KLEINHANS, Frederick William, 1943-
ELECTRON PARAMAGNETIC RESONANCE IN Mg-Mn.

The Ohio State University, Ph.D., 1971
Physics, solid state

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1971

ELECTRON PARAMAGNETIC RESONANCE IN 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

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* * * * *

The Ohio State University
1971

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ACKNOWLEDGEMENTS

I particularly want to thank my adviser, Professor Philip E. Wigen, whose boundless energy and enthusiasm has been a constant source of help and encouragement during this research. Many others have also given greatly appreciated help. Among them are Dale Zych, with whom I had several fruitful discussions concerning magnesium, Art Gossard of Bell Labs, and Albert Narath at Sandia. Ken Brog and Bill Jones, Jr. at Battelle Memorial Institute generously made facilities available for some initial work on alloys and have continued to be of assistance. During their summer NSF-URP programs, Mark Randles and Jim Long helped with setting up the equipment and taking data; and David Curry, at Denison University, provided the computer generated theoretical curves used in Figures 2 and 16. Mrs. Betty Watts cheerfully translated my scrawl into a typed draft for which I am deeply grateful, and my wife, Carroll, helped with numerous revisions and other tasks. Mrs. Cecelia Lombard quickly and efficiently typed the final draft. The support of a Battelle Memorial Institute Fellowship during the years 1968 to 1970 is gratefully acknowledged. This work was also supported in part by the National Science Foundation.

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PUBLICATIONS

"Logarithmic g Shift of Cobalt Paramagnetic Resonance in Molybdenum and Tungsten Host", P. E. Wigen, F. W. Kleinhans, M. H. Randles, K. C. Brog, and W. H. Jones, Jr., Bull. Amer. Phys. Soc. 14, 313 (1969).

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I. INTRODUCTION

Electron paramagnetic resonance (EPR)¹ observations of dilute magnetic alloys are of interest because of widespread theoretical and experimental activity directed toward a better understanding of s-d exchange interactions and local moments.^{2,3} Many interesting effects are associated with these phenomena, such as the Kondo effect, specific heat anomalies, and susceptibility anomalies. It is expected that a better understanding of isolated magnetic ions in a metallic environment will lead to a better quantitative understanding of magnetism in general.

EPR observations of transition metal ions dissolved in nonmagnetic host metals were first reported in 1956,^{4,5} 11 years after the observation of such resonances in insulators. Several factors were responsible for this delay. Resonance lines in metals and alloys are generally much broader than those in insulators and because the penetration depth of microwaves is very small in any

-
1. Some investigators prefer the term electron spin resonance (ESR).
 2. Alloys up to 50% solute have been investigated but "dilute" is generally accepted to mean less than 1 atomic percent, and sometimes much less.
 3. An excellent general review of dilute magnetic alloys by Heeger which includes a discussion of both EPR and NMR appears in Solid State Physics Vol. 23, (F. Seitz, D. Turnbull, and H. Ehrenreich, ed.) Academic Press, New York, 1969.
 4. J. Owen, M. Browne, W.D. Knight, and C. Kittel, Phys. Rev. **102**, 1501, (1956).
 5. J. Owen, M.E. Browne, V. Arp, and A.F. Kip, J. Phys. Chem. Solids **2**, 85, (1957).

good conductor it is not possible to use "large" samples. EPR has also been observed in alloys containing rare earth solutes, e.g. Gd^{+++} . This paper will primarily be concerned with alloys containing 3d transition series metals, but much of what is said also applies to rare earth alloys.

The early data for Cu-Mn⁶ of Owen, Browne, Arp, Kip, Knight, and Kittel (hereafter referred to as Owen et al.) are typical of microwave resonance in dilute alloys with 3d transition metal solutes. Briefly, they obtained the following results. J_{sd} , the exchange integral, was calculated using measurements of the shift of the resonance field position from the Mn^{++} free ion value (g shift). Their result was unexpectedly small and was subsequently found to be in error because of a then unknown "bottleneck" in the relaxation process. It was thought that the local moment relaxation rate was given simply by δ_{ds} , the local moment to conduction electron relaxation rate (because the S state local moments relax primarily via the conduction electrons which were believed to be in thermal equilibrium with the lattice). A relaxation bottleneck occurs when the conduction electrons relax too slowly to remain in equilibrium with the lattice, leading to a more complex relaxation process for the local moments which suppress the g shifts. Owen et al. also observed a rapid shift of the resonance field to lower

6. A small amount of EPR data was also obtained for Ag-Mn and Mg-Mn.

values as the temperature was decreased below a "critical" temperature. This was interpreted as a form of antiferromagnetic resonance (AFMR). The experimental results were reasonably well explained using the AFMR equations of Keffer and Kittel⁷ which were developed for insulators. However, they were unable to fully explain the sources of the exchange field $\vec{H}_E$ and the anisotropy field $\vec{H}_A$ necessary for AFMR. They were also unable to explain the lack of hyperfine structure in the spectra. Such structure would be expected because of the nonzero manganese nuclear moment.

The key to many of these difficulties was found by Hasegawa⁸ (1959) who recognized the possible existence of a bottleneck in the relaxation process and calculated what is still essentially the correct relaxation theory for dilute alloys in the paramagnetic region. His result explains the anomalously low g shifts and therefore the small J values obtained by Owen et al. It also predicts the interesting result that the linewidth should decrease as the paramagnetic impurity concentration is increased contrary to what might be expected. This last prediction was fully verified in 1967 by Gossard et al. with additional measurements on Cu-Mn⁹ and Ag-Mn.¹⁰ About this same time several investigators^{11,12} refined

7. F. Keffer and C. Kittel, Phys. Rev. 85, 329, (1952).
8. H. Hasegawa, Progr. Theoret. Phys. (Kyoto) 21, 483, (1959).
9. A.C. Gossard, A.J. Heeger, and J.H. Wernick, J. Appl. Phys. 38, 1251, (1967).
10. A.C. Gossard, T.Y. Kometani, and J.H. Wernick, J. Appl. Phys. 39, 849, (1968).
11. H. Cottet, P. Donzé, J. Dupraz, B. Giovannini, and M. Peter, Z. Angew. Phys. 24, 249, (1968).
12. D. Davidov and D. Shaltiel, Phys. Rev. Letters 21, 1752, (1968).

and extended Hasegawa's theory and explained the lack of hyperfine structure in bottlenecked systems.¹³ A complete treatment encompassing all of the previous results has recently been published by Dupraz et al.¹⁴ EPR investigations in bottlenecked systems provide information about relaxation processes occurring in dilute alloys and, in particular, can be used to measure spin-orbit induced spin-flip scattering of conduction electrons by impurities.^{9,10,15}

The resonance in the AFM region is not as well understood. No adequate theory for the linewidth exists and the source of the anisotropy field $\vec{H}_A$ is not clearly resolved yet. However, long range indirect exchange coupling via the conduction electron polarization (RKKY interaction) appears to be a reasonable source of the exchange field $\vec{H}_E$ necessary for alignment of the widely separated manganese local moments into antiparallel sublattices. Okuda and Date¹⁶ (1969) have suggested that the alignment of the nuclear magnetization by the manganese sublattices may be one source of $\vec{H}_A$ and have performed combined EPR-NMR experiments (ENDOR) in Ag-Mn which support their contention.

-
- 13. D.C. Langreth, D.L. Cowan, and J.W. Wilkins, Solid State Commun. 6, 131, (1968).
 - 14. J. Dupraz, B. Giovannini, R. Orbach, J.D. Riley, and J. Zitkova in Magnetic Resonance: Proceedings of the International Symposium on Electron and Nuclear Magnetic Resonance, Melbourne, 1969; Eds. C.K. Coogan, N.S. Ham, S.N. Stuart, J.R. Pilbrow, G.V.H. Wilson, Plenum Press, New York, 1970.
 - 15. Y. Yafet, J. Appl. Phys. 42, 1564, (1971).
 - 16. K. Okuda and M. Date, J. Phys. Soc. Japan 27, 839, (1969).

The system reported herein is Mg-Mn. Early resistivity^{17,18,19} and specific heat²⁰ data indicate manganese forms a local moment in magnesium. EPR was first detected in Mg-Mn by Owen et al. who investigated Mg-Mn(0.24%)^{21,22} and obtained susceptibility and EPR data similar to their results for Cu-Mn. Then in 1962 Collings and Hedgcock²³ reported on the susceptibility of several dilute Mg-Mn alloys and obtained detailed EPR data for Mg-Mn(0.38%).²⁴ Because EPR results are available at only one frequency and for two alloys of similar composition, it was decided that a more extensive EPR investigation of this alloy system was needed. In particular, measurements at more than one manganese concentration are necessary to extract information about the various relaxation processes occurring. To investigate the onset of antiferromagnetism, information is needed at both different manganese concentrations and different frequencies. This work reports the results of microwave resonance measurements on Mg-Mn alloys with Mn concentrations of

-
17. J.G. Thomas and E. Mendoza, *Phil. Mag.* 43, 900, (1952).
 18. F.T. Hedgcock, W.B. Muir, and E. Wallingford, *Can. J. Phys.* 38, 376, (1960).
 19. G. Gaudet, F.T. Hedgcock, G. Lamarche, and E.W. Wallingford, *Can. J. Phys.* 38, 1134, (1960).
 20. D.L. Martin, *Can. J. Phys.* 39, 1385, (1961).
 21. Adjusted value of the concentration. They quote $C_I = 0.67\%$. See section III-B-3.
 22. The notation X-Y(z%) will always mean z atomic percent of solute Y dissolved in solvent X.
 23. E.W. Collings and F.T. Hedgcock, *Phys. Rev.* 126, 1654, (1962).
 24. Adjusted value of the concentration. They quote $C_I = 0.59\%$. See section III-B-3.

0.49, 0.11, and 0.02 atomic percent at frequencies of 9.4 and 23.5 GHz and at temperatures as low as 2.1 K. The results are of particular interest, because heretofore extensive EPR data has only been available for manganese in cubic alloys and not for hexagonal systems.²⁵

The discussion will proceed along the following lines. Chapter II briefly reviews the magnetic properties of dilute alloys and then develops the theory of microwave resonance in such alloys for both the paramagnetic and the antiferromagnetic state. The theory of g shifts, the effect of the bottleneck, and the sources of exchange and anisotropy fields are considered in detail. In Chapter III the physical and metallurgical properties of the alloys used in this investigation are considered. Particular attention is devoted to the problem of determining the true manganese solid solution concentration and in establishing that the second phase material present does not contribute to the resonance. A discussion of experimental procedure appears in Chapter IV and the results with discussion are presented in Chapter V.

25. The only other hexagonal host in which Mn^{++} has been observed is Zn-Mn [E.W. Collings, F.T. Hedgcock, and W.B. Muir, LT-8: Proceed. Eighth Intern. Conf. Low Temp. Phys., London, 1962, R.O. Davies ed., Butterworths, Washington, 1963]. Data was obtained at X band in Zn-Mn (0.4%).

II. THEORY OF MICROWAVE RESONANCE IN DILUTE MAGNETIC ALLOYS

A. Magnetic Properties of Dilute Alloys

Electron paramagnetic resonance experiments involve transitions between the energy levels of well defined magnetic moments. Theoretically, it is a difficult problem to establish whether or not an ion such as Mn^{++} , Fe^{++} , or Co^{++} has a well defined magnetic moment (local moment) when dissolved in a metallic host.

The 3d electrons in transition series metals are known to have partially itinerant character because the d levels lie within the conduction band. Nevertheless, Friedel and his associates,²⁶ using the concept of "virtual bound states", were able to theoretically demonstrate the existence of electronic states localized in the vicinity of an impurity which are magnetic under the right conditions. They, and later Anderson,²⁷ found using a Hartree-Fock treatment that a magnetic state will exist if the intra-atomic coulomb interaction integral U is sufficiently large and the width of the d levels Δ is sufficiently narrow, i.e. $U/\pi\Delta > 1$. Within this scheme, alloys such as Au-Fe, Cu-Mn, and Mg-Mn are magnetic while others such as Al-Mn and Zn-Fe are nonmagnetic. Rare earth solutes also form local moments, which is not surprising because the rare earth 4f states are highly localized.

