-36}$$

and the linewidth is given by

$$\Delta H_0 = \delta_{se}/\gamma = \frac{\pi}{g\mu_B} (Jn(E_F))^2 kT \quad \text{II-37}$$

where $n(E_F)$ is the one spin density of conduction electron states per unit volume at the Fermi surface and N_0 is the number of atoms per unit volume.

Hasegawa solved the Bloch equations under the following conditions:

$$\delta_{es}, \delta_{se}, \delta_{el} \gg \delta_{sl} \quad (\text{No spin-orbit coupling})$$

$$\gamma_s = \gamma_e \equiv \gamma$$

$$\delta_{es}\chi_e = \delta_{se}\chi_s \quad (\text{detailed balance}) \quad \text{II-38}$$

$$\chi_s/\chi_e \equiv \chi_r \gg 1 \quad (\text{d-electron absorption dominates}).$$

For his Case B, the g shift and linewidth are altered by terms involving the ratio δ_{el}/δ_{es} , which is sometimes referred to as the bottleneck strength parameter.

$$\delta g = \delta g_0 \frac{(\delta_{el})^2}{(\gamma\lambda\chi_d H)^2 + (\delta_{el} + \delta_{es})^2} \quad \text{II-39}$$

(Bottlenecked:
 $\delta_{es} > \delta_{el}$)

$$\Delta H = \Delta H_0 \frac{(\delta_{el})^2 + (\delta_{es}^2 + (\gamma\lambda\chi_s H)^2)(\delta_{el}/\delta_{es})}{(\gamma\lambda\chi_s H)^2 + (\delta_{el} + \delta_{es})^2} \quad \text{II-40}$$

where δg_0 and ΔH_0 are defined in Eqns. II-36 and 37 respectively, and λ is the molecular field constant, defined in Eqn. II-31. In the non-bottlenecked regime, $\delta_{el} \gg \delta_{es}$, the g shift reduces to δg_0 and the linewidth to ΔH_0 . In this limit, the conduction electrons relax so rapidly to the lattice that all phase memory is lost, thus contributing an effective field to the magnetic impurities which is due only to their average longitudinal equilibrium magnetization. The other extreme is the strongly bottlenecked limit, $\delta_{es} \gg \delta_{el}$, in which the g shift and linewidth are severely reduced. The conduction and d electrons are strongly coupled, precess together in an external field, and therefore cannot exert a torque on one another. In this limit,

$$\delta g = \delta g_0 \frac{(\delta_{el})^2}{(\gamma\lambda\chi_s H)^2 + (\delta_{es})^2} \quad \text{II-41}$$

(Extreme bottleneck:
 $\delta_{es} \gg \delta_{el}$.)

$$\Delta H = \Delta H_0 (\delta_{el}/\delta_{es}) \quad \text{II-42}$$

The coupled Bloch Eqns. II-32 and 33 given by Hasegawa describe the coupled conduction electron-local moment system, but cannot incorporate in an obvious manner the effects of crystal fields which may split the local-moment resonance.

2. Fine Structure

Unresolved fine structure due to crystalline fields has been observed in single crystal Mg:Gd^{51,52} and Mg:Mn.⁴⁰ The analysis of the resonance spectrum was made using a spin Hamiltonian (after Abragam and Bleaney⁵³) for an S-state ion with an isotropic g value in an axial crystal field,

$$H = g\mu_B H_S z + 1/2 g\mu_B D(S_z^2 - 1/3 S(S+1))(3\cos^2\theta - 1)$$

$$-g\mu_B D(S_+ S_z + S_z S_-)\cos\theta\sin\theta + 1/4 g\mu_B D(S_+^2 + S_-^2)\sin^2\theta \quad \text{II-43}$$

where S_+ and S_- are raising and lowering operators. The resonance equation for the transition $M_S \leftrightarrow M_S - 1$ is

$$\hbar\omega = g\mu_B (H + 1/2 D(3\cos^2\theta - 1)(M_S - 1/2)) \quad \text{II-44}$$

The Hamiltonian, II-43, is correct when $D \ll H$, which holds experimentally for the alloys considered in this work. The parameter D is the crystal field constant, and it reflects the strength of the crystal field interaction. For ionic crystals the ESR spectrum resulting from

this Hamiltonian will exhibit 2S lines equally spaced, at intervals proportional to D, centered at the $D=0$ position. The splitting interval varies with angle as $(3\cos^2\theta-1)$, where θ is the angle between the applied field and the crystalline c-axis. This analysis is correct for insulating crystals, but not for metals, where the linewidth of the resonance may be larger than the splitting interval D. Furthermore, in metals, exchange narrowing, as well as a bottleneck, may occur. The result is a resonance spectrum which consists of a single line, whose position and linewidth vary with angle and temperature.

Before considering a detailed analysis of the unresolved ESR fine structure, a simple resonance spectrum is shown in Figs. 3-5. The single line observed in dilute metal alloys may be considered as the sum of 2S broadened fine structure lines, which are then exchange narrowed. At $\theta=0$, the (unresolved) fine structure line separation is a maximum. Rotating the sample in the field causes the single line to narrow as the angle θ is increased. When $\theta=55^\circ$, the angular term $3\cos^2\theta-1=0$; the (unresolved) fine structure lines collapse, and the metal alloy resonance linewidth should be a minimum. As θ increases to 90° , the (unresolved) line separation increases, causing the metal alloy resonance line to broaden again. The angular variation of the linewidth in this simple picture is indicated in Figure 6.

The observation of fine structure splitting and its magnitude, are related to the fundamental question of the character of the magnetic state in the metal. The rare earth impurities exhibit splittings representative of a well localized magnetic state. The Hartree-Fock

FIGURES 3-5. Typical resolved fine structure spectrum for an ionic $S=5/2$ impurity in an axial field for $\theta=0, 55, 90$ degrees; $kT \gg g\mu_B H$; $\hbar\omega = g\mu_B [H + 1/2 D(3\cos^2\theta - 1)(M'_S - 1/2)]$. Dashed line indicates a resonance where the linewidth $\Delta H \sim D$; the intensities are not to scale.

FIGURE 6. Approximate angular dependence of the linewidth for unresolved fine structure. Dashed line is typical variation for the second moment $\langle \Delta\omega^2 \rangle$.

Anderson model is inappropriate for rare earths, so that the Russell-Saunders ionic scheme is used for the magnetization. The ionic Hirst model³⁷ employs this idea for transition metal ions. Localization is achieved from the Coulomb potential U , then the mixing with conduction electrons is turned on to generate exchange coupling. Then intra-atomic exchange is introduced to give a definite Hunds rule ground state. This state is split by the crystal field, with spin-orbit coupling finally being invoked. The trouble with the ionic model is that it neglects the effects of the d level width and its influence on the Russell-Saunders coupling as well as the crystal field splitting. The finite temperature Hartree-Fock theory is not developed to the point where meaningful calculations can be made of local moment dynamics.

3. Resonance Field in the Presence of Fine Structure

The resonance field for dilute metal alloys occurs at the "center of gravity" of all the fine structure lines. In the temperature range where the M_s levels are equally populated, i.e. $kT \gg g\mu_B H$, each (unresolved) fine structure line has equal intensity and there is no dependence of the resonance field on the angle θ . For X-band frequencies (10 GHz) the requirement is $T \gg 0.5$ K, and for K-band (23 GHz), $T \gg 1$ K.

Boltzmann population factors must be taken into consideration as kT approaches the same energy as the M_s level splittings, $\sim g\mu_B H$. The center of gravity of the fine structure is determined by the weighted average,

$$\langle \omega \rangle = \frac{\sum_{M_S} C_{M_S} (E_{M_S} - E_{M_S-1})}{\hbar \sum_{M_S} C_{M_S}} \quad \text{II-45}$$

where

$$C_{M_S} = |\langle M_S | S_x | M_S - 1 \rangle|^2 (\exp(-E_{M_S-1}/kT) - \exp(-E_{M_S}/kT)) \quad \text{II-46}$$

and

$$E_{M_S} = g\mu_B (HM_S + 1/2 D(3\cos^2\theta - 1) [M_S^2 - 1/3 S(S+1)]) \quad \text{II-47}$$

The factors C_{M_S} reflect the intensity of each (unresolved) line. The term $C_{-3/2}$, e.g. represents the product of the probability that the $M_S = -5/2$ state is occupied, the $M_S = -3/2$ state is empty, and the transition probability, $|\langle -5/2 | S_x | -3/2 \rangle|^2$ where S_x represents the interaction of the transverse magnetization with the rf excitation field. Normalization is achieved by dividing the weighted sum by $\sum C_{M_S}$. Appendix A contains the details for calculating $\langle H \rangle$, the center of gravity of the lines in terms of the magnetic field, and a calculator program to find D and g from the fit of the angular variation of $\langle H \rangle$, to order (D^2/H) .

The first moment analysis for the resonance frequency has been used successfully for the Mg:Gd and Mg:Mn systems mentioned above.^{40,54} The computation of the second moment (arising from fine structure) was carried out according to the equation

$$\langle \Delta \omega^2 \rangle = \frac{\sum_{M_S} C_{M_S} (E_{M_S} - E_{M_S-1})}{\hbar^2 \sum_{M_S} C_{M_S}} - \langle \omega^2 \rangle \quad \text{II-48}$$

Using the value of D obtained from the low temperature resonance data, the second moment calculation using II-48 had roughly the same θ dependence as the measured linewidth, but II-48 gave a much greater amplitude, as shown in Figure 4. It appeared that the linewidth data required a value of D nearly an order of magnitude smaller than the value appropriate for the resonance field angular variation.

Tao, et al.,⁵² suggested that the unresolved fine structure lines had become exchange narrowed, in a manner similar to the hyperfine structure of local moments in a metal.^{55,56} The magnetization was pictured as "hopping" between axial-field-split resonance lines, broadened because of the near equality of δ_{se}/γ and D , allowing the lines to overlap.

4. Exchange Narrowing of Fine Structure in the Presence of a Relaxation Bottleneck

Using a Feynman diagram technique, Barnes⁹ has generalized an earlier paper⁵⁰ to include arbitrary spin, and has generated a set of Bloch equations to describe the coupled local moment-conduction electron system, including fine structure. In this model there are $2S+1$ coupled equations representing the manifold of $2S$ fine-structure

resonance lines and the conduction-electron resonance line. The equations are valid in the high temperature region where $kT \gg g\mu_B H$.

The notation used is different from that originally used by Hasegawa. The equations are linearized, and the transverse magnetization of the S_z level is written using $M_{S_z}^+ = M_{S_z}^x + iM_{S_z}^y$. For simplicity it is assumed that $g_e = g_s$ and that J is isotropic, although Barnes has treated the general case of anisotropic exchange and unequal g factors. Both Barnes' and Hasegawa's linearized equations of motion for the transverse magnetization are given below.

Hasegawa:

$$\frac{d}{dt} M_s^+ = -i(\omega_s + \lambda \chi_e^0 \omega_s) M_s^+ + i \chi_s^0 \omega_s (h_{rf}^+ + \lambda M_e^+)$$

II-49

$$- \frac{M_s^+}{T_{se}} + \frac{M_e^+}{T_{es}}$$

$$\frac{d}{dt} M_e^+ = -i(\omega_e + \lambda \chi_s^0 \omega_e) M_e^+ + i \chi_e^0 \omega_e (h_{rf}^+ + \lambda M_s^+)$$

II-50

$$- \left[\frac{1}{T_{es}} + \frac{1}{T_{el}} \right] M_e^+ + \frac{1}{T_{se}} M_s^+$$

$$\begin{aligned}
\frac{d}{dt} M_{S_z}^+ = & \left[-i(\omega_{S_z} + \lambda \chi_e \omega_s) M_{S_z}^+ \right] + \left[i \chi_{S_z}^o (\omega_{S_z} + \lambda \chi_e \omega_s) (h_{rf}^+ + \lambda M_e^+) \right] \\
& + \frac{1}{T_{S_z}^{S_z+1}} \left[M_{S_z+1}^+ - \chi_{S_z+1}^o (h_{rf}^+ + \lambda M_e^+) \right] + \frac{1}{T_{S_z}^{S_z-1}} \left[M_{S_z-1}^+ - \chi_{S_z-1}^o (h_{rf}^+ + \lambda M_e^+) \right] \\
& - \left[\frac{1}{T_{S_z}^{S_z e}} + \frac{1}{T_{S_z}^{S_z-1}} + \frac{1}{T_{S_z}^{S_z+1}} \right] \left\{ M_{S_z}^+ - \chi_{S_z}^o (h_{rf}^+ + \lambda M_e^+) \right\} \\
& + \left[\frac{1}{T_{e S_z}} + \frac{1}{T_{e S_z+1}} - \frac{1}{T_{e S_z}} \right] \left\{ M_e^+ - \chi_e^o (h_{rf}^+ + \lambda \sum_{-S}^{S-1} M_{S_z}^+) \right\}
\end{aligned} \tag{II-51}$$

and

$$\begin{aligned}
\frac{d}{dt} M_e^+ = & \left[-i(\omega_e + \lambda \sum_{-S}^{S-1} \chi_{S_z} \omega_e) M_e^+ \right] + \left[i \chi_e^o (\omega_e + \lambda \sum_{-S}^{S-1} \chi_{S_z} \omega_e) (h_{rf}^+ + \lambda \sum_{-S}^{S-1} M_{S_z}^+) \right] \\
& - \left[\frac{1}{T_{e S}} + \frac{1}{T_{e 1}} \right] \left\{ M_e^+ - \chi_e^o (h_{rf}^+ + \lambda \sum_{-S}^{S-1} M_{S_z}^+) \right\} \\
& + \sum_{-S}^{S-1} \left\{ \frac{1}{T_{S_z}^{S_z e}} [M_{S_z}^+ - \chi_{S_z}^o (h_{rf}^+ + \lambda M_e^+)] \right\}
\end{aligned} \tag{II-52}$$

The "hopping" of the magnetization between S_z levels is described by the relaxation times $T_{S_z}^{S_z \pm 1}$ and $T_{S_z}^{S_z}$. Hasegawa's conduction-localized-electron cross-relaxation times $T_{se} (=1/\delta_{se})$ and $T_{es} (=1/\delta_{es})$ are generalized by Barnes to include cross-relaxation between the conduction electrons and each S_z level. The physical meaning of the relaxation terms in II-51, 52 can be obtained by comparison with Hasegawa's collapsed equations, II-49, 50. The third and fourth terms

of II-51 represent a transfer of magnetization from the S_z+1 and S_z-1 levels, respectively, to the S_z level. The fifth term of II-51 represents the transfer of magnetization from the S_z level to the conduction electrons, to the S_z+1 level and to the S_z-1 level. The sixth term represents transfer of magnetization from the conduction electrons to the S_z level. Similar analogies can be drawn between Hasegawa's Eqn. II-50 and Barnes' II-52 for the equation of motion of the transverse conduction electron magnetization.