26. Metallic Solid Solution, (J. Friedel and A. Guinier, eds.) Benjamin, New York, 1963.

27. P.W. Anderson, Phys. Rev. 124, 41, (1961).

Traditionally, a system is magnetic if the local moments can be macroscopically detected by their temperature dependent contribution to the static magnetic susceptibility

$$\chi = \chi_p + \chi_{dia} + \chi_d(T) \quad (II.1)$$

where χ_p is the Pauli susceptibility of the conduction electrons, χ_{dia} is the diamagnetic term, and χ_d is the temperature dependent, local moment, paramagnetic contribution. The simplest form of χ_d is $\chi_d = C/T$; the usual Curie law behavior for the susceptibility of magnetic moments in a field H at temperature T and obeying Boltzmann statistics.²⁸ The Curie constant C can be theoretically calculated and has the value²⁹

$$C = \frac{Ng^2\beta^2J(J+1)}{3k} \quad (II.2)$$

where N is the number of magnetic ions per unit volume, g is the spectroscopic splitting factor of the magnetic moments ($g = 2$ for free electrons), β is the Bohr magneton $e\hbar/2mc$, k is Boltzmann's constant, and J is the total angular momentum of the local moment. For 3d local moments $J \sim S$ because crystalline field effects quench the orbital angular momentum.

It has been possible to explain a large number of interesting phenomena in dilute magnetic alloys, such as resistivity minima

28. The actual behavior is often of the more complicated Curie-Weiss form $\chi_d = C/(T-\theta)$ where the Curie-Weiss constant θ may be positive or negative.

29. C. Kittel, Introduction to Solid State Physics, 3rd ed.; Wiley, New York, 1966.

(the Kondo effect),³⁰ specific heat anomalies,³¹ and EPR g shifts,³² using the concept of local moments interacting with the conduction electrons via an exchange interaction. These interactions are referred to as s-d and s-f exchange interactions for local moments resulting from 3d and 4f (rare earth) electrons, respectively. They have been found to produce a spatially oscillating polarization of the electron gas around a local moment (RKKY polarization) which is discussed further in the section on exchange fields.

Recently the distinction between local moments and "non" moments has become blurred. According to the theory of spin fluctuations, the important factor determining local moment character is the average lifetime of these spin fluctuations (local moments).^{3,33,34} A local moment will be observed whenever the fluctuation time τ_{sf} is longer than the time scale of the experimental probe used. For instance, based on static magnetic susceptibility measurements, Au-V is a local moment system and Al-Mn is not. On the other hand, nuclear magnetic resonance (NMR) investigations detect no "essential" magnetic difference between the two.³⁵ In the spin fluctuation theory this is interpreted to mean that Au-V must have very low

-
- 30. J. Kondo, Progr. Theoret. Phys. (Kyoto) 32, 37, (1964).
J. Kondo in Solid State Physics Vol. 23 (F. Seitz, D. Turnbull, and H. Ehrenreich, eds.) Academic Press, New York, 1969.
 - 31. J. Kondo, Progr. Theoret. Phys. (Kyoto) 33, 575, (1965).
 - 32. K. Yosida, Phys. Rev. 106, 893, (1957).
 - 33. M. Levine and H. Suhl, Phys. Rev. 171, 567, (1968).
 - 34. N. Rivier and M. J. Zuckermann, Phys. Rev. Letters 21, 904, (1968).
 - 35. A. Narath and H. T. Weaver, Phys. Rev. Letters 23, 233, (1969).

spin fluctuation frequency $1/\tau_{sf}$ while Al-Mn has a higher $1/\tau_{sf}$ intermediate between zero and the NMR frequencies.

B. Paramagnetic Resonance Theory

EPR investigations of local moments have by and large been restricted to S state ions (Mn^{++} , Gd^{+++} , Eu^{++}) because of the severe line broadening associated with spin-orbit coupling in ions with $L \neq 0$. The magnetic ion can be added substitutionally to a pure metal (e.g. Cu, Ag, Au, Mg, Pd, Y), to an intermetallic compound (e.g. $LaNi_5$, YAl_2 , Pd_3U), or it may be one of the constituents of an intermetallic compound (e.g. $EuAl_2$, $GdAl_2$, $GdPt_2$).³⁶ It is generally found that the previously mentioned relaxation bottleneck is weak or absent for rare earth solutes, and it is therefore possible to calculate J_{sf} from g shifts in such alloys. This paper will concentrate on transition series alloys, which are generally bottlenecked. Recently the method of transmission electron spin resonance (TESR) has been used to investigate dilute magnetic alloys and has much in common with the theory discussed here.³⁷ Table 1 contains a comprehensive list of EPR, CESR, and TESR experimental papers applicable to metals.

36. The term alloy will be used loosely to apply to all of these cases, unless otherwise indicated.

37. S. Schultz, M.R. Shanabarger, and P.M. Platzman, Phys. Rev. Letters 19, 749, (1967).

TABLE 1

Experimental Papers

Listed below in chronological order are papers reporting the results of EPR, CESR, TESR, and AFMR investigations in metals and alloys. In each case the materials investigated are also listed. Round brackets indicate a material which was investigated but in which no resonance was seen.

T. W. Griswold, A. F. Kip, and C. Kittel, Phys. Rev. 88, 951 (1952), [CESR: Na].

A. F. Kip, C. Kittel, and A. M. Portis, Phys. Rev. 89, 518 (1953), [EPR: Gd].

A. F. Kip, Rev. Mod. Phys. 25, 229 (1953), [EPR: Gd].

G. Feher and A. F. Kip, Phys. Rev. 98, 337 (1955), [CESR: Li, Na, Be, (Mg, Al, Pd, W)].

J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids 2, 85 (1957), [EPR-AFMR: Cu-Mn, Ag-Mn, Mg-Mn].

M. Peter, Phys. Rev. 113, 801 (1959), [EPR: GdAl_2].

M. Peter and B. T. Matthias, Phys. Rev. Letters 4, 449 (1960), [EPR: Eu, GdIr_2 , (EuIr_2)].

V. Jaccarino, B. T. Matthias, M. Peter, H. Suhl, and J. H. Wernick, Phys. Rev. Letters 5, 251 (1960), [EPR: EuAl_2 , GdAl_2].

M. Peter, J. Appl. Phys. 32, 338S (1961), [EPR: GdAl_2 , EuAl_2 , EuMg_2 , and with added 4f impurities].

E. W. Collings, F. T. Hedgcock, and T. Sakudo, Can. J. Phys. 39, 1233 (1961), [EPR: (Au-Fe, Cu-Fe, Cu-Co)].

M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. 126, 1395 (1962), [EPR: GdAl_2 , LaAl_2 -Gd, Rh-Gd, Pd-Gd, Ag-Gd, Ag-Cd-Gd, Rh-Pd-Gd, Pd-Ag-Gd, (Au-Gd, Pt-Gd, Ir-Gd)].

E. W. Collings and F. T. Hedgcock, Phys. Rev. 126, 1654 (1962), [EPR-AFMR: Mg-Mn, (Al-Mn, Mg-Fe, Al-Fe)].

Table 1 (continued)

M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. Letters 9, 50 (1962), [EPR: Pd-Gd, and with added 4f impurities].

M. Peter in Metallic Solid Solution, J. Friedel and A. Guinier eds., Benjamin, New York, 1963, [EPR: Pd-Gd, and with added 4f impurities].

E. W. Collings, F. T. Hedgcock, and W. B. Muir, in LT8: Proceed. Eighth Int. Conf. Low Temp. Phys., London 1962, R. O. Davies ed., Butterworths, Washington, 1963, [EPR: Zn-Mn].

D. Shaltiel, J. H. Wernick, and H. J. Williams, Phys. Rev. 135, A1346 (1964), [EPR: Pd-Gd, and with added 3d and 4f impurities, UPd_3 -Gd and U-Pd-Gd, AB_5 -Gd where A = 4f or 5f and B = 3d or 4d].

D. Shaltiel and J. H. Wernick, Phys. Rev. 136, A245 (1964), [EPR: Au-Mn, Cu-Mn, Ag-Mn, Pd-Mn, and with 3d and 4f added impurities].

D. Shaltiel, J. H. Wernick, and V. Jaccarino, J. Appl. Phys. 35, 978 (1964), [EPR: AB_2 -Gd where A = 4f and B = 4d or 5d].

D. Shaltiel, A. C. Gossard, and J. H. Wernick, Phys. Rev. 137, A1027 (1965), [EPR: $La_{1-x}Th_xRu_2$ -Gd].

S. Schultz and C. Latham, Phys. Rev. Letters 15, 148 (1965), [TESR: Cu].

A. M. Harris, J. Popplewell, and R. S. Tebble, Proc. Phys. Soc. 85, 513 (1965), [EPR: Gd-Y, Gd-Lu, Gd-Pd].

R. G. Goodrich and G. E. Everett, Phys. Rev. 141, 541 (1966), [EPR: Ce].

S. Geschwind, G. E. Devlin, and J. H. Wernick, J. Appl. Phys. 37, 1221 (1966), [EPR: Cu-Mn].

D. M. S. Bagguley and J. Liesegang, J. Appl. Phys. 37, 1220 (1966), [Dy, Ho, Er].

R. G. Barnes, D. A. Cornell, and D. R. Torgeson, Phys. Rev. Letters 16, 233 (1966), [FMR: See A. C. Gossard and J. H. Wernick, Phys. Rev. Letters 16, 995 (1966)].

J. R. Asik, M. A. Ball, and C. P. Slichter, Phys. Rev. Letters 16, 740 (1966), [CESR: Li, Na, and with added impurities].

D. Griffiths and B. R. Coles, Phys. Rev. Letters 16, 1093 (1966), [EPR: Ag-Er].

Table 1 (continued)

- R. B. Lewis, G. C. Alexandrakis, and T. R. Carver, Phys. Rev. Letters 17, 854 (1966), [TESR: Gd].
- A. M. Harris, J. Popplewell, and R. S. Tebble, Proc. Phys. Soc. (London) 88, 679 (1966), [EPR-AFMR: Gd in Lu, Y, Sc, and La].
- D. Griffiths, Proc. Phys. Soc. (London) 90, 707 (1967), [EPR: Cu-Mn].
- S. Schultz and G. Dunifer, Phys. Rev. Letters 18, 283 (1967), [TESR: Na, K].
- M. Peter, J. Dupraz, and H. Cottet, Helv. Phys. Acta 40, 301 (1967), [EPR: Review article].
- A. Nakamura and N. Kinoshita, J. Phys. Soc. Japan 22, 335 (1967), [EPR-AFMR: Cu-Mn].
- A. Nakamura and N. Kinoshita, J. Phys. Soc. Japan 22, 449 (1967), [EPR: Cu-Mn].
- J. H. Wernick, H. J. Williams, and A. C. Gossard, J. Phys. Chem. Solids 28, 271 (1967), [EPR-AFMR: EuAl_4].
- A. C. Gossard, A. J. Heeger, and J. H. Wernick, J. Appl. Phys. 38, 1251 (1967), [EPR: Cu-Mn, and with added 3d impurities].
- D. L. Cowan, Phys. Rev. Letters 18, 770 (1967), [TESR: Cu-Mn].
- S. Schultz, M. R. Shanabarger, and P. M. Platzman, Phys. Rev. Letters 19, 749 (1967), [TESR: Cu-Mn, Ag-Mn, Ag].
- C. R. Burr and R. Orbach, Phys. Rev. Letters 19, 1133 (1967), [EPR: Mg-Er].
- C. E. W. Hahn and J. E. Enderby, Proc. Phys. Soc. 92, 418 (1967), [CESR: Li with added impurities].
- K. Okuda and M. Date, J. Phys. Soc. Japan 22, 1512 (1967), [EPR-AFMR: Cu-Mn with added Ni or Al].
- R. Dupree, C. T. Forwood, and M. J. A. Smith, Phys. Status Solidi 24, 525 (1967), [CESR: Au].
- A. C. Gossard, T. Y. Kometani, and J. H. Wernick, J. Appl. Phys. 39, 849 (1968), [EPR: Ag-Mn, and with added impurities].

Table 1 (continued)

- L. L. Hirst, G. Williams, D. Griffiths, and B. R. Coles, J. Appl. Phys. 39, 844 (1968), [EPR: Ag-Ge, Ag-Er, Au-Er, Au-Yb, (several rare earth solutes)].
- J. A. McElroy and A. J. Heeger, Phys. Rev. Letters 20, 1481 (1968), [EPR: Cu-Mn with added Si or Al].
- H. Cottet, P. Donzé, J. Dupraz, B. Giovannini, and M. Peter, Z. Angew. Phys. 24, 249 (1968), [EPR: LaRu_2 -Gd].
- P. Monod and S. Schultz, Phys. Rev. 173, 645 (1968), [TESR: Cu-Cr].
- D. Davidov and D. Shaltiel, Phys. Rev. Letters 21, 1752 (1968), [EPR: LaNi_5 -Gd].
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1. Original Molecular Field Theory of g Shifts

The original molecular field theory approach of Owen et al.⁵ as discussed by Hasegawa⁸ is briefly considered here, and demonstrates how the exchange integral may be determined from measurements of g shifts. Several subtleties are left to the next section. The treatment will be in terms of $\delta H/H$ which is equivalent to discussing g shifts because

$$\delta H/H = -\delta g/g. \quad (\text{II.3})$$

The shift δg is defined as $\delta g = g_a - g$ where g_a is the measured "g" value in the alloy and g is the measured value in an insulator. δH and H are similarly defined. Equation (II.3) follows immediately from the resonance relation $\hbar\omega = g\beta H$. The shift δH is the result of internal fields acting on the local moments in addition to the applied field.³⁸

Owen et al. calculated a first and second order shift as follows. The polarization of the conduction electrons by the applied field $\vec{H}_a$ is given by

$$\vec{M}_s = \chi_p \vec{H}_a \quad (\text{II.4})$$

where $\vec{M}_s$ is the magnetization of the conduction electrons and χ_p is the Pauli paramagnetic susceptibility (including diamagnetic corrections).

38. Crystalline electric field effects are not considered here. Their importance is diminished in metals by the shielding effect of the conduction electrons.

$$\chi_p = 2 \beta^2 \eta(E_f) \quad (II.5)$$

in the free electron model where $\eta(E_f) = 3n/4E_f$ is the density of states per unit volume of one spin direction at the Fermi surface, n is the number of conduction electrons per unit volume, and E_f is the Fermi energy. Then the effective internal field acting on the local moments is

$$\vec{H}_d = \lambda \vec{M}_s. \quad (II.6)$$

The molecular field constant λ can be expressed in terms of the zero-Fourier component $J(o)$ of the s-d exchange integral as

$$\lambda = J(o)/g^2 \beta^2 N_o \quad (II.7)$$

with N_o being the number of atoms per unit volume.^{39,40} $J(o)$ is related to the s-d Hamiltonian by

$$H_{sd}^o = -J(o) \vec{S} \cdot \vec{s}$$

where $\vec{S}$ is the local moment spin and $\vec{s}$ is the conduction electron spin. $J(o)$ is assumed temperature independent. Using equations (II.4-II.7), $\vec{H}_d$ can be obtained in terms of $J(o)$:

$$\vec{H}_d = \frac{3nJ(o)\vec{H}_a}{2N_o g^2 E_f}. \quad (II.8)$$

39. These definitions of N_o and N are opposite to those used by Hasegawa.

40. Theoretical papers generally use the term $2J(o)$ in place of our $J(o)$.

The true resonance field will be

$$\vec{H} = \vec{H}_a + \vec{H}_d ,$$

and with

$$\delta\vec{H} = \vec{H}_a - \vec{H}$$

we have

$$\vec{H}_d = - \delta\vec{H} .$$

The internal field $\vec{H}_d$ will be effective in producing a shift $-\delta\vec{H}$ only if the relaxation rate of the conduction electrons to the lattice δ_{sL} is fast enough to maintain $\vec{H}_d$ along the direction of $\vec{H}_a$ under the dynamic conditions of an EPR experiment. This is the assumption made by Owen et al. and leads to the first order shift⁴¹

$$\frac{-\delta H^{(1)}}{H} = \lambda\chi_p = \frac{3nJ(o)}{2N_0g^2E_f} \quad (II.9)$$

where $H_a \cong H$ for small shifts. This shift is analogous to the Knight shift in NMR and is sometimes referred to as an electronic Knight shift. In the literature (II.9) is often written in the form

$$\delta g_o = \lambda\chi_p g = 3nJ(o)/2N_0gE_f . \quad (II.10)$$

Note that for a negative s-d interaction (J negative), the g shift is negative. The assumption of fast relaxation is generally valid in rare earth alloys, but not for transition series alloys. This

41. In alloys with an exchange enhanced electronic susceptibility (e.g. Pd-Mn), the actual χ should be used rather than the free electron susceptibility, χ_p .

explains the small g shifts and calculated $J(o)$ values of Owen et al.

A second order or so called Kittel-Mitchell⁴² shift can also be calculated along the following lines. The magnetization $\vec{M}_d$ creates an additional polarization of the conduction electrons which produces an additional shift $\delta H^{(2)}$. Thus

$$\vec{M}_s = \chi_p (\vec{H}_a + \lambda \vec{M}_d) \quad (II.11)$$

and

$$\vec{H}_d = \lambda \chi_p \vec{H}_a + \lambda^2 \chi_p \vec{M}_d . \quad (II.12)$$

Using $\vec{M}_d = \chi_d \vec{H}_a$ gives

$$- \frac{\delta H^{(2)}}{H} = \lambda^2 \chi_p \chi_d . \quad (II.13)$$

The reasons why $H_d^{(2)}$ is not effective in producing an observable shift are discussed in the next section.

2. Theory of g Shifts Including Relaxation Effects

The importance of relaxation can be easily understood with the following simple example. Let the local moment and conduction electron unperturbed g values be equal, $g_s = g_d$, and allow strong cross relaxation between the two spin systems but only weak coupling to the lattice. Then there can be no shift of g_d by $\lambda \vec{M}_s$ because the two magnetizations, $\vec{M}_s$ and $\vec{M}_d$, remain parallel while precessing about the applied field and can therefore not exert a torque on each other. This is a completely bottlenecked system.

42. C. Kittel and A.H. Mitchell, Phys. Rev. 101, 1611, (1956).

The following treatment is based on the original theory of Hasegawa⁸ as modified by more recent investigators. The dynamical motion of the two spin systems is treated using phenomenological equations of the Bloch type. These are

$$\begin{aligned} \frac{d\vec{M}_s(t)}{dt} &= \gamma_s \vec{M}_s(t) \times [\vec{H}(t) + \lambda \vec{M}_d(t)] \\ &- \delta_{sL} (\vec{M}_s(t) - \vec{M}_s^0) - \delta_{sd} \vec{M}_s(t) + \delta_{ds} \vec{M}_d(t), \end{aligned} \quad (\text{II.14})$$

$$\begin{aligned} \frac{d\vec{M}_d(t)}{dt} &= \gamma_d \vec{M}_d(t) \times [\vec{H}(t) + \lambda \vec{M}_s(t)] \\ &+ \delta_{sd} \vec{M}_s(t) - \delta_{ds} \vec{M}_d(t). \end{aligned} \quad (\text{II.15})$$

Here δ_{sL} , δ_{sd} , and δ_{ds} are the relaxation rates of the conduction (s) electrons to the lattice, the conduction electrons to the local moment, d electrons; and the d electrons to the s electrons, respectively. The direct local moment to lattice relaxation rate δ_{dL} is assumed negligible for S state ions because such a process requires spin-orbit coupling. The magnetic field $H(t)$ includes both the applied static field and the rf field. The magnetomechanical ratios γ_s and γ_d are given by $\gamma_s = g_s \beta / \hbar$ and $\gamma_d = g_d \beta / \hbar$ where g_s and g_d are the unperturbed or "bare" spectroscopic splitting factors. Additional terms for δ_{dL} ,^{11,37} spin diffusion,^{37,43} spin fluctuations,³ and nuclear hyperfine fields¹³ have been considered by subsequent investigators. The first term in (II.14)

43. D.L. Cowan, Phys. Rev. Letters 18, 770 (1967).

and in (II.15) simply states that the time rate of change of the angular momentum of the spin system $\vec{M}_s$ or $\vec{M}_d$ is proportional to the torque acting on it. The other, relaxation terms provide for an exponential return to equilibrium if the exciting rf field is removed. There has been some difficulty in the past with the spin-lattice relaxation term

$$[\delta_{sL}] (\vec{M}_s(t) - \vec{M}_s^0) .$$

Hasegawa was unsure whether $\vec{M}_s^0$, the equilibrium value toward which $\vec{M}_s$ is relaxing, should be given by

$$\vec{M}_s^0 = \chi_p \vec{H}_a + \lambda \chi_p \vec{M}_d^0 \quad (\text{II.16})$$

or

$$\vec{M}_s^0 = \chi_p \vec{H}_a + \lambda \chi_p \vec{M}_d(t) \quad (\text{II.17})$$

where $\vec{M}_d^0$ is the time average, or equilibrium value, of $\vec{M}_d$, and $\vec{M}_d(t)$ is the instantaneous value of $\vec{M}_d$. Hasegawa thought (II.16) was probably correct (his case A) but also gave results using (II.17). In fact, Wangsness⁴⁴ has shown using dynamical equations of the Landau-Lifshitz form that for multiple sublattice systems ($\vec{M}_s$ and $\vec{M}_d$ here) relaxation must always occur toward the instantaneous value of the effective field. This is to insure positive energy absorption in a resonance experiment. This corresponds to Hasegawa's case B and results in the suppression of the Kittel-Mitchell shift.

44. R.K. Wangsness, Phys. Rev. 111, 813 (1958).

Equations (II.14) and (II.15) were solved by Hasegawa under the following assumptions,

$$\begin{aligned}
 \gamma_s &= \gamma_d = \gamma, \\
 \lambda \chi_s &\ll 1, \\
 \delta_{ds} \chi_d &= \delta_{sd} \chi_s, \\
 &\text{(Law of detailed balance)}^{45} \\
 \chi_d &\gg \chi_s. \\
 &\text{(i.e. d spin absorption dominates)}
 \end{aligned} \tag{II.18}$$

The results are

$$\delta\omega = \frac{-(\delta_{sL})^2}{(\delta_{sL} + \delta_{sd})^2 + (\gamma \lambda M_d^0)^2} (\gamma H_a \lambda \chi_p) \tag{II.19}$$

and

$$\delta_{\text{eff}} = \gamma \Delta H = \left(\frac{\delta_{sL}}{\delta_{sL} + \delta_{sd}} \right) \delta_{ds} \tag{II.20}$$

where ΔH is the observed linewidth.⁴⁶ EPR spectrometers generally operate at fixed frequency and variable field. The field shift is $\delta H = \delta\omega/\gamma$ and from (II.3) the g shift is $\delta g = -g\delta\omega/\gamma H_a$. The factor $(\gamma H_a \lambda \chi_p)$ in (II.19) can be written in terms of the unbottlenecked shift δg_0 of (II.10) as

$$\gamma H_a \lambda \chi_p = \gamma H_a \delta g_0 / g$$

which allows (II.19) to be expressed finally as

$$\delta g = \frac{+(\delta_{sL})^2}{(\delta_{sL} + \delta_{sd})^2 + (\gamma \lambda M_d^0)^2} \delta g_0. \tag{II.21}$$

45. Actually Hasegawa incorrectly stated this as $\delta_{sd} M_s^0 = \delta_{ds} M_d^0$.

46. To be completely explicit, ΔH is the half width at half height of the pure absorption curve.

FIGURE 1. Relaxation paths in the s-d spin system (after Hasegawa and Heeger).