For completeness, a list of the definitions of the terms in Eqns. II-51 and 52 is given in Appendix B.

The Bloch Eqns. II-51, 52 are solved by Barnes, and also by Smith and Haberkern,⁵⁷ in the following limits: presence or absence of a bottleneck, and strong or weak fine structure splitting (i.e. D large or small compared to $\gamma\delta_{se}$). The solution for the linewidth in the limits of $D \ll \gamma\delta_{se}$, and a bottleneck presence, gives a linewidth approximately equal to D^2/δ_{se} . The linewidth equations are

$$\text{Hasegawa:}^4 \quad \gamma\Delta H \simeq \left(\frac{\delta_{el}}{\delta_{es}} \right) \delta_{se} \quad \text{II-53}$$

$$\text{Barnes:}^9 \quad \gamma\Delta H = \left(\frac{\delta_{el}}{\delta_{se} + \delta_{es}} \right) \delta_{se} + \langle \Delta\omega^2 \rangle \left(\frac{\delta_{es}}{\delta_{es} + \delta_{se}} \right)^2 \frac{1}{3\delta_{se}} \quad \text{II-54}$$

Smith and Haberkorn:⁵⁷

$$\gamma\Delta H = \delta_{el} \left[\frac{\lambda^2 \omega_o^2 (\chi_e + \chi_s) \chi_e + \delta_{se} (\delta_{se} + \delta_{es})}{(\lambda \omega_o (\chi_e + \chi_s))^2 + (\delta_{se} + \delta_{es})^2} \right] + \frac{\langle \Delta \omega^2 \rangle}{3\delta_{se}} \quad \text{II-55}$$

where $\langle \Delta \omega^2 \rangle = 32/5 (\gamma D 1/2 (3 \cos^2 \theta - 1))^2$.

When $\chi_s > \chi_e$, the detailed balance Eqn. II-38 implies that $\delta_{es} > \delta_{se}$, so that the term $[\delta_{es}/(\delta_{es} + \delta_{se})]$ in II-54 approaches unity. Then the two results II-54 and 55 are nearly identical. Also, Hasegawa's result II-53 represents the limit of II-54 and 55 in the limit of no fine structure ($D \rightarrow 0$), and dominant d spin absorption ($\delta_{es} \gg \delta_{se}$).

5. Relaxation Rates

The linewidth Eqns. II-54 and 55 contain the relaxation rates δ_{el} , δ_{se} and δ_{es} . The cross-relaxation rates δ_{se} and δ_{es} are calculated using the analogous case of nuclear relaxation in metals via the hyperfine interaction $H_{hf} = -A \vec{I} \cdot \vec{S}$, by substituting $J(0)$ for A , and by substituting the impurity spin $\vec{S}$ for $\vec{I}$.

The nuclear rate was first calculated by Heitler and Teller,⁵⁸ and connection with the square of the Knight shift was made by Korringa.⁵⁹ For an isotropic delta function exchange interaction, the localized-to-conduction relaxation rate is

$$\delta_{se} = \frac{\pi (J\eta(E_F))^2}{\hbar N_o^2} \quad \text{II-56}$$

for temperatures such that $kT \gg g\mu H$.

The conduction-to-localized electron relaxation rate was first calculated for nuclei by Overhauser,⁶⁰ then adapted to the electron spin by Hasegawa.⁴ The high temperature expression for δ_{es} is

$$\delta_{es} = \frac{2\pi}{3\hbar} c \frac{n(E_F)}{N_0} J^2 S(S+1) \quad \text{II-57}$$

where in II-56 and 57 $n(E_F)$ is the one spin density of states per unit volume for the conduction electrons, N_0 is the number of atoms per unit volume, c is the fractional atomic impurity concentration, and J is the exchange constant.

The relaxation rate of the conduction electrons to the lattice, δ_{el} , has been calculated by Overhauser⁶⁰ and by Yafet.⁶¹ The rate calculated by Overhauser considers the interaction of the conduction electron spins with electric currents due to the translational motion of other electrons. The resulting rate was linear in temperature but several orders of magnitude too small to account for the observed line-width for impurities in metals.

The calculations by Yafet were based on the Anderson model.⁷ Yafet calculated the spin-flip scattering cross-section, σ_{sf} , of transition element impurities in copper. The conduction electrons at the Fermi level have some localized d state due to admixture, and the spin-orbit interaction enables the spin to flip. The two step process by which this occurs is first, the local moment and a conduction electron mutually flip their spins under the effect of exchange (at rates

δ_{es} and δ_{se}) and second, the conduction electron spin relaxes at a characteristic rate δ_{el} to the energy reservoir provided by the kinetic energy of the conduction electrons. The effect of impurity scattering dominates the relaxation process and results in a temperature independent δ_{el} .

In the presence of fine structure the value of δ_{el} is extracted from the temperature dependence of the linewidth at $\theta = 55^\circ$, the angle at which the second term in the linewidth Eqns. II-54 and 55 is zero. In an extreme bottleneck with dominant localized-spin absorption, i.e., $\chi_s \gg \chi_e$, (or $\delta_{es} \gg \delta_{sc}$, using detailed balance), the effective linewidth is

$$\theta=55^\circ : \quad \delta_{eff} = \gamma \Delta H = \delta_{el} \left[\frac{3n(F_F) kT}{2N_o S(S+1)c} \right] \quad \text{II-58}$$

which is obtained by substituting Eqns. II-56 and 57 for δ_{se} and δ_{es} , respectively, in Eqn. II-55. The value for δ_{el} is then obtained from the slope of linewidth vs. temperature.

6. Effects of Ordering on the Resonance Field

ESR studies of dilute metal alloys^{2,3} have shown a rapid decrease in the resonance field at a characteristic temperature which depended on the impurity concentration. This result had been interpreted in terms of the onset of antiferromagnetism. The antiferromagnetic resonance field was assumed to occur at the field

$$H = \sqrt{(\omega^2/\gamma^2 - H_C^2)} \quad \text{II-59}$$

where

$$H_C = \sqrt{2H_E H_A} \quad \text{II-60}$$

The microwave frequency is ω , γ is the gyromagnetic ratio, H_C is the critical field, H_E is the exchange field arising from direct exchange between magnetic impurities, and H_A is the anisotropy field which arises from the s-d exchange interaction. However, investigations^{62,63} in the Cu:Mn system, have shown a combination of ferromagnetic and anti-ferromagnetic exchange interactions. It is exactly this competition between ferro- and antiferromagnetic exchange interactions which has been used to describe the properties of a spin glass.⁶⁴⁻⁶⁷

A micromagnetic theory by Malozemoff and Jamet¹² has been proposed to describe the downward shift of the resonance field in amorphous films of $\text{Al}_{0.63}\text{Gd}_{0.37}$. This material is a spin-glass characterized by a Curie temperature of 30 K, and a spin-glass temperature of 18 K. Below the Curie temperature the resonance field shifts downfield at a rate of approximately 150 G/K. Due to severe line broadening, the resonance line can no longer be measured accurately below about 12.5 K.

The following explanation follows closely the treatment of Malozemoff and Jamet.¹²

The theory which explains this downfield shift in the field for resonance is based on the effect of inhomogeneities, which are present

in a spin-glass material with both ferro- and antiferromagnetic exchange interactions. Regions which are either rich in the magnetic impurity, or regions where nearest-neighbor interactions gives a high probability of ferromagnetic exchange, are surrounded by a matrix in which antiferromagnetic exchange dominates. The shapes of the ferromagnetic regions are presumed to have a statistical distribution of spheres, and prolate and oblate ellipsoids.

In an external magnetic field, the ferromagnetic regions which have their longest axis parallel to the field will have a higher magnetization. Regions which are oriented orthogonally, or spheres, magnetize less strongly due to higher demagnetization fields. The magnetization is approximated as $M_z(x,y)$, homogeneous in the z direction (along the applied field) but spatially varying in the x and y directions. The columnar pattern of induced inhomogeneous magnetization gives rise to an effective anisotropy field, H_{loc} , in the following way. It is assumed that the coupling between spins extends over distances greater than the intercolumnar separation, despite the inhomogeneity of the system, so that spins will precess together with the same phase. Further, it is supposed that the induced magnetization remains static during precession which implies that the longitudinal relaxation rate ($1/T_1$) is greater than the precession frequency. Both of these assumptions are valid for a bottlenecked system such as Mg:Mn.

Since there is a component of magnetization which is perpendicular to the applied field and which is spatially varying, there exists a

local magnetostatic energy density,⁶⁸ $1/2 H_d \Delta M \sin^2 \theta$. Here ΔM is the deviation $M(x,y) - \langle M \rangle$ of the magnetization from its spatial average $\langle M \rangle$, and H_d is the demagnetization field $2\pi \Delta M$ of a column. After spatially averaging this energy density and equating it to $K_u \sin^2 \theta$, an effective anisotropy field $H_{loc} = 2K_u / \langle M \rangle$ results,

$$H_{loc} = 2\pi \langle |M(x,y) - \langle M(x,y) \rangle|^2 \rangle / \langle M(x,y) \rangle \quad \text{II-61}$$

$$H_{loc} = 2\pi (\langle M^2 \rangle - \langle M \rangle^2) / \langle M \rangle \quad \text{II-62}$$

The columnar ferromagnetic regions have magnetization M_1 and occupy a volume fraction V_1 of the sample, while the remainder has a magnetization M_2 , with the average magnetization

$$\langle M \rangle = M_1 V_1 + M_2 (1 - V_1) \quad \text{II-63}$$

$$H_{loc} = 2\pi V_1 (1 - V_1) (M_1 - M_2)^2 / \langle M \rangle \quad \text{II-64}$$

Considering this local field to act along the applied field, the resonance equation for resolved fine structure becomes

$$\omega/\gamma = H + H_{loc} + 1/2 D(3\cos^2 \theta - 1) \quad \text{II-65}$$

where θ is the angle between the applied field and the crystalline c-axis. In these equations demagnetizing fields are neglected since even at 2K, χ is so small that in an applied field of 8000 G, $4\pi M$ is less than 10 Oe.

The resonance field for a system with unresolved fine structure is determined by substituting $H_{loc} + H$ for H in Eqns. II-45, 46, 47. The local field H_{loc} is obtained from the data, and the average magnetization $\langle M \rangle$ is computed from the measured susceptibility. M_2 is assumed to be very much smaller than M_1 . Then II-64 can be solved for V_1 .

III. SAMPLE CHARACTERISTICS

This chapter discusses the general physical properties of magnesium. The details of the growth of the single crystal alloys and the concentration analysis are also given.

A. Single Crystal Growth

The bulk alloy was prepared by Dow Chemical Company, Midland, Michigan from high purity ingredients in graphite crucibles. The spectroscopic analysis by Dow showed a concentration of .583 atomic percent manganese. Further analysis⁶⁹ showed a solid solute concentration of .49 atomic percent. The solubility phase diagram for Mg:Mn is shown in Figure 7. The low solubility is expected since the atomic radii of magnesium and manganese are 1.60 Å and 1.35 Å, respectively, and in general, two metals are insoluble if their size difference is greater than 15 percent.⁷⁰

Due to the rapid decrease in solubility of manganese in magnesium with decreasing temperatures, the material required rapid quenching. An oxygen-free atmosphere was also necessary to prevent the magnesium from oxidizing. The high vapor pressure of magnesium, 2.28 torr,⁷¹ at its melting temperature, ruled out the possibility of growing a crystal in vacuum. Therefore, graphite crucibles were constructed for use in a vacuum tight Bridgeman type resistance furnace with two sets of

FIGURE 7. Phase diagram for Mg:Mn. From: Constitution of Binary Alloys, First Supplement, Rodney P. Elliot, McGraw-Hill, Chicago, Ill., (1965).

windings. However, rather than move the sample through a fixed temperature gradient, the sample and crucible were held fixed and the temperature gradient was electrically controlled to move past the sample. The crucible had an inner diameter of approximately 1/2 inch and a depth of two inches with a 60 degree cone shaped tip. An outward taper of 1 degree made removal of the sample easier.

The furnace consisted of a vertical alumina tube 2 3/4 in. in diameter with O-ring sealed flanges at both ends. After establishing thermal equilibrium in the furnace, the temperature of an empty crucible was measured to characterize the temperature gradient. The pumping station maintained a pressure of less than 20 millitorr. During the growth run, two chromel-alumel thermocouples were inserted into small holes in the crucible, one at the top and one near the tip of the cone at the bottom. After baking the crucible at 800°C in vacuum for 8 hours to allow the empty crucible to outgas, a cleaned and etched Mg:Mn charge was inserted into the crucible and the entire assembly was reinserted into the furnace. After pumping out the furnace chamber the temperature was once again raised to 850°C, but with the crucible held in a cooler region at a temperature of about 200°C. The system was allowed to outgas for an hour. The furnace chamber was then backfilled with argon gas and a small flow of argon gas was maintained throughout the remainder of the growth run. The crucible was then raised to the position of steepest temperature gradient where the lowest temperature was at least 700°C, fifty degrees above the melting temperature, 650°C. The current in the furnace windings was then slowly decreased by a

clock motor connected to a Variac. Near the melting temperature, the temperature was decreasing at a rate of about 1.5 C/min. When the temperature of the charge reached 620°C, the crucible was lowered beyond the furnace windings and the flow of argon increased in order to quench the sample. The temperature of the sample decreased to 180°C in 5 minutes. After removing the cylindrical sample from the crucible, it was etched in an ultrasonic cleaner in an ethyl alcohol solution containing 2 percent nitric acid. No grain boundaries were observed after etching.

B. Composition and Structure Analysis

The sample was mounted on a goniometer and X-ray photographs were made using standard Laue backscattering techniques. The first photographs were taken with the cylindrical axis of the alloy transverse to the X-ray beam, at points 1 cm. apart. These photographs showed exact translational symmetry and verified the existence of a single crystal. The c-axis was identified and found to be approximately transverse to the cylindrical axis of the sample. This was expected since most crystals grow in the direction of densest packing.⁷²

The bulk crystal was cut into small samples using spark erosion techniques. A cylindrical sample 1/4 in. in diameter, 1 in. in length was cut from the bulk with the c-axis perpendicular to the cylinder axis. Thin slabs were also made for use in microwave resonant cavities at frequencies of 9.5 and 23 GHz. The thin slabs were cut so that the c-axis was in the plane of the slab. When mounted on the side walls of

the microwave cavity, the external magnetic field could be rotated so that when the field was parallel to the plane of the slab the c-axis was parallel to the field, and when the field was rotated so that it was normal to the slab, the c-axis was perpendicular to the field. Small slabs were cut from the bottom (near the cone shaped tip) and from the top of the crystal for a microprobe analysis.