The same result has been obtained by Davidov and Shaltiel¹² using Landau-Lifshitz damping terms as given by Cottet et al.¹¹

The physical meaning of (II.20) and (II.21) can be seen with the aid of the following picture (Fig. 1). If δ_{sL} is large, the s spins are in thermal equilibrium with the lattice and the relaxation rate of the d spins is determined by δ_{ds} . From (II.20) we see that δ_{sL} large means $\delta_{sL} \gg \delta_{sd}$ giving

$$\delta_{\text{eff}} = \delta_{ds} . \quad (\text{II.22})$$

In the opposite limit the conduction electrons do not rapidly relax to the lattice and therefore may relax back to the d spins. This "back flow" leads to a bottleneck in the local moment relaxation. In this limit (II.20) becomes

$$\delta_{\text{eff}} = \left(\frac{\delta_{sL}}{\delta_{sd}} \right) \delta_{ds} \quad (\text{II.23})$$

using $\delta_{sL} \ll \delta_{sd}$.

Equation (II.21) correctly gives the result, $\delta g = \delta g_0$ for $\delta_{sL} \gg \delta_{sd}$ (and $\gamma \lambda M_d^0$ not too large).⁴⁷ In the opposite limit, $\delta_{sL} \ll \delta_{sd}$ and (II.21) becomes

$$\delta g = \frac{(\delta_{sL})^2}{\delta_{sd}^2 + (\gamma \lambda M_d^0)^2} \delta g_0. \quad (\text{II.24})$$

In this case the shift is reduced by at least the factor $(\delta_{sL}/\delta_{sd})^2$.

Recently several investigators^{14,48-52} have applied Green's function and diagrammatic techniques to microscopically calculate the dynamics of localized moments. Spencer and Orbach⁵² obtain essentially the same g shift as Hasegawa, but question the simple expressions used for δ_{sd} and δ_{ds} (discussed in the next section) and suggest they are frequency dependent. Logarithmic g shifts^{52,53} associated with the Kondo effect are not expected in alloys such as Cu-Mn or Mg-Mn because of the general suppression of Kondo type anomalies by AFM ordering.^{54,55} If present these shifts will also be diminished by the relaxation bottleneck.

47. Davidov and Shaltiel [12] have investigated LaNi₅(Gd) in the temperature and concentration range over which the term $\gamma \lambda M_d^0$ is important.
48. B. Giovannini and S. Koide, Progr. Theoret. Phys. (Kyoto) 34, 705 (1965).
49. B. Giovannini, M. Peter, and S. Koide, Phys. Rev. 149, 251 (1966).
50. M.B. Walker, Phys. Rev. 176, 432 (1968).
51. B. Caroli, C. Caroli, and D.R. Fredkin, Phys. Rev. 178, 599 (1969).
52. H.J. Spencer and R. Orbach, Phys. Rev. 179, 683 (1969).
R. Orbach and H.J. Spencer, Phys. Rev. 179, 690 (1969).
53. H.J. Spencer and S. Doniach, Phys. Rev. Letters 18, 994 (1967).
54. S.D. Silverstein, Phys. Rev. Letters 16, 466 (1966).
55. R.J. Harrison and M.W. Klein, Phys. Rev. 154, 540 (1967).

3. Analysis of Relaxation and Linewidths in the Bottleneck Region

The development here is similar to that of Gossard et al.^{9,10} who have discussed the analysis of linewidths using Hasegawa's formulation. The starting point is (II.23) for the bottleneck region, $\delta_{sL} \ll \delta_{sd}$:

$$\gamma \Delta H = \delta_{\text{eff}} = \left(\frac{\delta_{sL}}{\delta_{sd}} \right) \delta_{ds} . \quad (\text{II.23})$$

Expressions for δ_{sd} and δ_{ds} are borrowed from the theory of nuclear relaxation in metals via the hyperfine interaction.⁵⁶ Replacing I by S and A by J(o), these expressions become

$$\delta_{sd} = \frac{2\pi}{\hbar} \frac{2\eta(E_f)J^2(o)}{N_o} \frac{N}{N_o} \frac{2}{3} S(S+1) \quad (\text{II.25})$$

and

$$\delta_{ds} = \frac{2\pi}{\hbar} \frac{2\eta(E_f)J^2(o)}{N_o} \frac{\eta(E_f)}{N_o} kT \quad (\text{II.26})$$

where $\eta(E_f)$ is the density of states per unit volume of one spin at the Fermi surface, N_o is the number of atoms per unit volume, N is the number of local moments per unit volume, and S is the local moment spin. Using these last two equation, (II.23) becomes

$$\delta_{\text{eff}} = \gamma \Delta H = \delta_{sL} \left(\frac{3 \eta(E_f) kT}{2N_o S(S+1)C_I} \right) \quad (\text{II.27})$$

where $C_I = N/N_o$ is the fractional concentration of the magnetic impurity. In a high purity metal δ_{sL} is proportional to kT because

56. W. Heitler and E. Teller, Proc. Roy. Soc. (London) A155, 637 (1936).

J. Korringa, Physica 16, 601 (1950).

A.W. Overhauser, Phys. Rev. 89, 689 (1953).

of the phonon temperature dependence. However, as shown in the conduction electron spin resonance (CESR) work of Feher and Kip,⁵⁷ even the slightest impurity concentration can dominate the relaxation and give an effective δ_{sL} which is temperature independent. Lattice defects and surface relaxation effects are also expected to contribute to δ_{sL} .⁵⁸ Thus the net temperature dependence of the linewidth is $\Delta H \propto kT$. This kT dependence arises from the term $(\eta(E_f)kT/N_O)$ in δ_{ds} and in that expression is just the number of conduction electron states at the Fermi surface to which the d spins can relax.

The effective spin-lattice relaxation rate δ_{sL} can be found from the slope of ΔH versus T . Specifically, the slope is

$$\frac{d(\Delta H)}{dT} = \delta_{sL} \left(\frac{3 \eta(E_f) k}{2 N_O \gamma S (S + 1) C_I} \right) \quad (\text{II.28})$$

where the only unknown is δ_{sL} . It will be found that δ_{sL} is a function of C_I as expected because of spin-orbit induced spin-flip scattering of the conduction electrons by the magnetic impurity cores. It should be stressed that this is a relaxation to the lattice through the impurity core electric fields. It is not related to δ_{sd} which refers to the process in which a conduction electron flips a local moment spin. The spin-flip scattering contribution to the linewidth should be proportional to C_I . Thus

57. G. Feher and F. Kip, Phys. Rev. 98, 337 (1955).

58. This effect is well illustrated in the data of Gossard et al. [10] who found a doubling of the relaxation rate in going from thin sheets to powder samples.

a plot of δ_{sL} versus C_I yields a straight line with a slope which can be expressed in terms of the spin-flip scattering cross section^{9,10,59}

$$\sigma_I = \frac{\Omega}{v_f} \left[d(\delta_{sL})/dC_I \right] \quad (II.29)$$

where Ω is the atomic, impurity volume; and v_f is the Fermi velocity.

Spin-flip scattering can be understood as follows: In transition metal alloys the s and d bands overlap resulting in the conduction electrons having some admixed d character, i.e. angular momentum, which couples with the lattice through the magnetic impurity core electric fields. The link between spin and lattice is completed by spin-orbit coupling. The impurity can either be the one responsible for the EPR or an added, second impurity. In either case, (II.29) is used to find σ_I . It has been found in copper that impurities having a local moment with some orbital character (e.g. Fe or Co) provide a very effective relaxation path for Mn spins.⁹ This appears to be a different case than that just described. Here the Mn spin can either relax to the conduction electrons (as above) or to the Fe or Co local moment via the RKKY interaction. The dominant path appears to be the one to the Fe or Co which then relax rapidly to the lattice via spin-orbit coupling. The theory of the effect of spin-orbit coupling on magnetic resonance relaxation has been discussed by Elliott,⁶⁰ Pines and Slichter,⁶¹ and with specific

59. J.R. Asik, M.A. Ball, C.P. Slichter, Phys. Rev. Letters 16, 740 (1966).

60. R.J. Elliott, Phys. Rev. 96, 266 (1954).

61. D. Pines and C.P. Slichter, Phys. Rev. 100, 1014 (1955).

reference to the applications here by Yafet.^{15,62}

In binary alloys without additional added impurities, the residual linewidths have the following interpretation. The value of δ_{sL} obtained by extrapolating C_I to zero is a measure of the unknown residual impurities and lattice defects. Extrapolating the temperature to zero in (II.27) yields $\Delta H = 0$. In actual fact, of course, there is generally always a residual linewidth at $T = 0$ K. In cubic alloys this residual linewidth is primarily attributed to direct relaxation of the local moments to the lattice rather than via the conduction electrons. Impurities can increase this relaxation rate in the following way: Admixing of conduction band states with the localized d states gives some long range character to the local moments. This allows the local moments to relax by distant impurity spin-orbit interaction. This is a temperature independent process and has been discussed by McElroy and Heeger.⁶³

In hexagonal Mg-Mn alloys, unresolved fine structure is expected to be an equally important contributor to the residual linewidth. In an environment with axial symmetry, the fine structure energy levels are given to lowest order in D by^{64,65}

$$g\beta H = g\beta H_0 - D(S_z^u - \frac{1}{2}) (3 \cos^2 \theta - 1) \quad (\text{II.30})$$

62. Y. Yafet, J. Appl. Phys. 39, 853 (1968), and in Solid State Physics, Vol. 14, (F. Seitz and D. Turnbull, eds.) Academic Press, New York, 1963.

63. J.A. McElroy and A.J. Heeger, Phys. Rev. Letters 20, 1481 (1968).

64. R.S. Alger, Electron Paramagnetic Resonance: Techniques and Applications, Interscience Publishers, New York, 1968.

65. B. Bleaney, Phil. Mag. 42, 441 (1951).

where $g\beta H_0 = \hbar\omega_0$ gives the resonance frequency in the absence of fine structure, S_z^u is the z component of the effective spin of the upper level involved in the transition ($\Delta S_z = \pm 1$), D is the fine structure constant appropriate for an environment with axial symmetry, and θ is the angle between the symmetry axis and the applied magnetic field. The spectroscopic splitting factor g has been assumed isotropic which is valid for S state ions in metals.^{66,67} For Mn^{++} , (II.30) predicts splittings on the order of several times D , depending on the angle θ . For polycrystalline samples an average must be taken over all angles. The value of D for Mg-Mn is not known. In general, fine structure splitting should be smaller in metals than in insulators because of conduction electron shielding of the crystalline electric field.

Line broadening due to hyperfine structure is believed to be negligible as discussed in the next section.

4. Hyperfine Splitting

Langreth et al.¹³ were the first to include the hyperfine fields in the equations of motion (II.14 and II.15), and established that the hyperfine splittings will be suppressed under the right conditions. This problem has also been discussed by Barnes et al.⁶⁸

66. S. Geschwind, G.E. Devlin, and J.H. Wernick, J. Appl. Phys. 37, 1221 (1966).

67. L.J. Tao, D. Davidov, R. Orbach, D. Shaltiel, and C.R. Burr, Phys. Rev. Letters 26, 1438 (1971).

68. S.E. Barnes, J. Dupraz, and R. Orbach, J. Appl. Phys. 42, 1659 (1971).

and Chui et al.,⁶⁹ who were the first to observe hyperfine splitting in metals (Ag-Er).⁷⁰ The criteria for the suppression of the splitting to first order are

$$\begin{aligned}\delta_{sL} &\ll \delta_{sd} \\ \omega_{hf} &\ll \delta_{ds}\end{aligned}\tag{II.31}$$

where ω_{hf} is the hyperfine splitting frequency. It will be shown in Chapter V that Mg-Mn easily meets these criteria. The line broadening caused by the "compressed" hyperfine lines is

$$\Delta H_{hf} \cong \omega_{hf}^2 / \gamma \delta_{ds}, \tag{II.32}$$

which is on the order of 1 or 2 gauss for Mg-Mn or Cu-Mn at low temperatures (1 K). Hyperfine lines should be observable in the bottleneck regime if $\omega_{hf} \gg \delta_{ds}$. This may hold for S state rare earth alloys at very low temperature, but is not likely to be true for transition metal alloys.⁶⁹

5. Theoretical Line Shapes

The penetration depth δ of microwaves into a metal is given by

$$\delta = (2/\omega\mu\sigma)^{\frac{1}{2}} \tag{II.33}$$

where ω is the microwave angular frequency, μ is the magnetic permeability, and σ is the conductivity. For typical frequencies,

69. R. Chui, R. Orbach, and B.L. Gehman, Phys. Rev. B 2, 2298 (1970).

70. More recently, fine structure splitting has been observed in Au-Er and Au-Yb [L.J. Tao, D. Davidov, R. Orbach, and E.P. Chock, Phys. Rev. B 4, 5 (1971)].

10 to 35 GHz, and good conductors, δ is on the order of a micrometer. This small penetration of microwaves into a sample, coupled with diffusion of electrons into and out of the skin depth, is responsible for the asymmetrical line shapes observed in metals (Fig. 2).

This effect was first treated by Bloembergen⁷¹ (1952), and in 1955 Dyson⁷² developed an essentially complete treatment of the problem which Feher and Kip⁵⁷ present in more usable form. These investigators were primarily interested in conduction electron spin resonance (CESR). For local moments in thick metal samples, the appropriate limit of their results is

$$T_T \gg T_D; T_T \gg T_2; T_D/T_2 \gg 1 \quad (\text{II.34})$$

where T_T is the traversal time for the local moment to diffuse through the entire sample thickness, T_D is the time for diffusion through the skin depth, and T_2 is the transverse relaxation time of the local moments. Then, assuming the undistorted line is Lorentzian,

$$\frac{dP(H)}{dH} = \left(\frac{HH_1^2 (\delta A) H_0 \chi_d T_2^2}{8} \right) \left(\frac{T_2^2 (H-H_0)^2 - 2T_2 (H-H_0) - 1}{[1 + T_2^2 (H-H_0)^2]^2} \right) \quad (\text{II.35})$$

where dP/dH is the derivative of the power absorbed, H is the static magnetic field, H_0 is the true resonance field, H_1 is the amplitude of the linearly polarized rf magnetic field, δ the skin depth, and

71. N. Bloembergen, J. Appl. Phys. 23, 1383 (1952).

72. F.J. Dyson, Phys. Rev. 98, 349 (1955).

FIGURE 2. Typical derivative of absorption curve for a local moment resonance. The asymmetrical line shape results from a mixing of absorption and dispersion. Measurement of W and y allows ΔH and H_0 to be determined.

A the sample area. The shape of this curve is shown in Figure 2 for the limiting case of infinite diffusion time. Analysis of this curve yields the following simple relations,^{5,73}

$$A/B = 2.55$$

$$h_2 = 0.3265 \Delta H_{\text{PTP}} \quad (\text{II.36})$$

$$\Delta H = 0.789 \Delta H_{\text{PTP}}$$

which can be used to analyze data. ΔH is the true line width, ΔH_{PTP} is the peak to peak width measured on the derivative curve, h_2 is the difference between the apparent and true resonance field values, and A/B is the ratio of "height" to "depth" of the curve.

Peter et al.⁷⁴ have developed an empirical method for the analysis of line shapes which has been used for this work. It is based on the principle that the asymmetrical resonance lines are a combination of absorption and dispersion. Assuming a Lorentzian line shape, absorption is proportional to χ'' ,

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

and dispersion to χ' ,

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

with

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

73. A.M. Harris, J. Popplewell, and R.S. Tebble, Proc. Roy. Soc. (London) 85, 513 (1965).

74. M. Peter, D. Shaltiel, J.H. Wernick, H.J. Williams, J.B. Mock, and R.C. Sherwood, Phys. Rev. 126, 1395 (1962).

Differentiating with respect to H and adding in the proportion, "a" parts absorption and "d" parts dispersion, yields

$$\frac{dP(H)}{dH} = \frac{1 - 2cx - x^2}{(1 + x^2)^2} \quad (II.37)$$

where $c = a/d$.

A family of these curves can be generated, measured, and a graph (Fig. 3) constructed which gives the true H_0 and ΔH using measured values of y_1 , y_2 , and W (see Fig. 2). y_1 is the base line to low field peak height, y_2 is the peak to peak height, W is the full width at half height of the low field peak, and h_1 is the field difference between the middle of W and the true resonance field H_0 . Note that the middle of W does not correspond to the low field peak position. In practice the method of Peter et al. is better because it easily handles variable mixtures of absorption and dispersion and W can generally be obtained quite accurately while measurements of ΔH_{PTP} are easily influenced by base line shift and a poorly defined high field peak.

FIGURE 3. Line shape analysis curves of Peter et al. [74] for finding H_0 and ΔH using measured values of y and W (Fig. 2).

C. ANTIFERROMAGNETIC RESONANCE THEORY

AFMR was first discussed by Kittel,⁷⁵ Nagamiya,⁷⁶ Keffer and Kittel,⁷⁷ Nagamiya et al.,⁷⁸ and others.^{79,80} More recently (1963) a review article by Foner has appeared.⁸¹ The theories are all for crystalline antiferromagnetic substances but, with care, can be applied to antiferromagnetic alloys. Typically, in dilute alloys (Cu-Mn, Ag-Mn, Mg-Mn) a single resonance is observed in the paramagnetic state. This resonance is observed to shift smoothly with the onset of the antiferromagnetic state. Only those AFMR modes for which this is true will be considered here. The biggest problem in the interpretation of the resonance is associated with the anisotropy field H_A which is discussed in Section II-C-4.

Calculations of the resonance modes are based on a two sublattice molecular field model for antiferromagnetism. In this model the magnetizations of the identical sublattices $\vec{M}_1$ and $\vec{M}_2$ are aligned antiparallel below the Neel temperature T_N by an effective (exchange) field $\vec{H}_E$. The exchange field acting on $\vec{M}_1$ is produced by $\vec{M}_2$ and vice versa. Thus, $\vec{M}_1$ and $\vec{M}_2$ experience fields $\vec{H}_E = -\Gamma\vec{M}_2$ and $\vec{H}_E = -\Gamma\vec{M}_1$, respectively. The molecular field constant Γ is

75. C. Kittel, Phys. Rev. 82, 565 (1951).

76. T. Nagamiya, Progr. Theoret. Phys. (Kyoto) 6, 342 (1951).

77. F. Keffer and C. Kittel, Phys. Rev. 85, 329 (1952).

78. T. Nagamiya, K. Yosida, and R. Kubo, Advances in Phys. 4, 1 (1955).

79. J. Ubbink, Physica 19, 9, 919 (1953).

80. D.M.S. Bagguley and J. Owen, Reports on Progress in Phys. 20, 304 (1957).

81. S. Foner in Magnetism, Vol. 1, (G.T. Rado and H. Suhl eds.), Academic Press, New York, 1963.

positive for antiferromagnetism. Uniaxial symmetry is assumed, and its effects are included by introducing an anisotropy field $\vec{H}_A$ parallel to the symmetry or "easy" axis of the system (usually the $\vec{c}$ axis).^{82,83} In the absence of external fields, $\vec{H}_A$ aligns $\vec{M}_1$ and $\vec{M}_2$ along the $\vec{c}$ and $-\vec{c}$ axis. In dilute, antiferromagnetic alloys H_E and H_A are on the order of 10's of kilogauss and 10's of gauss, respectively. In nonmetallic antiferromagnets the exchange field is typically 10 times larger, and the anisotropy field 100 to 1000 times larger. The equations of motion for $\vec{M}_1$ and $\vec{M}_2$ are (neglecting relaxation terms)

$$\begin{aligned}\frac{d\vec{M}_1}{dt} &= \gamma \vec{M}_1 \times \vec{H}_n \\ \frac{d\vec{M}_2}{dt} &= \gamma \vec{M}_2 \times \vec{H}_n\end{aligned}\tag{II.38}$$

where $\vec{H}_n$ is the net magnetic field acting on $\vec{M}_1$ and $\vec{M}_2$. In a resonance experiment H_n will include the exchange, anisotropy, applied, and microwave rf magnetic fields:

$$\vec{H}_n = (\vec{H}_E + \vec{H}_A + \vec{H}_a + \vec{H}_{rf}).\tag{II.39}$$

In the usual experimental arrangement $\vec{H}_{rf} \perp \vec{H}_a$, and only solutions corresponding to this case will be discussed. It is also assumed

82. $\vec{H}_A$ acts on $\vec{M}_1$ and $-\vec{H}_A$ acts on $\vec{M}_2$.

83. The anisotropy can also be expressed in terms of K , the anisotropy energy per unit volume. H_A and K are related by $2 H_E H_A = 2 \Gamma K$.

that $H_A \ll H_E$ and $H_a \ll H_E$ at all temperatures⁸⁴ and that at resonance the displacement of $\vec{M}_1$ and $\vec{M}_2$ from equilibrium is small.

Single crystals are almost always used in AFMR investigations of nonmetallic materials because the resonance frequency ω generally depends very strongly on the angle between $\vec{H}_a$ and the easy axis. However, if $\vec{H}_A$ is only a few gauss instead of several kilogauss, polycrystalline samples can be used without excessive line broadening as has been done for most resonance work in alloys. The actual angular dependence of ω is very complicated and only the limiting cases of $\vec{H}_a$ parallel and perpendicular to the $\vec{c}$ axis will be considered.

1. $\vec{H}_a \parallel \vec{c}, H_a < H_c$

With $\vec{H}_a$ parallel to the $\vec{c}$ axis two possible cases occur depending on whether or not H_a exceeds the critical field H_c given by

$$H_c^2 = \left(\frac{2H_E H_A}{1-\alpha} \right) \quad (\text{II.40})$$

where $\alpha = \chi_u / \chi_\perp$, the ratio of the static susceptibilities measured with $\vec{H}_a$ parallel and perpendicular to the $\vec{c}$ axis, respectively.⁸⁵ When H_a exceeds H_c it is energetically more favorable for $\vec{M}_1$ and $\vec{M}_2$ to flip over approximately perpendicular to the $\vec{c}$ axis but canted

84. At the Neel temperature $H_E = 0$ and $H_a \ll H_E$ is obviously not satisfied. However, H_E increases very rapidly toward a very large value just below T_N and therefore this is not a severe restriction.

85. Some authors use $\alpha = 1 - \chi_u / \chi_\perp$.

slightly toward the direction of $\vec{H}_A$ (while remaining approximately antiparallel to each other). This is the "spin floped" region and will not be considered because it results in a shift of the resonance to higher rather than lower fields in the AFM state.

Depending on the detailed temperature dependence of $\vec{H}_E$, $\vec{H}_A$, and α ; the critical field may increase or decrease as the temperature approaches T_N . This point has been occasionally overlooked by some investigators who use $H_C^2(T) = 2H_E H_A$ instead of the correct expression (II.40). The temperature dependence of $\chi_{||}$ and $\chi_{\perp}$ for a typical antiferromagnet are shown in Figure 4.

FIGURE 4. Typical susceptibilities of a two sublattice antiferromagnet.

FIGURE 5. The Brillouin function for a spin 1/2 system. See [98] for the functional form.

The exchange field H_E has a temperature dependence which generally follows the Brillouin function $B_S(x)$ having a maximum at $T = 0$ and the value zero at T_N , where $x = \mu H/kT$ (Fig. 5). In nonmetallic antiferromagnets the temperature dependence of H_A is also approximately that of the Brillouin function, or some power of the Brillouin function. In alloys the situation is considerably more complicated, but it is still generally true that H_A increases as the temperature decreases.