The 1" x 1/4" cylindrical sample was reoriented with X-ray techniques to affirm the single crystal nature and again showed exact translational symmetry and confirmed the location of the c-axis.

Further microprobe analysis at Battelle Memorial Institute was carried out on portions of the crystal to determine the existence of any axial or radial concentration gradients. The intensity of the K_{α} X-ray line of Mn was used to determine the concentration by comparison with a pure Mn standard. The analysis was carried out at points approximately 0.020 in. apart both radially and axially. The electron beam diameter was roughly 0.005 in. Each data point represented an average of 5 trials of 10 sec. each. The counting rate of the sample was approximately 7000 counts per second. A radial traversal was done on two pieces taken from both the top and the bottom of the crystal. An axial traversal was done on the cylindrical sample trepanned from the bulk crystal. The data indicated a constant concentration with no dependence on position to within the limits of the time drift of the standard. Thus it is concluded that there are no growth induced concentration gradients.

A quantitative measure of concentration could not be determined by comparison with a pure Mn standard due to the "matrix effect" of the host material. The intensity of the manganese K_{α} X-rays from the sample depends on the matrix in which the manganese is embedded. To obtain a quantitative concentration of manganese for an unknown sample, it is necessary to have a standard of known concentration of manganese in a magnesium matrix.

The manganese concentration in the crystal was determined from paramagnetic susceptibility measurements, assuming a Curie law behavior,

$$\chi = \frac{Np^2\mu_B^2}{3kT} = \frac{C}{T} \quad \text{II-1}$$

where χ is the magnetic susceptibility, N is the number of paramagnetic ions per unit volume, p is the effective number of Bohr magnetons,⁷³ μ_B is the Bohr magneton, k is Boltzmann's constant, C is the Curie constant, and T is the absolute temperature. Three polycrystalline Mg:Mn alloys of known manganese concentration provided the calibration.

Each sample was cylindrical in shape, 11 mm in length and 5 mm in diameter. After an acid etch, each sample was weighed and the volume calculated using a value of 1.738 g/cm³ for the density.⁷¹ A Princeton Applied Research (PAR) model 155 vibrating sample magnetometer mounted on a Varian model V-3603 12 inch electromagnet was used to measure the magnetic moment. Temperatures from 2 to 300 K were maintained in a Janis model 153 stainless steel variable temperature cryostat and were controlled by a PAR model 152 Cryogenic Temperature Controller.

The susceptibility vs. T^{-1} for each sample is shown in Figure 8. Each point represents a single measurement of moment. The (dimensionless) susceptibility was computed from

$$\chi = \frac{\mu}{VE} \quad \text{III-2}$$

where μ is the measured magnetic moment, V is the (computed) sample volume and E is the external field (10 kOe for all points). Because the susceptibility departs from T^{-1} dependence at about 20 K, the straight lines in the figure represent a best fit to

$$\chi = \chi_0 + \frac{C}{T} \quad \text{III-3}$$

in the temperature range $300 > T > 20$ K, where χ_0 allows for a temperature independent contribution to the total susceptibility. There was no significant difference in temperature dependence between a Brillouin function and a simple T^{-1} dependence for the susceptibility in this temperature range (20-300 K) and for the fields used (10 kOe). The Curie constants in the paramagnetic regime ($T > 20$ K) are shown in Table 1.

A plot of the Curie constant vs. manganese concentration is shown in Figure 9. The known values of manganese concentration of the three polycrystalline alloys provide the straight line fit, and the measured Curie constant of the single crystal alloy determines the concentration of .47 atomic percent manganese. Note that the fit goes through the origin, as expected.

FIGURE 8. Susceptibility vs. T^{-1} for four Mg:Mn alloys. The straight lines are linear least squares fit for points $T > 20$ K.

TABLE 1

Best fit to $\chi = \chi_0 + \frac{C}{T}$ for $T > 20$ K.

Alloy	$\chi_0 \times 10$	Curie constant $\times 10^4$	Bulk Mn conc. at. %	Solid solution Mn conc. at. %
95 ^a	1.24 ± 0.03	1.12 ± 0.01	0.062	0.02
96 ^a	1.51 ± 0.01	3.70 ± 0.007	0.217	0.11
98 ^a	0.48 ± 0.02	11.46 ± 0.01	0.583	0.49
BR2 ^b	0.96 ± 0.03	8.64 ± 0.01	0.470 ^c	0.35 ^d

a. polycrystalline alloy

b. single crystal alloy

c. inferred from Fig. 9

d. inferred from Fig. 10

FIGURE 9. Curie constant vs. bulk Mn concentration for the three polycrystalline alloys.

This estimate of manganese content is based on essentially a DC measurement, i.e. the static susceptibility. In a "difficult" metallurgical alloy such as Mg:Mn second phase manganese-rich regions are common. In the polycrystalline alloys this second phase material was studied in detail⁶⁹ using electron microprobe and transmission electron diffraction techniques. A dark phase was identified as MnO and a lighter phase of unknown composition was found. This phase was conjectured to contain one or more of the following: manganese carbide, α -Mn, MnS, MnS₂, or MnO₂. Table 2 lists some common manganese compounds along with their Néel temperatures. The existence of the sulfur compounds was thought possible because the ingots provided by Dow were grown in a protective SO₂ atmosphere. The relatively large Néel temperatures of these materials indicates large internal fields which would require high frequencies and/or high magnetic fields to observe any resonances. However, these materials are likely to contribute to the static paramagnetic susceptibility. Therefore any discussion of the manganese concentration must be prefaced by specifying the type of experiment to be carried out and the temperature range involved. A static measurement, such as dc resistivity or static susceptibility, with $T \geq 100$ K, will depend on the total bulk manganese content, including second phase material. Microwave resonance experiments in the temperature range from 2-100 K will involve only the manganese solid solution concentration.

The solid solution manganese concentration in the polycrystalline alloys was determined at Battelle⁶⁹ by carefully aligning the electron

TABLE 2

Néel temperatures of some common manganese compounds.

Materials	Neel Temperature T_N
α Mn	100 K
MnO	118
MnO ₂	92
MnS	160
MnS ₂	60

beam to avoid second phase regions (whose diameters were $\sim 3\mu$). The average values of several measurements determined the manganese solid solution concentration and these values are listed in Table 1. Figure 10 shows the solid solution manganese concentration vs. bulk manganese concentration (including second phase material) for the three polycrystalline alloys. The curve is a quadratic best fit of the three polycrystalline alloys. Using this curve, the solid solution concentration of manganese in the single crystal is estimated to be .35 atomic percent.

C. General Properties of Mg:Mn

1. Physical properties

In accordance with Vegard's Law⁷⁰ the lattice spacing of an alloy should not be appreciably changed from the pure host material if the atomic fraction of added impurities is small (<0.01):

$$d_{\text{alloy}} = n d_{\text{Mn}} + (1-n) d_{\text{Mg}}$$

where n is the atomic fraction of manganese, and d_{alloy} , d_{Mn} and d_{Mg} are the average interatomic distances in the alloy, pure manganese and magnesium, respectively. Because the changes are small, and for convenience, the pure magnesium lattice parameters will be used.

The crystal structure of pure magnesium is hexagonal close-packed (hcp) with lattice parameters⁷¹ at 25 C, $a = 3.2028 \pm 0.00003$ A.U. and $c = 5.1998 \pm 0.00005$ A.U. The axial ratio is $c/a = 1.6235$. The space

FIGURE 10 . Adjusted (solid solution) Mn concentration vs. bulk Mn concentration for three polycrystalline alloys 95, 96, 98.

group is D_{6h}^4 with two atoms per unit cell at coordinates (0,0,0) and (1/3,2/3,1/2) as shown in Figure 11. At room temperature the density of magnesium is 1.738 g/cm^3 ⁷¹ and by extrapolating to zero Kelvin the density is 1.76 g/cm^3 .⁷⁴ The number of atoms per unit is

$$N_0 = 4.37 \times 10^{23} \text{ atoms/cm}^3.$$

The electron configuration of magnesium is (Ne) $3s^2$ and manganese has the configuration (Ar) $3d^5 4s^2$. Both atoms give up their outer two, s electrons to the conduction band leaving the free electron per atom ratio in the alloy unchanged from pure magnesium. The number of conduction electrons per unit volume is then

$$n_0 = 2N_0 = 8.74 \times 10^{22}.$$

2. Free Electron Fermi Gas Model

Assuming that the conduction electrons in a metal behave like a gas of free and noninteracting particles which are subject to the Pauli exclusion principle (free electron Fermi gas), the conduction electrons states can be written in the form of traveling plane waves;

$$\psi_{\vec{k}}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}}, \quad \text{III-7}$$

provided that the components of the wavevector $\vec{k}$ satisfy $k_x = 0; \pm 2\pi/L_x; \pm 4\pi/L_x; \dots$ (Eqn. III-8) where L_x is the dimension of the sample along the x-axis. Similar equations hold for the k_y, k_z wave-vectors. The energy $\epsilon_{\vec{k}}$ of the state with wavevector $\vec{k}$ is

FIGURE 11. Unit cell for hexagonal close packed magnesium. There are 2 atoms per unit cell located at the origin and at $\vec{r} = \frac{2}{3} \vec{a} + \frac{1}{3} \vec{b} + \frac{1}{2} \vec{c}$.

$$\epsilon_{\vec{k}} = \hbar^2 k^2 / 2m = (\hbar^2 / 2m) (k_x^2 + k_y^2 + k_z^2). \quad \text{III-9}$$

The linear momentum $\vec{p}$ and velocity $\vec{v}$ of the electron can be written

$$\vec{p} = \hbar \vec{k} \quad \text{and} \quad \vec{v} = \hbar \vec{k} / m. \quad \text{III-10,11}$$

In the ground state of a system of N free electrons the occupied states may be represented as points inside a sphere in k space. The energy at the surface of the sphere is the Fermi energy; the wavevectors at the Fermi surface have a magnitude such that

$$\epsilon_F = (\hbar^2 / 2m) k_F^2. \quad \text{III-12}$$

From the periodic boundary conditions, Eqn. III-8, the total number of states in a sphere of volume $4\pi k_F^3 / 3$ must be

$$N = 2(4\pi k_F^3 / 3) / (2\pi/L)^3 = \frac{V}{3\pi^2} k_F^3, \quad \text{III-13}$$

where the factor of 2 arises from the two allowed values of m_s for each allowed value of $\vec{k}$. Then

$$k_F = (3\pi^2 n)^{1/3} \quad \text{III-14}$$

where n is the number of conduction electrons per unit volume. The Fermi energy has the value

$$\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}, \quad \text{III-15}$$

and the energy density of states at the Fermi surface is

$$n(\epsilon_F) = \frac{dN}{d\epsilon_F} = \frac{3N}{2\epsilon_F} . \quad \text{III-16}$$

In this work a more commonly used parameter is the energy density of states per unit volume and spin direction $\rho(\epsilon_F)$,

$$\rho(\epsilon_F) = \frac{3n}{4\epsilon_F} . \quad \text{III-17}$$

The values for these parameters for magnesium are a good approximation if a thermal effective mass of $m^* = 1.33 m$ is used, where m is the electron mass.⁷⁵ Table 3 lists several of the free electron gas parameters for magnesium at absolute zero.

TABLE 3

Physical parameters of Mg at $T = 0\text{K}$.

Lattice constant	$a = 3.19 \text{ \AA}$
Lattice constant	$c = 5.18 \text{ \AA}$
Volume of unit cell	$\Omega = 2.29 \times 10^{-23} \text{ cm}^3$
Density	$\rho = 1.76 \text{ g/cm}^3$
Atoms/unit volume	$N_0 = 4.37 \times 10^{22} \text{ atoms/cm}^3$
Free electrons/unit volume	$n = 8.74 \times 10^{22} \text{ electrons/cm}^3$
Wave vector	$k_F = 1.37 \times 10^8 \text{ cm}^{-1}$
Velocity	$v_F = 1.20 \times 10^8 \text{ cm/sec}$
Energy	$\epsilon_F = 7.1 \text{ eV}$
Density of states	$\rho(\epsilon_F) = 1.21 \times 10^{22} \text{ states/(eV-spin-cm}^3)$
Fermi temperature, E_F/k_B	$T_F = 6.67 \times 10^4 \text{ K}$

IV. EXPERIMENTAL PROCEDURE

This chapter details the apparatus used in the static susceptibility and the microwave resonance experiments. Information is given concerning sample preparation, method of temperature control and measurement, and data recording procedures.

A. Susceptibility Measurements

1. The Vibrating Sample Magnetometer

Measurements of magnetic moment were taken from 2 degrees Kelvin to room temperature, and in fields of 100 to 10,000 G. A Princeton Applied Research (PAR) model 155 Vibrating Sample Magnetometer (VSM) was used to measure the moment. A Block diagram for the VSM is shown in Figure 12.

The VSM is calibrated using a high purity nickel sample of known mass. The saturation field of nickel is about 8000 G and the saturation moment is 55.01 emu/G at 20°C. The sensitivity of the magnetometer is about 10^{-4} emu.

2. The Magnet

The external magnetic field was provided by a Varian model 3605 water cooled electromagnet powered by a Varian model 2503, 7kW solid state, water cooled power supply. The magnet coils are low impedance (1/8 ohm each) and series connected. The coil spacing is 6 inches,

FIGURE 12. Block diagram of PAR model 155 Vibrating Sample Magnetometer. Inset: Flux lines and current flow for the set of four pickup coils, for a dipole moment $\vec{\mu}$ moving downward.

with a pole diameter of 11.9 inches and an air gap of 2.7 inches (without tapered pole caps). The maximum energizing current is 160 Amperes, producing a maximum field of 11 kG. The field ripple is stated to be less than 1 ppm peak to peak at maximum field as measured in the air gap. The field is controlled by a Fieldial Magnetic Field Regulator Mark II, permitting a direct magnetic field selection by digital controls with visual indication in kilogauss. The field is maintained by a feedback circuit involving a temperature controlled, Hall effect probe mounted on one magnet pole piece. The field can be continuously swept by means of a sweep potentiometer connected through a slip clutch to the sweep motor. A selection of 17 different sweep ranges from 250 mG to 40 kG with sweep times from .5 to 100 minutes is possible. The sweep unit also provides a continuous output voltage from 0 (at +50% of the sweep range) to -15 Volts (at -50% of the sweep range) to drive an X-Y recorder. A Zero Sweep Unit applies a dc current in the reverse direction to the magnet coils in order to overcome any remanent field (typically 30 Gauss). The field can therefore be continuously swept through zero to a maximum reverse field of approximately 400 Gauss.

Because the measurement of susceptibility in this work did not involve a field sweep, but rather measurement of magnetic moment at a constant field, a Bell model 640 Gaussmeter was used to accurately set the desired field. The stated accuracy of the gaussmeter is $\pm .65\%$ of the meter reading.

3. Cryostat and Temperature Control and Measurement

A Janis model 153 stainless steel variable temperature cryostat was used to provide a stable temperature environment over a range from 2 K to 300 K for study of the temperature behavior of the Mg:Mn susceptibility. The cryostat was specially designed to be compatible with the PAR vibrating sample magnetometer.

The liquid helium capacity of the cryostat is 1.8 liters and the cryostat incorporates several layers of .00025 inch thick aluminized mylar in insulation in the vacuum spaces, eliminating the need for a separate liquid nitrogen reservoir. A variable flow of liquid helium is established from the helium reservoir through a diffuser by a needle valve and provides a constant rate of cooling. An electrical heater (~20 Ω of 28 gauge nichrome V wire) is positioned so that an adjustable amount of heat is provided to the vapor stream. A balance of heating and cooling can maintain any temperature between 4.2 K and room temperature, and temperatures below 4.2 K can be attained by pumping on the sample zone and adjusting the flow of heater current.

The current to the heater was controlled by a PAR model 152 Cryogenic Temperature Controller. The controller senses the temperature of the helium vapor stream emerging from the diffuser assembly of the cryostat and provides the amount of current to the heater (500 mA maximum) required to reach a preset temperature. The sensor is a gallium arsenide diode, and a typical voltage vs. temperature (for a constant 10 μA current) is shown in Figure 13. Gallium arsenide diodes have virtually no magnetoresistance below 20 kG, low heat dissipation

FIGURE 13. Typical diode voltage vs. temperature curve (GaAs diode number # 6150).

(15 μ watts maximum), repeatability of better than ± 0.1 K, quoted stability better than ± 0.01 K, and small mass for quick response. The sensor is attached to the diffuser assembly with Woods alloy for maximum thermal contact.

The optimum method of temperature control below 10 K was achieved by manual operation of the temperature controller: as the heat capacity drops at low temperatures, less heat is required to maintain stable temperatures and large fluctuations can occur in the heater output when controlling internally; these fluctuations cause varying levels of noise at the magnetometer output and can become quite severe when controlling below 4.2 K. Care must also be taken to insure that liquid helium does not collect in the sample zone. Not only is the effectiveness of the heater diminished, causing the liquid to bubble, the oscillations of the sample rod may become coupled to the cryostat, overloading the transducer, and possibly causing changes in the output of the magnetometer.

The temperature of the sample was measured by a calibrated gallium arsenide diode located at the tip of the sample rod adjacent to the sample. The current was provided by a PAR model 156 Cryothermometer, and the voltage measured to 4 places by a Hewlett Packard model 3465A digital multimeter.

B. Microwave Resonance Measurements

1. Microwave Resonance Spectrometer

The microwave resonance measurements carried out in this work were

made using microwave spectrometers of the balanced bridge type of 9.5 GHz (X-band) and 23.3 GHz (K-band). A block diagram of the X-band spectrometer is shown in Figure 14. The K-band spectrometer differs in that the circulator is replaced by a magic T.

Microwaves are generated by a reflex klystron, and first pass through a ferrite isolator which prevents the microwave network from acting back on, and influencing the stability of the klystron. A variable attenuator allows the microwave power to be adjusted to the desired level. In practice, no attenuation was used in this work in order to attain maximum incident microwave at the sample. At very low temperatures ($T \leq 5$ K), some attenuation was used in order to minimize heat dissipation in the sample. Microwaves enter port 1 of the circulator and exit through port 2 and pass through a slide screw tuner, and into the (reflection) cavity. The slide screw tuner introduces the proper impedance into the transmission line to allow an impedance match to the cavity. When the cavity is perfectly coupled to the waveguide, no power is reflected back through the circulator into the detector. When the magnetic field is adjusted for resonance, the sample absorbs power, loading the cavity and altering the cavity Q factor. The resulting impedance mismatch between the cavity and waveguide allows power to be reflected back into port 2 of the circulator, exiting at port 3 into the frequency meter and detector. In practice the cavity impedance match was accomplished using an adjustable iris at the cavity and the slide screw tuner was used only to "fine tune" the match, since the slide screw tuner introduces a certain amount of attenuation

FIGURE 14. Block diagram of a typical reflection microwave spectrometer.

of the microwave power. This "fine tuning" allowed the cavity to be slightly decoupled from the waveguide, permitting a certain amount of power to pass through the circulator to the detector, thus "biasing" the detector and allowing the detector to operate in its most sensitive range.

The cavities used were rectangular TE_{101} (X-band) and TE_{102} (K-band) mode cavities and gold plated to increase the cavity Q factor. The samples were placed on the narrow wall of the cavity in the region of most intense microwave field.

Conventional lock-in detection methods were used to improve the signal to noise ratio by shifting the essentially dc resonance signal to an audio frequency. This method of operation allows a high gain, low noise, narrow band amplifier to be used: a Princeton Applied Research (PAR) model 124 lock-in amplifier. An audio frequency signal is generated by the PAR reference oscillator, amplified by an audio amplifier, passed through a capacitance impedance matching network, and applied to a pair of Helmholtz coils mounted on the magnet pole pieces. The dc magnetic field is then modulated at the audio frequency. The choice of frequency is a compromise between high frequencies which reduce $1/f$ noise, and low frequencies which readily pass through the stainless steel walls of the dewar and through the walls of the microwave cavity. For this work, the choice of frequency was approximately 80 Hz., with an amplitude such that a peak to peak modulation field of approximately 40 Gauss was produced.

The modulated absorption signal from the detector is amplified and demodulated by the PAR lock-in amplifier. The demodulator is a full wave rectifier driven at the reference oscillator frequency with phase adjustable to the input signal. Hence, the term "phase sensitive detection." Because the modulation field "samples" the slope of the resonance absorption, the output signal from the amplifier is the derivative of the power absorption, dP/dH .⁷⁶

The microwave sources at X-band and K-band were, respectively, Varian V-58 and EM1188M reflex klystrons. The power source was a Hewlett Packard model 716B Klystron Power Supply. The maximum power output of each klystron was rated 600 mW, but each was operated somewhat below the rated maximum power. The X-band klystron was cooled in an oil bath, while the K-band klystron was air cooled. The klystron frequency is stabilized to the cavity resonant frequency by means of an automatic frequency control (AFC). This device modulates the frequency of the klystron⁷⁷ by applying a 10 kHz, low voltage signal to the klystron reflector which is normally at about 400 Vdc. The resultant variation in the detector is passed through a lock-in amplifier similar in principle to the PAR amplifier. The rectified AFC output is applied to the klystron reflector and always has the correct polarity necessary to reduce the deviation between the klystron frequency and cavity resonant frequency.

The spectrometers were used in conjunction with a 12 inch Harvey Wells electromagnet controlled by a Walker Magnion FFC-4D field controller which used a temperature stabilized rotating coil gaussmeter as

its sensing element. The magnet was calibrated using a Ventron ("Pound box") nuclear magnetic resonance gaussmeter.

The microwave frequency was measured by a Hewlett Packard X532B wavemeter at X-band and a K532A wavemeter at K-band. Both wavemeters were calibrated by measuring the field with the NMR gaussmeter while making spin resonance measurements with α, α' -diphenyl- β -picryl hydrazyl (DPPH) in the cavity. The known DPPH g-factor is $g = 2.0036$; this allowed a calibration to within 1 part in 1000.

2. Cryostat

The cryostat used for the microwave resonance studies operated essentially in the same manner as the variable temperature stainless steel cryostat used with the magnetometer. The cryostat was manufactured by Andonian (model O-25/7N-II) and incorporates an extra outer chamber which is filled with liquid nitrogen. The cryostat is thus precooled as well as radiation shielded. The bore of the dewar is 1-3/4 inches, which easily incorporates an X-band waveguide arm and cavity.

For early microwave measurements, the temperature of the cavity was controlled and stabilized using a Leeds and Northrup Electromax temperature controller. The emf of a gold-chromel thermocouple mounted on the cavity was compared with an internal, variable reference voltage. Deviation between the two signals indicated a deviation from the set temperature (reference voltage) and if the cavity was too cold, heat was supplied by a manganin heater wire wrapped around the cavity in a

bifilar configuration, and encased in epoxy. At the set temperature the controller provided just enough heater current to oppose the cooling, rather than cycling off and on.

The temperature of the cavities was measured using two Crvo Cal, Inc., CR-1000 four terminal Germanium Resistance Thermometers, one each for the X-band and K-band cavities. The sensitivity of the germanium thermometers improves as the temperature lowers: at 4.2 K, 350 Ω /K; at 20.4 K, 19 Ω /K; at 77.4 K, 0.3 Ω /K. These thermometers lack sufficient sensitivity to be used above 100 K. The resistance was measured by a Hewlett Packard model 3450A Multi-Function Meter. The current supplied to the resistance thermometer was 1 mA for resistances up to 100 ohms (about 10 K), and then switched to 10 μ A for resistance values greater than 100 ohms ($T \leq 10$ K). This procedure minimized Joule heating of the resistance thermometer at the lowest temperature range. The measured temperature was found to drift during the 2 or 5 minute time period required for magnetic field sweeps through the resonance line. In addition, the thermometers were calibrated at only two points, LHe and LN₂ temperatures, and the full resistance vs. temperature extrapolation was based on the resistance vs. temperature behavior for a "typical" germanium resistor. These problems led to the later use of a gallium arsenide diode (similar to that previously described) for temperature control and measurement. A calibrated gallium arsenide diode was used for both temperature control and temperature measurement, with a constant current of 10 μ A supplied to the diode by a FAR model 152 Temperature Controller.

C. Data Recording and Reduction

1. Static Susceptibility

The static susceptibility χ is not directly measured by the VSM; rather, the output is the dipole component of the induced moment, μ , an extensive quantity. The conversion to susceptibility is made using the definition

$$\chi = \frac{1}{V} \left. \frac{\partial \mu}{\partial B} \right|_{B=0} \quad \text{IV-1}$$

where V is the sample volume, and B is the applied magnetic field. Assuming a linear dependence of χ on the applied field B , and zero remanent moment, the static susceptibility can be reduced to

$$\chi = \frac{\mu}{V} \frac{1}{B} \quad \text{IV-2}$$

In practice the magnetic field B was measured using the Bell gaussmeter, and the moment was obtained from the digital meter of the VSM. The volume of the sample was obtained from the mass using a value of 1.75 g/cm^3 for the density of the alloy at room temperature.

2. Resonance Field and Linewidth

The microwave resonance data were recorded on a Hewlett Packard model 7046A X-Y recorder. The X axis drive was provided by the magnet controller and the Y axis drive was supplied by the lock-in amplifier. Because the magnetic field was modulated at 80 Hz., the derivative of the resonance absorption dF/dH was recorded.

Because of the broad linewidth ($H \geq 120$ Gauss) of the Mg:Mn resonance line, fields sweeps of 2000 to 3000 Gauss were made at a sweep time of five minutes. Sweep times of ten minutes were used for temperatures greater than 30 K. In this temperature range the signal to noise ratio became so small that a time constant of one second in the filter circuits of the lock-in amplifier was required.

As shown in Figure 15, the sample was mounted in the cavity with the c-axis of the crystal horizontal. When the magnet was rotated about its vertical axis, the angle ϕ_H between the magnetic field and the crystalline c axis could be varied over a range of 180° .

Figure 16 shows two typical resonance lines at X-band taken directly from the X-Y recorder. The temperature of the sample was 4.4 K. The upper trace was made with the magnet angle $\phi_H = 0^\circ$. The anisotropy is clearly evident.

The method of Peter, et al.,⁷⁸ was used to obtain the resonance field H_c and the absorption resonance linewidth ΔH , from the derivative absorption signal. The complex metallic impedance of the sample causes the absorptive and dispersive parts of the resonance to become mixed, resulting in the asymmetric lineshape. Assuming a Lorentzian lineshape, the absorption line is proportional to the imaginary part of the complex dynamic susceptibility χ'' ,

$$\chi'' = \frac{1}{1+x^2}$$

IV-3

FIGURE 15. Geometry of the sample c -axis and applied magnetic field $\vec{H}$.

FIGURE 16. Typical X-band spectrum.

and the dispersion line is proportional to the real part of the susceptibility χ' ,

$$\chi' = \frac{x}{1+x^2} \quad \text{IV-4}$$

where

$$x = \frac{H-H_0}{\Delta H} \quad .$$

H_0 is the resonance field and ΔH is the half-power half-width of the absorption part of the resonance line. Combining "a" parts absorption and "d" parts dispersion, the derivative of the power absorbed with respect to H , for a ratio $a/d = c$, is

$$\frac{dP}{dH} = \frac{1-cx+x^2}{(1+x^2)^2} \quad \text{IV-6}$$

The value of c is varied from 0 to 1, and a series of asymmetric line-shapes are generated and analyzed by a computer to find the parameters v_1 , v_2 , W , and h . These quantities are exhibited in Figure 17. The low field peak height measured from the baseline is v_1 , the peak to peak height is v_2 , W is the width of the low field peak at half-height, and h_1 is the difference between the resonance field H_0 and the field H_W at the middle of W . Calibration curves were generated and a computer program was written to give the resonance field H_0 , and linewidth ΔH for an input of v_1/v_2 , W , and H_W .

Because the resonant frequency of the cavity changes due to the change in dimensions of the cavity as the temperature is changed, or because below 4.2 K the cavity fills with liquid helium, the resonance

FIGURE 17. Data reduction scheme of Peter, et al.⁷⁸

field undergoes an apparent shift. This frequency induced shift is compensated for by normalizing the microwave frequency to 9.5 GHz. at X-band and 23.3 GHz. at K-band. The induced field shift δH is computed from the frequency shift δf by

$$\delta H = \frac{h}{g\mu_B} \delta f \quad . \quad \text{IV-7}$$

This correction was included in the computer program and for each sweep the following quantities were calculated and stored on magnetic tapes: the frequency normalized resonance field, H_0 ; the resonance absorption linewidth, ΔH ; the absolute temperature; the angle between the applied field and the c axis of the sample $\phi_{||}$; and the g value, calculated using the normalized frequency.