The treatment of Foner⁸¹ is outlined below for the case $H_a < H_c$ (and $\vec{H}_a \parallel$ to the $\vec{c}$ axis, assumed along $\vec{z}$; Fig. 6). The development is in terms of fixed magnetic field $H_a = H_0$ and variable frequency ω . For small amplitude oscillations, $M_{1z} \cong M_1^0$ and $M_{2z} \cong M_2^0$. The transverse components of (II.38) become

FIGURE 6. The AFMR normal mode ω_h^+ .

$$\begin{aligned}
 j(\omega/\gamma)M_{1x} &= (H_0 + H_A - \Gamma M_{2z} + H_z^{rf})M_{1y} - (H_y^{rf} - \Gamma M_{2y})M_{1z} \\
 j(\omega/\gamma)M_{1y} &= -(H_0 + H_A - \Gamma M_{2z} + H_z^{rf})M_{1x} + (H_x^{rf} - \Gamma M_{2x})M_{1z}
 \end{aligned}
 \tag{II.41}$$

where a time dependence $e^{j\omega t}$ has been assumed for the transverse components, and for small oscillations, all products of transverse components are neglected. The equations for M_{2x} and M_{2y} are obtained by interchanging 1 and 2 everywhere in the above equations. The resonance frequencies are obtained by setting $H^{rf} = 0$ and

solving the secular equation. This latter step is simplified by substitution of the circularly polarized components

$$M_1^\pm = M_{1x} \pm jM_{1y}$$

into (II.41) yielding

$$\begin{aligned} (\pm\omega/\gamma)M_1^\pm &= -(H_0 + H_A - \Gamma M_{2z})M_1^\pm - (\Gamma M_{1z})M_2^\pm \\ (\pm\omega/\gamma)M_2^\pm &= -(\Gamma M_{2z})M_1^\pm - (H_0 - H_A - \Gamma M_{1z})M_2^\pm. \end{aligned} \quad (\text{II.42})$$

Diagonalization of the secular determinant yields the eigenvalues⁸⁶

$$\begin{aligned} \omega_\ell^\pm/\gamma &= \mp \{-H_0(1 - \alpha/2) + [2H_E H_A + (\alpha H_0/2)^2]^{1/2}\} \\ \omega_h^\pm/\gamma &= \pm \{+H_0(1 - \alpha/2) + [2H_E H_A + (\alpha H_0/2)^2]^{1/2}\} \end{aligned} \quad (\text{II.43})$$

where ω_ℓ (ω_h) refers to the mode whose frequency is lowered (increased) in an applied field H_0 . In a resonance experiment with a fixed microwave frequency and a varying magnetic field this result can be rewritten as

$$\omega/\gamma = \omega_0/\gamma = H_0 = H_A (1 - \alpha/2) \pm [2H_E H_A + (\alpha H_A/2)^2]^{1/2} \quad (\text{II.44})$$

where $\omega_0/\gamma = H_0$ is the resonance field in the paramagnetic state

86. The dependence on α is a result of $|M_{1z}| \neq |M_{2z}|$ at $T > 0$. Specifically, the magnetization, say M_{1z} , parallel to $\vec{H}_a$ is greater than that antiparallel to $\vec{H}_a$. In this case $\Gamma(M_{1z}+M_{2z}) = \alpha H_a$ and an average temperature dependent H_E can be defined by $2H_E = \Gamma(M_{1z}-M_{2z})$.

and H_0 in (II.43) becomes H_a , the field for resonance in the antiferromagnetic state. For temperatures just below the Néel temperature $\alpha \sim 1$ and $1 - \alpha$ is very small. It is then possible to have $2H_E H_A \ll H_a^2$ and at the same time have $H_a < H_c$. Using this approximation (II.44) becomes

$$H_0 = \frac{1}{2}H_a \pm (H_a/2 + 2 H_E H_A/H_a). \quad (\text{II.45})$$

Keeping only the plus sign to prevent a discontinuity at T_N , this becomes

$$\delta H = H_a - H_0 = -2 H_E H_A/H_a. \quad (\text{II.46})$$

The resonance mode for this case is shown in Figure 6. For $T \geq T_N$, H_E and H_A are zero and $H_0 = H_a$ as desired. As the temperature is decreased below T_N the product $2H_E H_A$ increases and the resonance shifts to lower fields. In typical nonmetallic crystalline AFM substances, lowering the temperature below T_N leads to a very rapid increase in $H_E H_A$ resulting in a decrease in H_a to zero field and the resonance disappears. For instance, in $\text{CuCl} \cdot 2\text{H}_2\text{O}$ this rapid shift occurs between $T_N = 4.3$ K and 4.2 K.⁷⁹ In MnTiO_3 the shift is less rapid, occurring over the temperature range $T_N = 63$ K to 45 K.⁸⁷ In a dilute, structurally disordered alloy, the transition to an antiferromagnetic state is expected to be less abrupt, allowing the downfield shift described by (II.46) to occur over a broad temperature range. At higher spectrometer frequencies (II.46) predicts a

87. J.J. Stickler and G.S. Heller, J. Appl. Phys. 33, Suppl., 1302 (1962).

decrease in the shift δH because of the higher H_O . This effect has been observed in Cu-Mn^{5,16} and Ag-Mn⁵.

2. $\vec{H}_a \perp \vec{c}$

With this geometry the resonance fields can be derived in a similar fashion to that for $\vec{H}_a \parallel \vec{c}$ and are

$$H_O \cong \pm (2H_E H_A + H_a^2)^{\frac{1}{2}} . \quad (\text{II.47})$$

As before, only the plus sign is kept, giving

$$\delta H = H_a - H_O = -H_E H_A / H_a . \quad (\text{II.48})$$

This predicts the same shift as (II.46) to within a factor of 2. This difference may, in part, be responsible for the observed line-width in the antiferromagnetic state of a polycrystalline sample, and is discussed later.

3. The Exchange Field $\vec{H}_E$

There seems little doubt that the Ruderman-Kittel-Kasuya-Yosida^{88,89,32} (RKKY) indirect exchange interaction is responsible for the AFM ordering observed in dilute magnetic alloys, as was first suggested by Yosida³² in reference to the Cu-Mn investigation of Owen et al.⁵ According to this interaction, a localized magnetic moment produces a damped oscillation in the polarization of the

88. M.A. Ruderman and C. Kittel, Phys. Rev. 96, 99 (1954).

89. T. Kasuya, Progr. Theoret. Phys. (Kyoto) 16, 45 (1956).

surrounding conduction electron gas given by

$$\chi(r) \propto \frac{1}{r^4} \{2k_f r \cos(2k_f r) - \sin(2k_f r)\} e^{-r/\zeta} \quad (\text{II.49})$$

where $\chi(r)$ is the local electron susceptibility at a distance r from the magnetic moment, k_f is the Fermi wave number, and ζ is the mean free path of the electrons. The form given here is that of de Gennes^{26,90} who introduced the exponential damping term to include the effects of finite, electron mean free path. Expression (II.49) can be approximated by

$$\chi(r) \propto \frac{\cos(2k_f r)}{r^3} e^{-r/\zeta} \quad (\text{II.50})$$

which more clearly indicates the nature of the oscillating polarization. Although damped out rapidly by the exponential and $1/r^3$ terms, this interaction is still of much longer range than direct exchange interactions which require direct overlap of wave functions between two interacting moments. Numerous calculations of NMR linewidths,^{88,91} specific heat,^{92,93} EPR linewidths and line shifts,⁹⁴ magnetic susceptibility,⁹³ and electrical resistivity^{54,55} in dilute magnetic alloys have demonstrated the basic correctness of (II.50).

90. P.G. de Gennes, J. Phys. Radium 23, 630 (1962).

91. A.J. Heeger, A.P. Klein, and P. Tu, Phys. Rev. Letters 17, 803 (1966).

92. W. Marshall, Phys. Rev. 118, 1519 (1960).

93. M.W. Klein and R. Brout, Phys. Rev. 132, 2412 (1963).

94. D. Shaltiel, J.H. Wernick, H.J. Williams, and M. Peter, Phys. Rev. 135, A1346 (1964).

However, the disordered nature of alloys leads to some difficulties in its application, particularly in explaining all the magnetic properties. For instance, the high temperature susceptibility data of Owen et al. for Cu-Mn yield a positive, ferromagnetic θ ; but the low temperature data exhibit a peak in χ indicating an antiferromagnetic behavior. In addition thermoremanent magnetization and magnetic hysteresis are observed in samples cooled to helium temperature in a magnetic field. To explain some of these anomalies it has been suggested that Cu-Mn may consist of small ferromagnetic domains which are antiferromagnetically coupled together.^{5,95,96} These complications must be kept in mind when using a simple two sublattice, molecular field model. Nevertheless, this model gives very good qualitative results in many complicated systems and is a useful phenomenological model to use here.

For example, this model allows a simple calculation of H_E in terms of T_N . The usual expressions⁹⁷ for the exchange field $\vec{H}_E$, the magnetization $\vec{M}_1$ (or $\vec{M}_2$), the Curie constant C and the Néel temperature T_N are

$$\begin{aligned}\vec{H}_E &= -\Gamma \vec{M}_1 \\ \vec{M}_1 &= \vec{M}_0 B_S \left(\frac{\mu H}{kT} \right) \\ \vec{M}_0 &= \left(\frac{1}{2} N \right) g \beta \vec{S}\end{aligned}$$

95. J.S. Kouvel, J. Phys. Chem. Solids 21, 57 (1961) and 24, 795 (1963).

96. D. Griffiths, Proc. Phys. Soc. (London) 90, 707 (1967).

97. J. Samuel Smart, Effective Field Theories of Magnetism, W.B. Saunders Co., Philadelphia, 1966.

$$C = \frac{Ng^2\beta^2S(S+1)}{3k} \quad (\text{II.51})$$

$$T_N = \frac{\Gamma C}{2}$$

where $\vec{M}_0$ is the sublattice, saturation magnetization; B_S is the Brillouin function⁹⁸ for spin S (L assumed = 0), and N is the number of magnetic ions per unit volume. The exchange field H_E can be found in terms of T_N yielding

$$H_E = \frac{3kT_N B_S(x)}{g\beta(S+1)} \quad (\text{II.52})$$

The Brillouin function $B_S(x)$ varies between 0 and 1 for positive argument x (Fig. 5). For a manganese alloy with a typical Néel temperature of 10 K, the saturation value of the exchange field $H_E(T=0) = H_E^0$ is 64 kilogauss. For comparison, in the antiferromagnetic crystals MnCO_3 and MnF_2 the best experimental values are $T_N = 32$ K, $H_E^0 = 334$ kG and $T_N = 68$ K, $H_E^0 = 556$ kG, respectively.^{99,100} It is difficult to obtain good experimental values for H_E , but the trend is toward slightly larger exchange fields than predicted by (II.52). Exchange fields are discussed further in the following section on anisotropy fields, because of the difficulty in obtaining separate values for the two.

98. $B_S(x) = \frac{2S+1}{2S} \coth \frac{(2S+1)x}{2S} - \frac{1}{2S} \coth \frac{x}{2S}$, $x = \mu H/k_B T$.

Values of $B_S(x)$ are tabulated (e.g. reference 97).

99. H. Fink and D. Shaltiel, Phys. Rev. 136, A218 (1964).

100. F.M. Johnson and A.H. Nethercot, Jr., Phys. Rev. 114, 705 (1959).

4. Anisotropy Field $\vec{H}_A$

To explain the experimental data for Cu-Mn,^{5,16} Ag-Mn,^{5,16} and Mg-Mn^{23,101} an anisotropy field on the order of 10's of gauss having a temperature dependence of roughly $1/T$ rather than a Brillouin function is required. Three sources of $\vec{H}_A$ will be considered here: (a) the usual anisotropy field $\vec{H}_{AC}$ associated with the crystalline easy axis, (b) the anisotropy field $\vec{H}_{AE}$ associated with the conduction electron polarization, (c) the anisotropy field $\vec{H}_{AN}$ associated with the nuclear polarization. There is an important distinction between the latter two fields and the first. The nuclear and electronic anisotropy fields are approximately parallel to the sublattice magnetizations, independent of the particular orientation of the crystalline symmetry axis. Thus, if $\vec{H}_{AE}$ and $\vec{H}_{AN}$ dominate, it is possible to use polycrystalline samples without obtaining the usual line broadening associated with $\vec{H}_{AC}$. The theory for $\vec{H}_{AE}$ was developed by Owen et al. but must be modified in light of the more recent knowledge about relaxation rates and processes. Nuclear anisotropy fields have been discussed by Okuda and Date¹⁶ with reference to Ag-Mn. Both theories will be reviewed here.