V. RESULTS AND DISCUSSION

The static susceptibility has been measured, and the ESR spectrum obtained from a single crystal of Mg:Mn with a Mn concentration of 0.35 at. percent. The static susceptibility is used to verify that a local moment exists and to measure the effective moment per Mn^{2+} ion, and also to determine the temperature of the transition from the paramagnetic state to the spin glass state. The angular dependence of the ESR resonance field is used to find the crystal field parameter D. The resonance field shifts rapidly downfield at low temperatures ($<4\text{K}$), indicating the onset of an internal field. A comparison of the measured shift at different frequencies is made with that predicted by a recently formulated micromagnetic theory.¹²

The exchange parameter J is determined by fitting the ESR linewidth data to Eqn. II-55. This relation expresses the angle and temperature dependence of the linewidth for an exchange narrowed system in the presence of a relaxation bottleneck. Anisotropy in the linewidth at low temperatures ($<7\text{K}$) suggests the possibility of anisotropy in the exchange parameter, J.

The results obtained from the susceptibility measurements are discussed in section A. The measured effective moment per Mn^{2+} ion in Mg:Mn agrees with that obtained for Mn^{2+} in other hosts, and agrees qualitatively with the value predicted using the s-d exchange model, Eqn. II-18.

A discussion of the crystal field parameter D is contained in section B. The value of D obtained in this work disagrees with that found using TESR in a less concentrated Mg:Mn crystal,⁴⁰ and both values are inconsistent with the value of D obtained in crystalline Mg:Gd.⁵²

A discussion of the low temperature resonance field shift is contained in section C, and a discussion of the effects of spin glass order is contained in section D.

A general discussion of the exchange integral J and its value are included in section E, and a summary is found in section F.

A. Susceptibility

1. The effective moment

The dilute alloy Mg:Mn obeys a Curie-Weiss susceptibility,

$$\chi(T) = N(p_{\text{eff}}\mu_B)^2/3k_B(T+\theta) \quad \text{V-1}$$

where θ is the Weiss temperature, and N is the number of magnetic impurities per unit volume and p_{eff} is the effective number of Bohr magnetons per ion. For this reason, Mg:Mn is a class (b) dilute magnetic alloy in Rizzuto's classification scheme³² (see section B of Chapter II). The effective magnetic moment per Mn^{2+} ion, p_{eff} , and the Weiss temperature, θ , are determined by the slope of the inverse susceptibility vs. temperature. Their values, obtained from the data in Figure 18, are listed in Table 4 for the polycrystalline alloy # 98 and for the single crystal alloy BR2.

FIGURE 18. Inverse static susceptibility, χ^{-1} , vs. T for the Mg:Mn single crystal sample BR2 (solid line) and for the polycrystalline sample 98 (broken line). Inset: low temperature susceptibility.

TABLE 4

Weiss temperature θ and effective number of Bohr magnetons per atom, P_{eff}

Alloy	Solid solution concentration (at.%)	Measured P_{eff}	Free ion $P_{\text{eff}} = g\sqrt{S(S+1)}$	θ
98 ^a	0.49	5.5	5.9	4.22±.05
BR2 ^b	0.35	5.6	5.9	3.41±.05

^a polycrystalline alloy
^b single crystal alloy

The difference between the analysis of the susceptibility reported here, and that reported in Chapter III should be noted.

In Chapter III, the susceptibility for temperatures between 20 and 300 K was used. For the temperature range involved, the susceptibility is very nearly proportional to T^{-1} . The Curie constant, C was determined by fitting the susceptibility to

$$\chi(T) = \chi_0 + C/T \quad \text{V-2}$$

where χ_0 is a temperature independent term. The susceptibility of three polycrystalline samples whose Mn concentrations were determined by independent measurements (atomic spectroscopy and electron microprobe) were used to establish a standard for correlating the measured Curie constant with the three known Mn concentrations. This standard curve was then used to determine the Mn concentration of the single crystal alloy, BR2 by interpolation.

The Weiss temperature, θ , and the effective moment, p_{eff} , were determined by fitting the susceptibility for temperatures between 2 and 300 K to Eqn. V-1. (In this temperatures range, a significant departure of the susceptibility from a T^{-1} behavior at temperatures ≤ 20 K prevents the use of Eqn. V-2.) In Eqn. V-1 the value used for N , the number of Mn^{2+} ions per unit volume is that obtained from the concentration analysis of Chapter III.

Values for p_{eff} and θ could not be accurately determined for the two most dilute polycrystalline alloys, #95 and #96, because the temperature independent Pauli susceptibility is on the same order as the

susceptibility of the Mn ion in the contribution to the total susceptibility and therefore difficult to separate. For the two alloys #98 and BR2, whose susceptibilities obey the Curie-Weiss law, μ_{eff} is comparable with that obtained for Mn in other host metals (see Figure 1). The reduction in measured effective moment from the free ion value is $\approx 5\%$, in qualitative agreement with the 10% reduction predicted by the s-d model, Eqn. II-18.

Anisotropy in the susceptibility was sought, but none was observed. The expected absence of crystalline anisotropy in the static susceptibility is discussed in section B-3 of Chapter III.

2. Determination of the magnetic state.

The fact that the measured susceptibility obeys a Curie-Weiss law indicates that not only do the Mn^{2+} ions in Mg possess a local moment, but that the system is paramagnetic.

Previous work^{62,63} has indicated the presence of both ferro- and antiferromagnetic exchange in dilute alloys. Since this is a necessary requirement⁶⁴⁻⁶⁷ for the transition from a paramagnetic state to a spin glass state, the spin glass transition temperature, T_g was sought. The transition is signified by a cusp in the low field susceptibility, which becomes rounded at higher fields.⁴¹ The absence of a minimum in the susceptibility in Figure 18 is unexpected. If Mg:Mn undergoes a spin glass transition, then T_g is less than 2 K.

B. Determination of the Crystal Field Parameter D

The spin Hamiltonian for an isolated S state ion in a hexagonal crystal is

$$H = g\mu_B H S_z + g\mu_B D(0.5(3\cos^2\theta - 1))(S_z^2 - 1/3 S(S+1)) \quad \text{II-43}$$

+ h.o.t.

where D is the crystal field strength and θ is the angle between the applied field and the crystalline c-axis. In an ionic crystal, the ESR spectrum would consist of 2S equally spaced lines whose separation would be proportional to D and centered at the D=0 position, and the splitting interval would vary with angle as $0.5(3\cos^2\theta - 1)$.

In the single crystal dilute alloy Mg:Mn, the presence of a strong bottleneck plus exchange narrowing causes the spectrum to collapse to a single unstructured line. The line position is determined by a thermally weighted average of the positions of the 2S lines. This first moment analysis is outlined in detail in Appendix A. Crystalline anisotropy is observed in the ESR spectrum of a metal alloy when the 2S+1 crystal field split energy levels become differentially populated due to the Boltzmann factors. When $kT < g\mu_B H$, the position of the single line of the spectrum is more heavily weighted by the transitions between the lowest energy levels. At low temperatures and at large fields, the differences in level populations will be greater, producing a variation of resonance field with angle whose amplitude can be greater than D.

1. Determination of D at Constant Temperature

At a constant temperature, the resonance field was measured at eight to ten angles between 0° and 90° inclusive. These measurements were done at several temperatures, and at two frequencies, X-band (9.5 GHz.) and K-band (23.3 GHz.). Despite efforts to maintain temperature stability while recording the angular spectrum, temperature drifts up to 0.5 K occurred.

Typical data is shown in Figure 19. The temperature is 4.5 K and the frequency is 23.3 GHz. From the data in Figure 19, the value obtained for D is 117 G, while the variation in the resonance field at $\theta=0^\circ$ to $\theta=90^\circ$ is 138 G. This analysis to determine D cannot be used at temperatures below 4 K due to the onset of an anisotropic internal field at about this temperature. The angular variation of the resonance field at X-band at temperatures below 4 K is shown in Figure 20. The contributions to the anisotropy from different sources nearly cancel at 2.5 K. The large uncertainty for the data at 2.5 K is due to noise created by the bubbling of liquid helium in the resonant cavity. At 1.75 K and at 1.84 K, the resonance field for $\theta=0^\circ$ is lower than that for 90° , indicating a negative D (-55 G) if the crystal field were the only source of anisotropy. Thus it is evident that there is a significant contribution to the anisotropy from the internal field.

As the temperature is increased, the amplitude of the variation of the resonance field with angle decreases, and the uncertainty in the value of D increases. The values of D obtained from X-band and from K-band data for several temperatures are listed in Table 5, as

FIGURE 19. Typical K band data showing anisotropy in the resonance field. The temperature is 4.5 K. The angle $\theta=0^\circ$ is parallel to the c axis. The least square values of g and D determined from the analysis in Appendix A are $g=2.013$ and $D=117$ G.

FIGURE 20. Anisotropy of the X band resonance field due to the combined effects of the crystal field interaction and anisotropic internal fields. A least chi squared fit is obtained for $D=-56$ G, $g=2.114$ and $D=-54$ G, $g=2.112$ for the data at 1.75 K and 1.84 K, respectively.

TABLE 5

Values of D and g determined from the present work, and the values of D determined by Oseroff, et al.³⁹

Frequency (GHz.)	T (°K)	D (Gauss)	<D> (Gauss)	g
9.5	4.2	162±25 ^a		2.026±.003
	5.8	198±28 ^a		2.011
	7.4	116±40		2.000
	9.4	125±48		1.997
	9.5	161±46		1.998
	11.0	144±53		1.999
	13.5	138±62		1.999
	14.4	142±64		2.000
	16.8	173±87		2.000±.005
	20.3	128±83		2.000±.004
23.3	4.5	117±12 ^a	137±19 ^b	2.015±.001
	4.9	117±12		2.012
	17.6	162±20		2.014
	13.7	128±34		2.011
			124±7 ^c	
9.2 ^e	1.4	69.5±2	[79]	
	2.0	63 ±3	[76]	
	3.5	57.5±10	[78]	
	5.0	50 ±4	[75]	
			126±7 ^d	
35 ^e	1.33	61±3	[72]	
	3.0	46±7	[60]	
	5.0	41±14	[62]	

^aThese values for D may be incorrect due to the presence of anisotropy in the internal field, H_{loc} .

^bThis average value excludes those values obtained at X band at 4.2 and 5.8 K.

^cThis average value includes all values obtained at K band.

^dThis average value includes all X and K band data except those noted in [b].

^eThis data is taken from S. Oseroff, et al., ref. [39]. The values of D shown in brackets are modified by a susceptibility factor.

well as the average value of D . Included in the table are the values of D obtained by S. Oseroff, et. al., from TESR measurements using a 60 ppm Mn single crystal alloy of Mg:Mn.

In the work reported here, the determination of D is complicated by the onset of an anisotropic internal field, which causes a downfield shift of the observed resonance. As can be seen in Figures 21 and 22, the onset of the shift for $\theta=0^\circ$ is sharp, occurring at ~ 4 K for both X- and K-band frequencies. The onset of the internal field for $\theta=90^\circ$ is more gradual, occurring at ~ 4 -8 K at X-band, but at a temperature perhaps as low as 2 K at K-band.

Since the source and the angular dependence of the internal field are unknown, it is not possible to separate that portion of the anisotropy which is due to the crystal field from that portion which is due to anisotropy in the internal field. Thus the data below ~ 4 K, which would give more reliable estimates for D , cannot be used. In fact there is doubt that the values of D in Table 5, which were determined using X-band data below 8 K, and K-band data below 5 K, are accurate due to the possible presence of additional anisotropy from the internal field. In particular, the values of D obtained at X-band at 4.2 K, and at 5.8 K, are suspect. It is possible that a gradual onset of the internal field at $\theta=90^\circ$ with a negligible internal field at $\theta=0^\circ$, occurs at 6 K. The splitting of the resonance field from 0° to 90° would then be larger than that produced solely by the crystal field, resulting in a larger value of D . At 4.2 K, the same argument holds, except that there may be a non-negligible internal field at 0° , i.e. the internal field at

FIGURE 21. Temperature dependence of the resonance field at X band (9.5 GHz.) for $\theta=0^\circ$ (circles) and for $\theta=90^\circ$ (crosses). A least squares fit for temperatures $T>7.5$ was obtained for $D=135\pm 18$ and $g=2.001\pm .001$.

FIGURE 22. Temperature dependence of the resonance field at K band (23.3 GHz.) for $\theta=0^\circ$ (circles) and for $\theta=90^\circ$ (crosses). A least squares fit for temperatures $T>4K$ was obtained for $D=101\pm 5$ G and $g=2.0077\pm 0.0005$.

0° has begun to "catch up" with the internal field for 90° at this temperature.

2. Determination of D at constant angle

In order to determine a single value of D appropriate to the X-band data, shown in Figure 21, a two parameter (D and g) least squares fit was made using the resonance field data for $\theta=0^\circ$ and $\theta=90^\circ$ for all $T \geq 7.5K$. In the fitting routine an uncertainty of 15 G in the resonance field was included, corresponding approximately to the scatter in the data. In the figures, the circles represent the resonance field for $\theta=0^\circ$, and the crosses represent the resonance field for $\theta=90^\circ$. The dashed line represents the resonance field in the absence of anisotropy. The best fit values of g and D are shown in the figures. For the X-band data, $D=136 \pm 18$ G with $g=2.001 \pm .001$, and for the K-band data, Figure 22, $D=101 \pm 5$ G with $g=2.0077 \pm .0005$. The difference in D determined from the X-band and from the K-band data is unexpected because of the absence of frequency dependent terms in the spin Hamiltonian, Eqn. II-43. However, due to the spread in values of resonance field in Figures 21 and 22, it is not surprising that a significant uncertainty for D is obtained. Although these values of D are nearly twice as large as those obtained by Oseroff, et al., the trend of decreasing D with increasing frequency is also observed in his experiment. The scatter in the values of D in Table 5 prevents the determination of any temperature or frequency dependence of D. An investigation of the angular dependence of the resonance field at higher frequencies may give further

information about trends.

3. Sources of uncertainty in the measured resonance field

The overall scatter in the data results from possible thermoremanent effects associated with the onset of internal fields, from uncertainties in measuring both the applied field and the sample temperature, from poor signal-to-noise ratio at temperatures above 25 K, and from noise problems due to the bubbling of liquid helium at temperatures between the lambda point and the boiling point of helium. This combination of factors leads to an uncertainty in the resonance field of ~5-10% of the linewidth, a feature common in the ESR of dilute alloys.

For one set of data taken on any given day, the resonance field and linewidth vary smoothly with temperature, as shown in Figure 23 and Figure 24, respectively. When the collected data from several runs for either X band or K band frequencies is displayed, the points form a "band" 20 to 30 G wide, as shown in Figures 21 and 22. The most likely explanation for this lack of reproducibility is the change in effective Mn concentration at the surface of the sample due to the periodic acid etching of the sample. Each etch removed approximately 300 microns of material from each side of the sample. The etch prevented spurious signals, e.g. from MnO, from Mn in amorphous MgO, or from surface contaminants. However, over a period of a few weeks, it is possible that due to concentration inhomogeneities, regions rich in Mn were exposed, and then eroded away by the etching process. This would produce a

FIGURE 23. Smooth variation of the temperature dependence of the resonance field for one set of data.

FIGURE 24. Smooth variation of the temperature dependence of the linewidth for one set of data.

discontinuous variation in the Mn concentration in the "effective" sample region, i.e., the skin depth ($\sim 1\mu$).

It should be noted that the values of D derived by Oseroff, et. al.,⁴⁰ were obtained using transmission resonance (TESR) of a Mg:Mn single crystal with a Mn concentration of 60 ppm. The same first moment analysis as described in Appendix A of this work was used to obtain D. These values of D were then modified by a susceptibility factor, $(\chi_r+1)/\chi_r$, where χ_r is the static susceptibility ratio, $\chi_r \equiv \chi_d/\chi_e$, where the subscripts d and e refer to the local moments and the conduction electrons, respectively. The argument for the correction factor maintains that the amplitude of the angular variation of the resonance field actually observed is reduced from that due to D by the factor $\chi_r/(\chi_r+1)$. The spin system is regarded as consisting of five independent subsystems each with an appropriate "g_d" value determined from the full coupled bottleneck Eqns. II-51 and 52. (For the present work, the susceptibility ratio correction would be negligible since with an Mn concentration of 0.35 at.%, $\chi_r \gg 1$ for temperatures below 20 K.) Using the modified values for D shown in brackets in Table 5, Oseroff, et.al. estimate that $D=70 \pm 10$ G. They report that this is comparable to a value of 54 G for D reported from an analysis of the susceptibility anisotropy.⁷⁹

Although the modified values of D obtained by Oseroff are slightly increased by the correction factor, the values obtained in the present work are still larger by nearly a factor of two. Oseroff uses transmission resonance with the sample c-axis oriented normal to the sample plane, whereas in the present work standard reflection resonance is

used, and the sample c-axis is located in the plane of the sample. One important difference between the present work and that of Oseroff is the difference in the Mn concentration. His samples contained 60 ppm Mn vs. 0.35 at.% (3500 ppm) Mn in the work reported here. Impurity-impurity interactions, which may greatly affect the local spin dynamics, are much more likely to be present at the higher concentrations of Mn. (An indication of the importance of impurity interactions is that the static susceptibility of the 60 ppm sample departs from a Curie law only below 60 mK,⁴⁰ whereas the susceptibility of the 0.35 at.% sample has a Weiss temperature of 3.4 K.) Further investigation using Mg:Mn crystals with a wide range of Mn concentrations would be necessary to determine any effect of impurity-impurity interactions on the crystal field interaction. A complicating factor in the determination of D from transmission resonance data is that the resonance field of the localized electrons is not measured directly. The g-value of the observed resonance line is determined from the combined susceptibility weighted g-values of the conduction electrons, g_e , and the localized electrons, g_s . In the work reported here using reflection resonance, the position of the resonance line is determined solely by the g-value of the localized electrons, since $\chi_s \gg \chi_e$. Thus an error in either the Mn susceptibility, χ_s , or the conduction electron susceptibility, χ_e , will affect the transmission resonance line, but it will not affect the reflection resonance line.

C. Measurement of the Internal Field

A downfield shift of the observed resonance field at a characteristic temperature, T_0 , which depends on the impurity concentration is a feature common to dilute alloys.¹⁶ The shift was originally interpreted^{2,3} as indicating the onset of antiferromagnetism. However, susceptibility measurements failed to show the expected departure from a paramagnetic Curie law behavior at T_0 . In addition, further investigations^{62,63} in dilute alloys have shown that both ferromagnetic and antiferromagnetic exchange interactions exist, and that the competition between them leads to the random freezing of the local moments at the spin glass temperature T_g .

The Cu:Mn system has been thoroughly investigated because of the favorable solubility of Mn in Cu over a large concentration range. The spin glass temperature, T_g has been obtained⁸ for Cu:Mn from low field susceptibility measurements, and a reexamination of the ESR of Cu:Mn² shows that the onset of the downfield shift occurred at $\sim T_g$.

A generalization of this result for the ESR in all spin glasses cannot be made. An investigation¹² of the magnetic properties of a concentrated (amorphous) spin glass, $Gd_{0.37}Al_{0.63}$, has revealed a Curie temperature of 30 K, and a spin glass temperature of 16 K. The downfield shift of the ESR resonance field occurred at 30 K, the Curie temperature. A theory for the shift, based on the effect of columnar inhomogeneities, was proposed. Since the details of the theory are contained in Chapter II, only a brief description will be contained here.

A field-induced columnar magnetization inhomogeneity gives rise to an effective anisotropy field, H_{loc} , where

$$H_{loc} = 2\pi V_1(1-V_1)(M_1-M_2)^2 / \langle M \rangle \quad \text{II-64}$$

$$\langle M \rangle = M_1 V_1 + M_2(1-V_1) \quad \text{II-63}$$

The average magnetization $\langle M \rangle$ is the sum of the magnetization M_1 of the ferromagnetic region (occupying a volume fraction V_1), and the magnetization M_2 of the remainder of the sample (volume fraction $V_2 = 1-V_1$). These equations are valid so long as the exchange coupling between spins is sufficiently strong that in spite of the inhomogeneity of the system, the spin precession angle during resonance is essentially constant over the characteristic intercolumnar separation.

The analysis of the Al:Gd system by Malozemoff and Jamet is the following. The average magnetization $\langle M \rangle$ is obtained from the static susceptibility. Then M_1 is calculated assuming each Gd^{3+} ion has a spin of 7/2 and that in the volume fraction V_1 , all Gd spins are aligned ferromagnetically. Assuming $M_2 \ll M_1$, Eqn. II-63 gives a value for V_1 , which, when substituted in II-64, along with $\langle M \rangle$ and M_1 , gives a value for H_{loc} which is larger than the measured value. Working backward from the observed H_{loc} , a smaller value for V_1 is found, and a non-zero value for M_2 is obtained.

The observed shift in the resonance field in Al:Gd agrees with the calculated local field. In addition, the observed shift in the series of Cu:Mn alloys with concentrations between 11.1 and 1.4 at.%

Mn examined by Owen, et al., can also be explained in terms of the onset of a local field.

The measured H_{loc} in the Al:Gd system was determined from the difference between the expected resonance field in the absence of H_{loc} and the measured resonance field, including effects of demagnetizing fields. In the Mg:Mn system reported here, the magnitude of the local field was determined from the difference between the measured field and the calculated resonance field using the spin Hamiltonian, Eqn. II-43. The effects of demagnetization fields were ignored since $4\pi\langle M \rangle \sim 2$ G at 2 K and at K band. The temperature dependence of the local field is shown in Figures 25 and 26 at X band and at K band, respectively. The circles represent data with the applied field parallel to the c-axis, $\theta=0^\circ$, and the crosses, $\theta=90^\circ$.

For Mg:Mn at $\theta=0^\circ$ the maximum observed value of H_{loc} is ~ 370 G at 1.6 K at X band, where $\langle M \rangle \approx 0.7$ G. If the system were fully ferromagnetically aligned, $M=8.1$ G. Assuming that $M_2=0$, and that $M_1=8.1$ G, Eqn. II-63 gives a value of $V_1=0.08$, and Eqn. II-64 gives $H_{loc}=45$ G. This is the greatest possible value for H_{loc} using the local field theory. Including a non-zero value for M_2 will decrease H_{loc} .

The same analysis, when carried out for $\theta=0^\circ$ at K band at 1.6 K, gives $\langle M \rangle \approx 1.7$ G, $M_1=8.1$ G, and $V_1=0.20$ which result in $H_{loc}=40$ G. The observed maximum value of H_{loc} is ~ 350 G for $\theta=0^\circ$ at 1.6 K.

It may be that the estimate of M_1 is not correct. If the ferromagnetic regions occupying a volume fraction V_1 are rich in magnetic impurity as the result of clustering, then it is not possible to

FIGURE 25. Temperature dependence of the local field, H_{loc} , at X band (9.5 GHz). The data points represent the difference between the measured resonance field and the resonance field calculated using a first moment analysis with $D=135$ G and $g=2.001$ (Figure 21). The circles represent $\theta=0^\circ$ and the crosses, $\theta=90^\circ$.

FIGURE 26. Temperature dependence of the local field, H_{loc} , at K band (23.3 GHz.). The data points represent the difference between the measured resonance field and the resonance field calculated using a first moment analysis with $D=101$ G and $g=2.008$ (Figure 22). The circles represent $\theta=0^\circ$ and the crosses, $\theta=90^\circ$.

calculate M_1 , since the concentration of magnetic ions in the volume V_1 would be unknown.

Assuming that $M_2 \ll M_1$, Eqns. II-63 and 64 can be combined to eliminate M_1 , so that the local field can be expressed

$$H_{loc} = 2\pi(1-V_1)\langle M \rangle / V_1 \quad . \quad V-2$$

Substituting the observed value of 350 G for H_{loc} , and using $\langle M \rangle \approx 0.7$ G and 1.7 G for X and K band respectively,

$$V_1 = \begin{cases} 0.011 & \text{at X band} \\ 0.028 & \text{at K band} \end{cases} .$$

The value of M_1 then obtained from these values of V_1 using Eqn. 11-63 is $M_1 \approx 60$ G, which implies a concentration of Mn of ≈ 2.8 at.% in the volume fraction V_1 . Such a large concentration of Mn in solid solution in Mg is inconsistent for a single phase material, as shown by the phase diagram in Figure 7.

The quantitatively inconsistent results obtained using the local field theory are probably due to a breakdown in the theory at low concentrations (≤ 1 at.%). The qualitative behavior predicted by the theory is still observed, however. Table 6 lists the resonance field shifts at 2 K observed in a series of polycrystalline Mg:Mn alloys,¹¹ at X band as well as the shift reported here. The decrease in the shifts with decreasing Mn concentration is consistent with the prediction of the theory.

TABLE 6

Observed line shifts in Mg:Mn at 2 K

Alloy	Conc. (at.%)	ν (GHz.)	observed δH (Gauss)
#98 ^a	0.49	9.4	370
BR2 ^b	0.35	9.5	350
#96 ^a	0.11	9.4	130
#95 ^a	0.02	9.2	20

^a polycrystalline alloy, see ref. [11].

^b single crystal alloy, $\theta=0^\circ$

D. Effects of Spin Glass Ordering on ESR

There is evidence that the effects of spin glass ordering can be detected by the presence of a maximum in the ESR linewidth at T_g when the sample is cooled in an external field. The effect was observed in 1967 by Griffiths⁸⁰ in an investigation of the effects of field cooling on the ESR of Cu:Mn. The specimens were powdered samples with Mn concentrations of 4.4 and 14.9 at.%. When the samples were cooled to 2 K in a field of 5kG, a maximum in the linewidth, and a pronounced minimum in the peak to peak signal amplitude occurred at temperatures of 21 K and 60 K for the 4% and 15% alloys respectively. Neither effect was observed when the samples were cooled in zero field. The temperatures at which this anomalous behavior in the ESR data occurred corresponds with the spin glass temperature T_g in Cu:Mn as determined later⁴¹ by a cusp in the low field susceptibility.

The effects of field cooling in Mg:Mn in the present work was sought, but none was observed. This negative result supports the contention that $T_g < 2$ K for the Mg:Mn alloy studied herein.

In the review by Mydosh,⁴¹ a log-log plot of T_g vs. concentration of impurity for the alloys Au:Mn, Cu:Mn, and Ag:Mn shows that in these alloys, for a Mn concentration of 0.35 at.%, T_g is between 5 K (for Cu:Mn) and 2.5 K (for Au:Mn and Ag:Mn). Thus it is not unreasonable that T_g for a 0.35 at.% Mg:Mn alloy is less than about 2 K.

For all alloys studied to date, $T_g \propto c^m$, where m is between 0.5 and 0.75, and for many alloys⁴¹ $m=2/3$. A systematic measure of the low field susceptibility of several Mg:Mn alloys with varying concentrations

is needed to verify its expected spin glass behavior. This sort of investigation has probably not been carried out for Mg:Mn due to the fact that it is a "difficult" metallurgical system, and the maximum concentration of Mn as determined by the phase diagram, Figure 7, is 1.5 at.% at the melting point, 650°C.

E. Linewidth Analysis

That the Mg:Mn system reported here is bottlenecked is shown by comparing δ_{e1} and δ_{es} . The relaxation rate δ_{e1} is estimated from the thermal slope of the high temperature ($T > 15K$) linewidth, $\delta_{e1} = 1.7 \times 10^{11} s^{-1}$ and using a reasonable value of 0.2 eV for J , δ_{es} is $\approx 1.2 \times 10^{12} s^{-1}$. The bottleneck condition $\delta_{es} > \delta_{e1}$ is thus satisfied, and the linewidth is given approximately by

$$\Delta H = \delta_{se} (\delta_{e1} / \delta_{es}) + \Delta H_0 \quad . \quad \text{II-53}$$

The presence of the crystal field interaction introduces an additional term to the linewidth for a bottlenecked system.

The temperature dependence of the linewidth, Eqn. II-55, arises from the relaxation term δ_{se} which is linear in T .

$$\Delta H = (\delta_{e1} / \gamma) \frac{\lambda^2 \omega_0^2 (\chi_e + \chi_s) \chi_e + \delta_{se} (\delta_{se} + \delta_{es})}{(\lambda \omega_0 (\chi_e + \chi_s))^2 + (\delta_{se} + \delta_{es})^2} + \frac{.32 \gamma}{15 \delta_{se}} [D(.5) (3 \cos^2 \theta - 1)]^2 + \Delta H_0 \quad \text{II-55}$$

where

$$\gamma = g\mu_B/\hbar = 1.76 \times 10^7 \text{ s}^{-1}/\text{G}$$

$$\lambda = 2J/g^2\mu_B^2 N_0 = 2.13 \times 10^5 \text{ J}$$

$$\chi_e = g^2\mu_B^2 n(E_F) = 2.6 \times 10^{-6}$$

$$\chi_s = 9.95 \times 10^{-4} / (T + 3.4)$$

$$\delta_{se} = \frac{\pi [J n(E_F)]^2}{\hbar N_0^2} kT = 3.15 \times 10^{10} \text{ J}^2 \text{ T s}^{-1}$$

$$\delta_{es} = 2\pi c n(E_F) J^2 S(S+1) / 3\hbar N_0 = 3.08 \times 10^{13} \text{ J}^2 \text{ s}^{-1}$$

and where δ_{el} is the lattice relaxation rate of the conduction electrons, ($\approx 1.7 \times 10^{11} \text{ s}^{-1}$) ω_0 is the angular microwave frequency, D is the crystal field parameter, and ΔH_0 is the residual ($T=0$) linewidth; J is the exchange integral in eV, $n(E_F)$ is the one spin density of states at the Fermi energy, E_F , N_0 is the number of atoms/cm³, and c is the atomic fraction of Mn.