First consider the investigations of $\vec{H}_{AN}$ in insulators^{99,102,103,104} where its existence has been well established. Essentially,

101. This work.

102. D.T. Teaney, M.J. Freiser, and R.W.H. Stevenson, Phys. Rev. Letters 9, 212 (1962).

103. A.J. Heeger, A.M. Portis, D.T. Teaney, and G. Witt, Phys. Rev. Letters 7, 307 (1961).

104. P.G. de Gennes, P.A. Pincus, F. Hartmann-Boutron, and J.M. Winter, Phys. Rev. 129, 1105 (1963).

$\vec{H}_{AN}$ is the result of a two-step interaction in which the exchange fields $\vec{\Gamma}\vec{M}_1$ and $\vec{\Gamma}\vec{M}_2$ polarize the nuclear spins forming two anti-parallel sublattices which, in turn, produce a field $\vec{H}_{AN}$ acting back on the electronic spins. The coupling mechanism is the hyperfine interaction A. This anisotropy field $\vec{H}_{AN}$ can of course exert no torque on $\vec{M}_1(\vec{M}_2)$ if it is parallel to $\vec{M}_1(\vec{M}_2)$ as will be the case under static conditions. However, in an EPR experiment the precessional frequency of $\vec{M}_1$ and $\vec{M}_2$ is too high for the nuclear spins to follow, and therefore $\vec{H}_{AN}$ will continue to point along the average direction of $\vec{M}_1(\vec{M}_2)$. In this model $\vec{H}_{AN}$ can be written as

$$\vec{H}_{AN} = A \langle \vec{I} \rangle / \gamma_e \hbar \quad (\text{II.53})$$

where $\langle \vec{I} \rangle$ is the thermal average of the nuclear spins given by the usual Curie law behavior

$$\langle \vec{I} \rangle = \hbar \gamma_n I(I+1) \vec{H}_{hf} / 3kT \quad (\text{II.54})$$

and H_{hf} is just the hyperfine field

$$\vec{H}_{hf} = A \langle \vec{S} \rangle / \hbar \gamma_n \quad (\text{II.55})$$

with γ_e and γ_n the electronic and nuclear magneto-mechanical ratios, respectively. Combining (II.53-55) gives

$$\vec{H}_{AN} = I(I+1)A^2 \langle \vec{S} \rangle / 3\hbar \gamma_e kT. \quad (\text{II.56})$$

Below the Néel temperature, $\langle \vec{S} \rangle$ is proportional to $B_S(x)$ and as the temperature decreases it rapidly approaches the saturation value

$\langle \vec{S} \rangle = \vec{S}$. Therefore, at low temperatures H_{AN} is proportional to $1/T$. Typical values for AFM insulators are $H_{AN} = 8.6 \text{ G}/T_n$ in MnCO_3 ⁹⁹ and $H_{AN} = 9.43 \text{ G}/T_n$ in RbMnF_3 ¹⁰² where T_n is the nuclear spin temperature. The obvious test of this scheme is to raise the nuclear spin temperature by saturation of the NMR resonance and observe changes in the EPR resonance associated with a diminished $\vec{H}_{AN}$. This has been done in MnCO_3 ⁹⁹, RbMnF_3 ¹⁰², and KMnF_3 ¹⁰³ with essentially the expected result. The detection of H_{AN} in these materials depends on their exceptionally low crystalline anisotropy fields of only a few gauss.

A look at typical A values for manganese indicates $\vec{H}_{AN}$ will be about 4 times smaller in metals. Specifically, for manganese in insulators, A is $88 \times 10^{-4} \text{ cm}^{-1}$ (94 gauss); while in metals,¹⁰⁵ it has the value $A \approx 45 \times 10^{-4} \text{ cm}^{-1}$. Using the values $I = 5/2$, $\langle S \rangle = 5/2$, and $A = 45 \times 10^{-4} \text{ cm}^{-1}$ in (II.56) yields the value

$$H_{AN} = 2.3/T \text{ G.} \quad (\text{II.57})$$

Motivated by the work in insulators, Okuda and Date¹⁶ have made ENDOR measurements in Ag-Mn. This alloy has the usual downfield

105. This value is the average of the following measurements: Mn in Ag, $A = 40.0 \times 10^{-4} \text{ cm}^{-1}$ from ENDOR data of Okuda and Date [16]; Mn^{54} in Cu, $A = 39 \times 10^{-4} \text{ cm}^{-1}$ and Mn^{54} in Ag, $A = 44 \times 10^{-4} \text{ cm}^{-1}$ from γ ray polarization data of [J.A. Cameron, I.A. Cambell, J.P. Compton, R.A.G. Lines, and G.V.H. Wilson, Phys. Letters 20, 569 (1966)]; Mn in Al, $A = 59 \times 10^{-4} \text{ cm}^{-1}$ from Knight shift data of [H. Launois and H. Alloul, Solid State Commun. 7, 525 (1969)]; and Mn in Al, $A = 45 \times 10^{-4} \text{ cm}^{-1}$ from Knight shift data of Narath and Weaver [35]. The specific value for Mn in Mg is not available, but there is no reason to suppose it should differ substantially from the above values.

shift of the EPR resonance field below T_N which they described using (II.48)

$$\delta H = -H_E H_A / H_a. \quad (\text{II.48})$$

Saturation of the manganese nuclear resonance produced a very slight reduction (a few percent) of the shift δH , clearly indicating a nuclear polarization contribution to $\vec{H}_A$. It does not, however, appear to be the major source of $\vec{H}_A$ as Okuda and Date claim. It is true, as they point out, that δH will only be partially diminished when using a single NMR frequency to saturate an inhomogeneously broadened line. However, the major problem is with their calculated value of H_E^0 . The measured value of $\nu_{\text{NMR}} = 300 \text{ MHz}$ yields $A = 40. \times 10^{-4} \text{ cm}^{-1}$ where¹⁰⁶

$$\nu_{\text{NMR}} = \frac{A \langle S \rangle}{h}. \quad (\text{II.58})$$

Using this value to calculate $\vec{H}_{AN}$ (II.56) and substituting into the formula for δH (II.48) along with the measured values of δH yields $H_E^0 = 590 \text{ kG}$ in Ag-Mn(2%). This is at odds with their T_N of 12 K, evidently obtained from the EPR field shift data (i.e. onset of AFMR). However, this T_N is in agreement with the susceptibility data of Owen et al. who obtain $T_N = 12$ to 20 K in Ag-Mn(4%). Using $T_N = 12 \text{ K}$ in (II.52) yields $H_E^0 = 77 \text{ kG}$. Additional evidence for a smaller H_E^0 is obtained from the work of Chari.¹⁰⁷ Using resistivity

106. Corrections to this formula due to "pulling" of ν_{NMR} are negligible in this alloy [104].

107. M.S.R. Chari, Phys. Stat. Sol. 9, 103 (1965).

data he obtains $H_E^0 = 30, 33, \text{ and } 42 \text{ kG}$ in silver samples containing 0.14, 0.32, and 0.55 atomic percent manganese, respectively. Extrapolating to Ag-Mn(2%) gives $H_E^0 \cong 80 \text{ kG}$. And finally, these values of T_N and smaller values of H_E^0 are consistent with results obtained in Cu-Mn and Mg-Mn. It thus appears that the value of 590 kG is about $7\frac{1}{2}$ times too large or, stated differently, the value of $\vec{H}_{AN}$ is $7\frac{1}{2}$ times too small to explain the observed shifts in Ag-Mn(2%). Since the calculation of $\vec{H}_{AN}$ seems well founded on both theoretical and experimental grounds, there must be some other source of $\vec{H}_A$ with the value

$$H_A' (T = 1 \text{ K}) \cong 7\frac{1}{2} \times (2G) - 2G \cong 13 \text{ G}.$$

It is extremely difficult to estimate the possible contribution of $\vec{H}_{AC}$ to $\vec{H}_A$ but for the reasons discussed below, it is thought to be much less than $\vec{H}_{AE}$ in cubic hosts (Cu, Ag, Au) and perhaps on the order of $\vec{H}_{AE}$ in hexagonal hosts (Mg, Zn).

An excellent discussion of $\vec{H}_{AC}$ appears in Nagamiya et al.⁷⁸ which is drawn on here, in Yosida et al.,¹⁰⁸ and in J. Kanamori.¹⁰⁹ There are three contributions to H_{AC} . Anisotropic crystalline field effects depend on $\vec{L} \cdot \vec{S}$ and $\vec{L} \cdot \vec{H}_a$ coupling and should therefore be relatively small in Mn^{++} . Also, as noted previously, the crystalline field is shielded by the conduction electrons. Magnetic

108. K. Yosida, A. Okiji, and S. Chikazumi, Proc. Int. Conf. Magnetism, Nottingham (1964), published by the Inst. of Phys. and the Phys. Soc. London, p 22.

109. J. Kanamori in Magnetism, Vol. 1, G.T. Rado and H. Suhl, eds., Academic Press, New York, 1963.

dipolar interactions will be small owing to the large average spacing between neighboring magnetic ions in a dilute alloy. Finally, anisotropic exchange interactions (pseudo-dipolar interaction) could result from anisotropic RKKY interactions^{93,110} and may be a source of $\vec{H}_{AC}$. Anisotropic exchange interactions and anisotropic crystalline field effects are responsible for anisotropic g values. The best measurement of this to date has been made by Geschwind et al.⁶⁶ in a single crystal of Cu-Mn(0.1%). They find g isotropic to 1 part in 4000 indicating a very small effect in Cu-Mn.

A more direct measure of the net H_{AC} is obtained from the investigation of Owen et al. on a single crystal of Cu-Mn(5.6%). In the AFM state they found an angular dependence in δH of less than ± 30 gauss compared with a total shift of 1,100 gauss.

Another way of getting at $\vec{H}_{AC}$ follows from considerations of the EPR linewidth in the AFM region. Equations (II.46) and (II.48) predict a difference by a factor of 2 in the shift δH for $\vec{H}_A \parallel$ and $\perp$ to the easy axis, respectively. As a result, a crystalline anisotropy contribution to the linewidth of roughly $\Delta H = \frac{2}{3} \delta H$ is expected for polycrystalline samples in which $\vec{H}_{AC}$ dominates (Fig. 7).

On the other hand, as discussed at the beginning of this section, $\vec{H}_{AE}$ and $\vec{H}_{AN}$ do not lead to line broadening in polycrystalline samples. Data are available for Cu-Mn¹⁶, Mg-Mn¹¹¹, and Zn-Mn.²⁵

110. C. Kittel, J. Appl. Phys. 39, 637 (1968).

111. This work.

FIGURE 7. The crystalline field contribution to the AFMR linewidth in polycrystalline samples.

In Cu-Mn(2%), ΔH is constant at 100 gauss while δH increases to 350 gauss indicating a small $\vec{H}_{AC}$. In Mg-Mn(0.49%), ΔH increases from 225 gauss to 425 gauss with a corresponding shift of $\delta H = 350$ gauss. The data for Zn-Mn is poor because of the large linewidth, but there appears to be a definite broadening of the resonance line in the AFM state. Thus, as might reasonably be expected, $\vec{H}_{AC}$ appears more important in the hexagonal systems than in cubic systems. This assumes that the inhomogeneous broadening due to spatial variations in $\vec{H}_E$ and $\vec{H}_A$ is no greater in hexagonal alloys than in cubic alloys. The data of Tao et al.⁶⁷ for Mg-Gd (discussed in Chapter V) support the hypothesis of significant crystalline field effects in Mg.

The temperature dependence of δH argues against $\vec{H}_{AC}$ being the major source of anisotropy. If it were, we would expect

$$\delta H = -H_E H_A / H_a \propto -B^2(x) / H_a \quad (\text{II.59})$$

which saturates below $T \lesssim T_N/2$ giving a rapidly diminishing $d(\delta H)/dT$

as the temperature is lowered. This is opposite to the observed dependence in Cu-Mn¹⁶ and Mg-Mn²³ which have an increasing $d(\delta H)/dT$ as would be expected for a δH of the form

$$\delta H \propto - B^2(x) T^{-1}/H_a, \quad (\text{II.60})$$

with $H_E \propto B(x)$ and $H_A \propto B(x)T^{-1}$. It is true that in these dilute magnetic materials H_E and H_A probably increase less rapidly than $B(x)$ as the temperature is lowered, but it is unlikely that they could increase toward saturation slowly enough to explain the observed results. For instance, in Cu-Mn(2%) with a T_N of $\cong 23$ K, Okuda and Date¹⁶ found δH still increasing rapidly at 1.5 K.