At high temperatures, the first term of II-55, which is roughly linear in T , dominates, while at low temperatures, the second term, which is proportional to T^{-1} , dominates. Thus, Eqn. II-55 predicts a linewidth which decreases with decreasing temperature at high temperatures, reaches a minimum, and then increases with decreasing temperature at low temperatures.

The first two terms of Eqn. II-55 are plotted individually in Figure 27 for $J = 0.1, 0.12$, and 0.3 eV, with $\theta=0^\circ$, $\delta_{el}=1.7 \times 10^{11} \text{s}^{-1}$, and $D = 134$ G. The strong J^{-2} dependence of the second term at low temperatures, and the weak J dependence of the first term is evident.

1. Contributions to the Exchange Integral, J

The form of the exchange interaction,

$$H = -J \vec{S} \cdot \vec{s} \quad , \quad \text{II-8}$$

results from assuming an isotropic, purely local interaction (delta function potential) leading to a constant value for J . Both assumptions are in general incorrect.

The origin of Eqn. II-8 is a complicated question. Since the interaction resembles intra-atomic exchange, there is almost certainly a contribution of that nature, which Slater showed is always positive.⁸¹ The interatomic exchange contribution is non-local, and therefore cannot be written as II-8, although for dilute alloys interatomic exchange is usually a small contribution. The last contribution is due to an admixture between the local moment and the conduction electrons,

$$J_{\text{mix}} = |V_{kd}|^2 [(E_d - E_F)^{-1} + (E_F - E_d - U)^{-1}] \quad . \quad \text{II-9}$$

This admixture repels localized and conduction electron spins which are parallel, and lowers the energy of opposite spin-direction states, leading to an effective antiferromagnetic interaction ($J_{\text{mix}} < 0$).

Figure 27. The first and second terms of Eqn. II-51 plotted separately for $J = 0.1, 0.2, \text{ and } 0.3 \text{ eV}$ with $D=134 \text{ G}$, $\delta_{e1}=1.7 \times 10^{11} \text{ s}^{-1}$, and $f=9.5 \text{ GHz}$.

These ideas can be treated more quantitatively. The following discussion is based on the treatment of exchange by J. Kondo.²⁰

The exchange integral is defined by

$$\langle \vec{k}n | n\vec{k}' \rangle = \iint \phi_{\vec{k}}^*(\vec{r}_1) \phi_L^*(\vec{r}_2 - \vec{R}_n) V(r_{12}) \phi_L(\vec{r}_1 - \vec{R}_n) \phi_{\vec{k}'}(\vec{r}_2) d^3r_1 d^3r_2 \quad V-3$$

where $\phi_{\vec{k}}(\vec{r})$ is a Bloch function representing a conduction electron at $\vec{r}$ with wave vector $\vec{k}$, $\phi_L(\vec{r} - \vec{R}_n)$ represents the orbital of an impurity atom located at $\vec{R}_n$, and $V(r_{12})$ represents an effective two body interaction.

When the Bloch functions are expanded in terms of the Wannier function, the result is

$$\phi_{\vec{k}}(\vec{r}) = N^{-1/2} \sum_i e^{i\vec{k} \cdot \vec{R}_i} w(\vec{r} - \vec{R}_i) \quad V-4$$

where the sum is over all atomic sites $\vec{R}_i$. Introducing V-4 into V-3, and translating the origin to $\vec{R}_n$.

$$\begin{aligned} \langle \vec{k}n | n\vec{k}' \rangle &= N^{-1} \exp[i(\vec{k}' - \vec{k}) \cdot \vec{R}_n] \sum_{i,j} \exp[i(\vec{k}' \cdot \vec{R}_j - \vec{k} \cdot \vec{R}_i)] \\ &\times \iint w^*(\vec{r}_1 - \vec{R}_i) \phi_L^*(\vec{r}_2) V(r_{12}) \phi_L(\vec{r}_1) w(\vec{r}_2 - \vec{R}_j) d^3r_1 d^3r_2 \quad V-5 \\ &\equiv N^{-1} \exp[i(\vec{k}' - \vec{k}) \cdot \vec{R}_n] J(\vec{k}, \vec{k}') \quad . \end{aligned}$$

The last equation defines $J(\vec{k}, \vec{k}')$ as,

$$J(\vec{k}, \vec{k}') = \sum_{i,j} \exp [i(\vec{k}' \cdot \vec{R}_j - \vec{k} \cdot \vec{R}_i)] f(\vec{R}_i, \vec{R}_j) \quad . \quad V-6$$

If interatomic exchange is not important, then the $i=j=0$ term in the sum is dominant. In this case J is independent of $\vec{k}$ and $\vec{k}'$, and J reduces to the atomic exchange integral when the Wannier function reduces to an atomic orbital. If the d-orbital ϕ_L is degenerate, then S in II-8 may be taken to be the total spin operator if the intra-atomic exchange interaction is strong enough to retain Hund's rule coupling in the metal. Then J denotes an average of various exchange integrals.

Estimates of J can be obtained from the g shift, Eqn. II-41, and from the linewidth, Eqn. II-55. If the condition of a delta function range potential is relaxed, the exchange integral J can be written (with the restriction of a spherical Fermi surface)

$$J(\vec{k}, \vec{k}') = J(\vec{q}) = \sum_L (2L+1) P_L(\cos\theta) J^{(L)}(k_F, k_F) \quad V-7$$

where $\vec{q} = \vec{k} - \vec{k}'$ and $|\vec{q}| = 2k_F(1 - \cos\theta)^{1/2}$. With this form, since the g shift is proportional to the $\vec{q}=0$ component of the exchange (because the measuring rf wavelength is large compared to the sample size), the J determined by the g shift, Eqn. II-41, is replaced by¹⁵

$$J(0) = J^{(0)} + 3J^{(1)} + 5J^{(2)} + 7J^{(3)} + \dots \quad V-8$$

For the linewidth, the important parameter is the square of $J(\vec{q})$, summed over all wave vectors from 0 to $2k_F$. The effective square of the exchange which should replace J^2 in δ_{es} and δ_{se} is

$$\langle J^2(\vec{q}) \rangle = (J^{(0)})^2 + 3(J^{(1)})^2 + 5(J^{(2)})^2 + 7(J^{(3)})^2 + \dots \quad V-9$$

Each partial wave has a (positive) contribution from atomic exchange which Watson⁸² has shown falls off rapidly with increasing L . The (negative) contribution from interband mixing is a maximum for $L = L$, the orbital angular momentum for the electron in question. Thus, for d electrons, Eqn. V-7 can be terminated after $L=2$.

The g shift and the linewidth give two equations for the L wave coefficients, and the electrical resistivity and Kondo resistivity give two more. Thus, in principle, all significant partial wave amplitudes can be determined. For the Mg:Mn system reported here, the Kondo temperature is below presently available temperatures. Also, the g shift is so small that only a crude estimate of $J^{(0)}$ can be made. Finally, the magnetic contribution to the electrical resistivity is small for such a "difficult" metallurgical system, due to the large contribution from dislocation scattering. Dislocations and imperfections in the Mg:Mn crystal result from the quenching necessary to "freeze" Mn ions into solid solution. Of the four observable quantities used to determine J , only the linewidth can be used for single crystal Mg:Mn.

A least chi squared fit of the linewidth data at the angles $\theta=0$, 15, 30, 45, 65, 80, and 90° to Eqn. II-55 was obtained for the values of ΔH_0 , δ_{e1} and $|J|^{83}$ listed in Table 7, and plotted in Figures 28-30. Since the statistical uncertainties in ΔH_0 and δ_{e1} were large, they were assumed isotropic, and their weighted mean values determined. The mean values are listed at the bottom of Table 7.

Since the values for $|J|$ seemed to vary systematically with angle, the linewidth data was reexamined in terms of a one parameter fit. The values of $|J|$ thus obtained are listed in the last column of Table 7, and vary only slightly from the values of $|J|$ determined by the three parameter fit. The systematic angle dependence was again obtained.

Eqn. II-55 gives a qualitative description of the temperature and angular dependence of the linewidth, but it has a critical failure at $\theta=55^\circ$. The linewidth at $\theta=55^\circ$ is shown in Figure 31. At this angle, the second term of II-55 should be zero, and at low temperatures the predicted linewidth (solid line) departs only slightly from a straight line (due to the growing importance of χ_s). However, the data shows a marked upturn at about 7 K.

Several factors may be responsible for the apparent angular dependence of J and for the failure at $\theta=55^\circ$. If the Malozemoff model for the local field H_{loc} is correct, then inhomogeneous broadening will occur as H_{loc} increases. If inhomogeneous broadening due to the onset of an isotropic local field is present, then the departure of the linewidth at $\theta=55^\circ$ from the solid line in Figure 31 gives an estimate of the broadening. However, if H_{loc} has a preferred orientation, there

TABLE 7

Values of ΔH_o , δ_{el} and $|J|$ determined by a least squares fit of line-width data to equation II-51.

θ	$ J $ ^a (eV)	ΔH_o (Gauss)	$\delta_{el} \times 10^{-11}$ (s ⁻¹)	$ J $ ^b (eV)
0	.295±.018	74±13	1.63±.13	.269±.005
15	.280±.036	62±29	1.87±.27	.256±.013
30	.197±.027	54±28	1.86±.26	.184±.010
45	.085±.014	37±42	1.76±.30	.090±.006
55	-	-	-	.065±.006
65	.076±.016	18±55	1.75±.38	.095±.009
80	.153±.028	60±33	1.55±.27	.148±.011
90	.154±.010	35±13	1.56±.11	.180±.007
Weighted Average				
	.152±.006	52±8	1.64±.07	.147±.002

^a These values of $|J|$ are determined from a three parameter fit.

^b These values of $|J|$ are determined from a one parameter fit.

FIGURE 28. Values of δ_{e1} determined from a least squares fit of the temperature dependence of the Eqn. II-55.

FIGURE 29. Values of J determined from a least squares fit of Eqn. II-55.

FIGURE 30. Values of ΔH_0 determined from a least squares fit of Eqn. II-55.

Figure 31. Temperature dependence of the linewidth for $\theta=55^\circ$. The solid line results from a least squares fit of data for $T > 10$ K with $\delta_{e1} = 1.75 \times 10^{11} \text{ s}^{-1}$, $J = 0.065$ eV, and $\Delta H_0 = 50$ G using Eqn. 11-51 with the second term deleted. The broken line represents a least squares fit as above but for all data, with $\delta_{e1} = 1.47 \times 10^{11} \text{ s}^{-1}$, $J = 0.065$ eV, and $\Delta H_0 = 88$ G.

will be some anisotropy in the broadening. Also, since Eqn. II-55 is the result of solving a set of six coupled Eqns. (II-51 and 52) in the limit of zero anisotropy and extreme bottleneck, ($\delta_{es} \gg \delta_{el}$), it may be that higher order angle dependent terms have been omitted which may become important at low temperature.

2. Anisotropic Exchange

It is possible that II-55 accurately predicts the linewidth, and that s-wave scattering is dominant (only $L=0$ in Eqn. V-7). A least squares fit of the values of J determined from the one parameter fit can be made to the relation

$$|J(\theta)| = j_0 + j(0.5(3\cos^2\theta - 1))^2$$

with $j_0 = 0.083 \pm 0.003$ eV and $j = 0.199 \pm 0.006$ eV. The angular dependence of J is shown in Figure 32.

It must be noted that most of the J dependence is found in the second term of Eqn. II-55. Since this term is nonnegligible only below about 10 K, the determination of J is based almost entirely on data taken at temperatures below 10 K. For some angles, there is insufficient data below 10 K to justify the small uncertainties in J in Table 7 which result from the least squares fit.

The weighted mean value of $|J|$ determined from the one parameter least squares fit value is 0.147 ± 0.002 eV. This is smaller than the estimate $|J| \geq 0.24$ eV determined by Kleinhans¹¹ in polycrystalline Mg:Mn using Eqn. II-53. The linewidth data for this polycrystalline

FIGURE 32. Values of J determined from the one parameter fit of linewidth vs. temperature using Eqn. II-51, with $\delta_{el}=1.64 \times 10^{11} \text{ s}^{-1}$, and $\Delta H_0=52 \text{ G}$. The solid line represents $J=j_0 + j(0.5(3\cos^2\theta-1))^2$ with $j_0=0.083$ and $j=0.199 \text{ eV}$.

alloy can be used to determine $|J|$ in the manner as described for the single crystal alloy. Assuming that a large number of randomly oriented crystallites are present in the polycrystalline alloy, the average value of θ in Eqn. II-55 can be determined from the value of $(0.5(3\cos^2\theta-1))^2$, averaged over all solid angle. The result is $\langle\theta\rangle = 37^\circ$. Using the values of χ_s , δ_{se} , δ_{es} , δ_{el} and ΔH_o intrinsic to the polycrystalline alloy, and $D=135$ G, a least chi squared fit is obtained for $|J|=0.098$ eV. This value is consistent with the values obtained for $|J|$ in the single crystal alloy at $\theta=45^\circ$, and 30° .

The value of J calculated using susceptibility, specific heat, and optical measurements⁸⁴ is $J=-0.5$ eV for Mn^{2+} in metallic hosts. Using NMR techniques in Cu:Mn,⁸⁵ a value of $J=-0.2$ eV has been determined, and studies of the concentration dependence of the superconducting critical field H_{c2} for Mn in Mo_7Ga_{31} have yielded a value of $J=-0.34$ eV.⁸⁶

Since, due to the dynamic character of resonance experiments, the wavevector dependence of $J(\vec{k},\vec{k}')$ results in smaller estimates of J than other measurements, the value of $|J|=0.147$ eV is not inconsistent with other determinations.

F. Summary

A systematic study of single crystals of Mg:Mn with both larger and smaller Mn concentrations than the alloy studied here, is needed. The more dilute alloys would allow a more accurate determination of the crystal field parameter D because the onset of the local field, H_{loc}

should occur at lower temperatures. The crystal field splitting of the resonance field, which increases with decreasing temperature, could then be measured at lower temperatures. If a larger concentration alloy can be made whose spin glass temperature is in the temperature range available in ESR experiments, the field cooling effects, similar to that found in Cu:Mn, could be examined.

A more realistic treatment of the conduction electrons is needed to understand the dynamics of the problem in dilute metallic alloys. To the present, only free electrons, restricted to a spherical Fermi surface, have been used in the calculation of the g shift and linewidth for ESR. However, the band structure has yet to be introduced. As a result, the coupling parameters deduced from experiment may be meaningless. Although it is appropriate to use the calculated value of the $\vec{q}=0$ component of the conduction electron susceptibility to obtain $J(\vec{q}=0)$ from the g shift, the wavevector dependent, imaginary part of the conduction electron susceptibility must be used for the linewidth. The resulting wavevector dependence of the exchange makes the estimate of $J(\vec{q})$ difficult.

Appendix A: First Moment Analysis of the Resonance
Field in the Presence of Crystalline
Fine Structure.

The Hamiltonian for a magnetic moment in a crystal field of axial symmetry in an external field is

$$\begin{aligned}
 H &= g\mu_B H S_z + 1/2 g\mu_B D [S_z^2 - 1/3 S(S+1)] [3\cos^2\theta - 1] \\
 &\quad - g\mu_B D (S_x S_z + S_z S_x) \cos\theta \sin\theta \\
 &\quad + 1/4 g\mu_B D (S_+^2 + S_-^2) \sin^2\theta \\
 &= H_0 + H_1 + H_2 + H_3
 \end{aligned}$$

where H is the external field, D represents the strength of the crystal field interaction, θ is the angle between the external field and the crystalline c -axis, and S_+ and S_- are raising and lowering operators.

The first two terms, H_0 and H_1 , have diagonal matrix elements ($\Delta m_s = 0$). The matrix elements of the third term $\langle m_s | H_2 | m_s \rangle$ are found on the immediate off-diagonal ($\Delta m_s = \pm 1$), and the matrix elements of the fourth term $\langle m_s | H_3 | m_s \rangle$ are found on the second nearest off-diagonal ($\Delta m_s = \pm 2$).

Specifically, the non-zero off-diagonal matrix elements are $\langle \pm 5/2 | H_2 | \pm 3/2 \rangle$, $\langle \pm 3/2 | H_2 | \pm 1/2 \rangle$, $\langle -1/2 | H_2 | +1/2 \rangle$, and $\langle \pm 5/2 | H_3 | \pm 1/2 \rangle$ and $\langle \pm 3/2 | H_3 | \mp 1/2 \rangle$, for a spin 5/2 particle.

Dropping the subscript of m_s , the energy can be expressed to second order as

$$E_m = E_m^0 + E_m^1 + E_m^2 + E_m^3$$

where

$$E_m^0 = g\mu_B H m_s \equiv Gm; m = \{-5/2, -3/2, -1/2, 1/2, 3/2, 5/2\}$$

$$E_m^1 = \frac{1}{2} g\mu_B D (3\cos^2\theta - 1) (m^2 - \frac{1}{3} S(S+1)) ; m = \{-5/2, \dots, 5/2\}$$

$$E_m^2 = - \sum_{n \neq m} \frac{|\langle n | H_2 | m \rangle|^2}{E_n^0 - E_m^0} = \frac{(g\mu_B D)^2}{4G} \cos^2\theta \sin^2\theta [(2m+1)^2 (S(S+1) - m(m+1)) \{m \leq 3/2\} - (2m-1)^2 (S(S+1) - m(m-1)) \{m \geq -3/2\}]$$

$$E_m^3 = - \sum_{n \neq m} \frac{|\langle n | H_3 | m \rangle|^2}{E_n^0 - E_m^0} = - \frac{1}{2G} (g\mu_B D)^2 \sin^2\theta / 4 [(S(S+1) - (m-1)(m-2)) (S(S+1) - m(m-1)) \{m \geq -1/2\} - (S(S+1) - (m+1)(m+2)) (S(S+1) - m(m+1)) \{m \leq 1/2\}]$$

The resonance frequency is then determined by

$$\hbar\omega = E_m - E_{m-1} = G + g\mu_B D \frac{1}{2} (3\cos^2\theta - 1) (2m-1) +$$

$$E_m^2 - E_{m-1}^2 - E_m^3 + E_{m-1}^3$$

The first moment of the frequency at fixed magnetic field is¹³⁷

$$\langle \omega \rangle = \hbar^{-1} \left[\sum_{m=-S}^{S-1} C_m (E_m - E_{m-1}) \right] / \left\{ \sum_{m=-S}^{S-1} C_m \right\} .$$

The first moment calculation for the resonance field at fixed frequency is

$$g\mu_B \langle H \rangle = \left\{ \sum_{m=-S}^{S-1} C_m \right\}^{-1} \left\{ \sum_{m=-S}^{S-1} C_m (\hbar\omega - g\mu_B D \frac{1}{2} (3\cos^2\theta - 1)(2m-1) + E_m^2 - E_{m-1}^2 + E_m^3 - E_{m-1}^3) \right\} ,$$

where

$$C_m = |\langle m | S_x | m-1 \rangle|^2 (\exp(-E_{m-1}/kT) - \exp(-E_m/kT)) ,$$

$$E_m = \hbar\omega m - \frac{1}{2} g\mu_B D (3\cos^2\theta - 1) \{m(m-1) + 35/12\} +$$

$$(m-1)E_m^2 - mE_{m-1}^2 + (m-1)E_m^3 - mE_{m-1}^3 \} ,$$

$$E_{m-1} = E_m - \hbar\omega .$$

It should be noted that the first moments of H and ω are not related by any simple equation due to the nonlinear dependence of the energy on magnetic field.

The calculator program which computes a value of g and D from the data (H_{res} , T , θ , and ω) follows. The program is designed for a Hewlett-Packard model 9825A calculator and uses a least squares search routine ("Curfit") given originally in FORTRAN.⁸⁷

Program to compute g and D from the angular variation of the resonance field at constant temperature using a least squares fit.


```

0: "Curfit Hres vs. Theta at const. T for g,D + sigmas;file9"
1: ent "Number of data pairs",N,"Number of parameters",M
2: enp "Temp",T,"Freq. in GHz",Q;6.6254e-18*Q+Q;spc
3: dim A[M],B[M],C[M],D[M],F[N],G[M,M],H[M]
4: dim I[M],J[M,M],L[N],S[N],W[N],X[N],Y[N]
5: dim AS[3]
6: enp "Sigma Hres",S;ina S:S;spc
7: prt "Theta i","Hres i";spc ;fxd 2
8: for I=1 to N
9: ent "Theta",X[I],"H res",Y[I]
10: prt X[I],Y[I]
11: spc
12: next I
13: spc
14: prt "Initial parameters";spc
15: enp "D/100=",A[1],"g=",A[2];spc 2
16: prt "Reduced Chi squared:"
17: spc ;smpy .01A+D
18: .001+F;c11 'Curfit'
19: fxd 4;C+A;prt A
20: "Loopstart":c11 'Curfit'
21: if (C-A)/A<=.01;gto "Done"
22: fxd 4;C+A;prt A
23: gto "Loopstart"
24: "Done":
25: fxd 4;prt C;spc
26: fxd 2;prt "Best D",100A[1];prt "Sigma",100C[1];spc
27: fxd 4;prt "Best g",A[2];prt "Sigma",C[2];spc 2
28: end
29: "Curfit":
30: N-M+P;if P<=0;0+C;ret
31: ina W:1,H,G,L:1
32: ara S*S+W;ara L/W+W
33: for I=1 to N
34: c11 'Fderiv'
35: for J=1 to M
36: H[J]+W[I]*(Y[I]-'Functn'(I))*I[J]+H[J]
37: for K=1 to J
38: G[J,K]+W[I]*I[J]*I[K]+G[J,K]
39: next K
40: next J
41: next I
42: for J=1 to M;for K=1 to J;G[J,K]+G[K,J];next K;next J
43: for I=1 to N
44: 'Functn'(I)+F[I];next I
45: 'Fchisq'+D

```

```

46: "71":for J=1 to M
47: for K=1 to M
48: G[J,K]/√(G[J,J]G[K,K])→J[J,K]
49: next K
50: l+F→J[J,J]
51: next J
52: inv J→J
53: for J=1 to M
54: A[J]→B[J]
55: for K=1 to M
56: B[J]+H[K]*J[J,K]/√(G[J,J]G[K,K])→B[J]
57: next K
58: next J
59: for I=1 to N
60: 'Functn'(I)→F[I];next I
61: 'Fchisq'→C
62: if D<C;l0F→F;gto "71"
63: for J=1 to M
64: B[J]→A[J]
65: √(J[J,J]/G[J,J])→C[J]
66: next J
67: .lF→F
68: ret
69: "Fderiv":
70: for J=1 to M
71: A[J]→X;D[J]→Z;X+Z→A[J]
72: 'Functn'(I)→Y
73: X-Z→A[J]
74: (Y-'Functn'(I))/2Z→I[J]
75: X→A[J]
76: next J
77: ret
78: "Fchisq":
79: 0→C
80: for I=1 to N
81: C+W[I]*(Y[I]-F[I])^2→C
82: next I
83: ret C/P
84: "Functn":0→p25;-1.5→p4;9.2741e-21*A[2]→p8;100*p8*A[1]→p7
85: 1.38e-16*T→p9;.5(3cos(X[p1])^2-1)→p5
86: -p4*Q+p7p5(p4(p4-1)+35/12)→p10
87: (.25(exp((p10+Q)/p9)-exp(p10/p9))(8.75-p4(p4-1))→p13)
    +p12→p12
88: p13(Q-p7p5(2p4-1))+p11→p11
89: if 2.5>p4;l+p4→p4;gto -3
90: p11/p12→p25
91: -1.5→p4;0→p11→p12
92: sfg 3
93: -(2p4+1)^2(8.75-p4(p4+1))(p4<=1.5)→p19
94: p19+(2p4-1)^2(8.75-p4(p4-1))(-1.5<=p4)→p19
95: (8.75-(p4-2)(p4-1))(8.75-p4(p4-1))(-.5<=p4)→p18
96: p18-(8.75-(p4+1)(p4+2))(8.75-p4(p4+1))(p4<=.5)→p18

```

```

97: if flg3;p19(p7cos(X[p1])sin(X[p1]))^2/4p25+p14;
    p4-1→p4
98: if flg3;p18(p7sin(X[p1])^2)^2/32p25+p16;cfg 3;gto -5
99: p19(p7cos(X[p1])sin(X[p1]))^2/4p25+p15
100: p18(p7sin(X[p1])^2)^2/32p25+p17;1+p4→p4
101: p4*Q-p7p5(p4(p4-1)+35/12)-(p4-1)(p14+p16)+p4(p15+p17)
    +p10
102: (.25(exp((-p10+Q)/p9)-exp(-p10/p9))(8.75-p4(p4-1))
    +p13)+p12+p12
103: p13(Q-p7p5(2p4-1)-p14+p15-p16+p17)+p11→p11
104: if 2.5>p4;p4+1→p4;gto -12
105: p11/p12p8+p20
106: ret p20
107: end

```

Appendix B: Equations of Motion of the Transverse Magnetization in the Presence of Fine-Structure

The equations II-51 and 52 hold for temperatures such that $kT \gg \hbar \omega_{S_z}$, where $\hbar \omega_{S_z} = E_{S_z+1} - E_{S_z}$, and E_{S_z} is the bare Zeeman plus fine structure energy of the localized spin level characterized by S_z .

The transverse magnetization associated with the transition $S_z \leftrightarrow S_z+1$ is $M_{S_z}^+ = \chi_{S_z}^+ (\omega_0) h_{rf}^+$ and the total magnetization is $M_e^+ + \sum_{S_z=-S}^{S-1} M_{S_z}^+$, where h_{rf}^+ is the microwave field in the x-y plane.

The following equations define the remaining parameters in equations II-51 and II-52:

$$\begin{aligned}\lambda &= J/g_e g_s \mu_B^2 \\ \omega_e &= g_e \mu_B H/\hbar \\ \omega_s &= g_s \mu_B H/\hbar\end{aligned}$$

where g_e and g_s are the gyromagnetic ratios of the conduction electron and localized electron spins, respectively;

$$\begin{aligned}\chi_e &= \chi_e^0 \left[1 + \sum_{S_z=-S}^{S-1} (\omega_{S_z}/\omega_s) \chi_{S_z}^0 \right] C^{-1} \\ \chi_{S_z} &= \chi_{S_z}^0 \left[(\omega_{S_z}/\omega_s) - \lambda^2 \chi_e^0 (\omega_{S_z}/\omega_s) \sum_{S_z'=-S}^{S-1} \chi_{S_z'}^0 + \lambda^2 \chi_e^0 \sum_{S_z'=-S}^{S-1} \left(\frac{\omega_{S_z}}{\omega_s} \right) \chi_{S_z'}^0 \right. \\ &\quad \left. + \lambda \chi_e^0 \right] C^{-1} \\ C &= 1 - \lambda^2 \chi_e^0 \sum_{S_z=-S}^{S-1} \chi_{S_z}^0\end{aligned}$$

$$\chi_e^o = 1/2 (g_e \mu)^2 c$$

$$\chi_{S_z}^o = [S(S+1) - S_z(S_z+1)] \frac{c(g_s \mu_B)^2}{2} \frac{n_{S_z+1} - n_{S_z}}{\hbar \omega_{S_z}}$$

$$n_{S_z} = (e^{-E_{S_z}/kT}) / Z_S$$

$$Z_S = \sum_{S_z=-S}^S e^{-E_{S_z}/kT}$$

where ρ is the atomic density of states for conduction electrons for one spin direction evaluated at the Fermi energy and c is the atomic fraction of impurities. The relaxation rates in Eqns. II-51 and II-52 are

$$1/T_{S_z e} = 2\pi(\rho J)^2 [kT - (S_z + 1/2)\omega_s]$$

$$1/T_{S_z}^{S_z \pm 1} = 2\pi[S(S+1) - S_z(S_z+1)](\rho J)^2 (kT \mp 1/2 \omega_s)$$

$$1/T_{e S_z} = \pi c \rho J^2 \{ (n_{S_z+1} + n_{S_z}) S(S+1) + n_{S_z+1} (S_z+1)(S_z+2) + n_{S_z} S_z(S_z-1) \}$$

$$1/T_e^{S_z} = 2\pi c \rho J^2 S_z [S(S+1) - S_z^2]$$

$$1/T_{es} = \left\{ \sum_{S_z=-S}^{S-1} 1/T_{e S_z} \right\} + 1/T_e^S - 1/T_e^{-S}$$

An equivalent set of equations to II-51 and II-52 can be written in collapsed form⁵⁴ as a set of coupled linear equations of dimension $2S+1$, as

$$(M - \omega_0) \chi = \eta$$

where χ and η are column vectors. The full expression can be found in reference (9), with the full response of the system described by

$$\chi^{+-}(\omega_0) = \sum_{S_z=-S}^{S-1} \chi_{S_z}^{+-}(\omega_0) + \chi_e^{+-}(\omega_0)$$

where the individual $\chi_{S_z}^{+-}$ and χ_e^{+-} are found from the solutions to the matrix equation.

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