This brings us to a discussion of $\vec{H}_{AE}$, which can only be considered in a very qualitative way. Owen et al.⁵ proposed the following hypothesis (related to the Kittel-Mitchell shift). In the AFM state half of the conduction electrons will experience an effective field $\lambda \vec{M}_1$ due to sublattice M_1 and half will experience a field $\lambda \vec{M}_2$ due to sublattice M_2 . This polarizes the conduction electrons,

$$\begin{aligned} \vec{M}_S^1 &= \chi_p (\lambda \vec{M}_1) \\ \vec{M}_S^2 &= \chi_p (\lambda \vec{M}_2) \end{aligned} \quad (\text{II.61})$$

which in turn creates a field $\vec{H}_{AE}$ acting back on M_1 and M_2 ;

$$\begin{aligned} \vec{H}_{AE}^1 &= \lambda^2 \chi_p \vec{M}_1 \\ \vec{H}_{AE}^2 &= \lambda^2 \chi_p \vec{M}_2 \end{aligned} \quad (\text{II.62})$$

where χ_p , λ , and $\vec{M}_1$ ($\vec{M}_2$) are given by (II.5), (II.7), and (II.51), respectively. Equations (II.61) and (II.62) must be interpreted with caution. First, a uniform magnetization of the conduction electrons as implied by (II.61) does not exist, but rather an oscillatory polarization given by the RKKY interaction. Second, unlike the situation for $\vec{H}_{AN}$, $\gamma_e \cong \gamma_d$, and therefore the electronic magnetization $\vec{M}_s^1$ and $\vec{M}_s^2$ can, in principle, remain parallel to $\vec{M}_1$ and $\vec{M}_2$, respectively, even under dynamic conditions. In this case $\vec{H}_{AE}$ produces no torque on $\vec{M}_1$ or $\vec{M}_2$. Owen et al. resolved this problem by arguing that under conditions of rapid relaxation of the conduction electrons to the lattice, $\vec{H}_{AE}$ will remain parallel to $\vec{M}_1^0$ and $\vec{M}_2^0$. It is now recognized that this condition of rapid relaxation is not generally met; and further, as Wangsness⁴⁴ has demonstrated, the relaxation of $\vec{M}_s^1$ and $\vec{M}_s^2$ is always toward the instantaneous values of $\vec{M}_1$ and $\vec{M}_2$, respectively, and not their average values. The initial assumption of $\gamma_e = \gamma_d$ suggests a way out of this dilemma. In the AFM state only a small contribution to $\vec{H}_A$ by the nuclear and crystalline field terms is needed to increase the effective γ_d above γ_e .¹¹² The situation is then similar to that for the nuclear anisotropy field and under dynamic conditions $\vec{H}_{AE}$ may be partially effective. The differences in γ are much smaller here than in the nuclear case, but the coupling J is much stronger than A . It is thus conceivable that $\vec{H}_{AN}$ could contribute to the aniso-

112. Equation (II.48) gives a downfield shift for fixed frequency ω_0 . Then with $\omega_0 = \gamma H$ we have $\delta\gamma \propto -\delta H$.

tropy field. A similar situation occurs in alloys containing two paramagnetic impurities with unequal γ .^{94,113} The polarization of the conduction electrons by the one impurity shifts and broadens the resonance of the other.

The most convincing evidence for a significant $\vec{H}_{AE}$ is provided by the results of investigations in ternary alloys by Okuda and Date.^{16,114} For instance, the addition of 0.3% Ni to Cu-Mn(2%) quadruples the shift δH from 350 to 1400 gauss and the linewidth ΔH from 80 to 320 gauss (measured at 1.5 K).¹¹⁴ It is difficult to see how the addition of this small amount of Ni could have any effect on $\vec{H}_{AC}$ or $\vec{H}_{AN}$. The most reasonable interpretation is that by adding a new relaxation path the nickel has changed the dynamics of the local moment-conduction electron interaction in such a way as to enhance the effective $\vec{H}_{AE}$. The effect is not unique to nickel. More recent work by Okuda and Date¹⁶ show similar effects when the added element is Co, Fe, Pd, Ti, and Zn. The addition of aluminum has little effect on either δH or ΔH which reinforces the hypothesis that altered relaxation dynamics increases the effectiveness of $\vec{H}_{AE}$. The theoretically expected temperature dependence of $\vec{H}_{AE}$ is not obvious, but the Cu-Mn data suggest something on the order of $1/T$.

Generalizing, it appears that in cubic systems $\vec{H}_{AC}$ and $\vec{H}_{AN}$ are too small to account for the observed shifts δH , and therefore $\vec{H}_{AE}$

113. M. Peter, J. Dupraz, and H. Cottet, *Helv. Phys. Acta* 40, 301 (1967).

114. K. Okuda and M. Date, *J. Phys. Soc. Japan* 22, 1512 (1967).
Note that Ni does not form a local moment in Cu.

must be an important contributor to the anisotropy field. In hexagonal systems, crystalline field effects are larger, and $\vec{H}_{AC}$ and $\vec{H}_{AE}$ are estimated to be roughly comparable in magnitude.

5. Linewidth and Intensity

There is no adequate theory of linewidths in AFM insulators or metals. The review article by Foner⁸¹ discusses the situation up to 1963 for insulators; and papers by Gerritsen et al.,¹¹⁵ Dayhoff,¹¹⁶ Johnson and Nethercot,¹⁰⁰ and Heller et al.¹¹⁷ are typical of the diversity of results and explanations. Table 1 includes the papers reporting AFMR in metals. None contain theoretical calculations of linewidth.

There are two readily identifiable line broadening mechanisms in addition to those discussed for the paramagnetic region. First, broadening in polycrystalline samples due to crystalline field effects is discussed in the previous section and may be important in noncubic alloys. Second, magnetic inhomogeneities resulting from the random nature of dilute magnetic alloys must be responsible for some of the observed broadening.

Two rough generalizations can be made about the existing linewidth data. First, the linear decrease in linewidth with decreasing

115. H.J. Gerritsen, M. Garber, and G.W.J. Drewes, *Physica* 22, 213 (1956).

116. E.S. Dayhoff, *Phys. Rev.* 107, 84 (1957).

117. G.S. Heller, J.J. Stickler, and J.B. Thaxter, *J. Appl. Phys.* 32, 307S (1961).

temperature observed in the paramagnetic region stops at the Néel temperature (defined here as the point at which the resonance field starts shifting to lower values). Second, as the temperature is lowered below T_N the linewidth usually remains approximately constant in cubic alloys but generally increases in hexagonal alloys.

Line intensities have been found both theoretically^{7,118} and experimentally^{23,96,119} to be comparable to those in EPR. Measurements in metals^{23,96} reveal a decreasing line intensity as the temperature is lowered in the AFM region. As expected for the paramagnetic region, the line intensity increases as the temperature is decreased.

118. H.J. Gerritsen and M. Garber, Commun. Kamerlingh Onnes Lab., Leiden Suppl. #110C.

119. H.J. Gerritsen and M. Garber, Physica 22, 197 (1956).

III. CHARACTERIZATION OF THE Mg-Mn SAMPLES

This chapter will discuss the preparation, analysis, and properties of the Mg-Mn alloys used in this investigation. The parameters needed for the theoretical analysis in Chapter II are obtained and compiled in Table 4. There are several references to the book on magnesium by Raynor¹²⁰ which should be consulted for original references to the literature.

A. Preparation and Analysis

1. Sample Preparation

The alloys were prepared in carbon crucibles using "high purity" materials by Dow Chemical Company, Midland, Michigan. The spectroscopic analysis provided by Dow is included in Table 2. To insure homogeneity the ingots were annealed at 590°C (melting point is 650°C) for 10½ hours under a protective atmosphere of SO₂ and then rapidly quenched in water.¹²¹ Metallurgically Mg-Mn is a "difficult" system. Two metals are generally insoluble in each other if their size difference is greater than 15 percent.¹²² For Mg-Mn the difference

120. G.V. Raynor, Physical Metallurgy of Magnesium and Its Alloys, Pergamon, Elmsford, New York, 1959.

121. In retrospect, it would have been better to cold work the alloys and then heat treat them as this usually results in greater homogeneity. [D.K.C. MacDonald and W.B. Pearson, *Acta Metallurgica* 3, 392 (1955).]

122. Raynor, p.117-118.

TABLE 2

Spectroscopic and Electron Microprobe Analysis of the Mg-Mn Alloys.

Spectroscopic weight per cents											Electron Microprobe atomic per cent
#	<u>Al</u>	<u>Ca</u>	<u>Cu</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Pb</u>	<u>Si</u>	<u>Sn</u>	<u>Zn</u>	<u>Mn</u>
94	<.03	<.01	<.001	<.001	0.090 (0.04 at. %)	<.001	<.01	<.01	<.01	<.02	-
95	<.03	<.01	<.001	<.001	0.14 (0.062 at. %)	<.001	<.01	0.012	<.01	<.02	0.02
96	<.03	<.01	<.001	<.001	0.49 (0.217 at. %)	<.001	<.01	<.01	<.01	<.02	0.11
98	<.03	<.01	<.001	0.001	1.31 (0.583 at. %)	<.001	<.01	<.01	<.01	<.02	0.49

is just 15 percent, so their mutual solubility is expected to be low, as is found experimentally.¹²³ At 650°C the solubility of Mn in Mg is ~1.5 atomic percent and drops very rapidly to <<0.04 atomic percent at 200°C.^{124,125} Thus, for all but the lowest concentrations, it is necessary to quench the ingots rapidly in order to "freeze" the manganese ion into the magnesium lattice.¹²⁶ The manganese enters the magnesium, hexagonal close-packed (hcp) lattice as a substitutional impurity (it is too large to enter interstitially), and the system appears to be free of intermetallic compounds.^{125,127}

2. Sample Composition

The spectroscopic analysis of the bulk material (Table 2) loses much of its value for inhomogeneous samples. Because of the low solubility of manganese in magnesium, it was in fact doubted whether the samples were homogeneous, and therefore a detailed analysis was made at Battelle Memorial Institute (Columbus) by experienced metallurgists. Although second phase material was found to be present, it was possible to quantify the sample properties sufficiently to maintain confidence in the final results of this investigation.

Metallographic examinations were made on sections of each sample which had been polished to 0.05 μ M alumina finish. For all three

123. The metallic radii of Mn and Mg are 1.35 Å and 1.60 Å, respectively. [122]

124. Raynor, p. 432.

125. M. Hanson, Constitution of Binary Alloys, McGraw-Hill, New York, 1958.

126. It is still not possible, of course, to exceed the high temperature solubility limit of 1.5 atomic percent.

127. Raynor, p. 434.

samples, two phases consisting of individual particles less than $3 \mu\text{M}$ in diameter were detected in addition to the matrix phase. One of these phases appeared dark, while the other had a metallic luster and polished in relief, indicating that it was harder than the bulk matrix. Together these two phases represent approximately two percent by volume of sample #96 and somewhat less for the other two. This is not surprising as it is typical to have on the order of one percent second phase present in "difficult" alloy systems.¹²⁸

Electron microprobe and transmission electron diffraction techniques were used to analyze the second phase material. Both the light and dark particles were found to be high in manganese content, but a quantitative determination was not possible because the electron beam diameter of the microprobe was greater than the diameter of the particles being investigated. The dark particles fluoresced under the electron beam which generally indicates the presence of oxygen. To investigate this more thoroughly some of the particles were removed using a replication technique and analyzed in an electron microscope by transmission electron diffraction. The standard pattern for MnO was obtained indicating that the dark phase particles are probably of this composition. The light phase particles were not positively identified but may be manganese carbide. Free manganese seems less likely because of the amount available.

128. Discussion with J.F. Pashak, Dow Chemical Company; and K.C. Brog, Battelle Memorial Institute.

Clearly, a large portion of the manganese has been removed from the magnesium matrix by the second phase particles. This is not necessarily a serious problem if (a) the true manganese, solid solution concentrations can be determined and (b) the second phase particles do not contribute to the resonance. The manganese concentrations were readily obtained with the electron microprobe by carefully aligning the beam so that it missed the second phase particles and only impinged on the bulk matrix. The averages of several measurements yielded manganese concentrations of 0.49, 0.11, and 0.02 atomic percent in samples #98, #96, and #95, respectively. The differences between the spectroscopic and microprobe values (see Table 2) can be explained in the following way.¹²¹ In the high concentration samples a fixed amount of manganese is removed from solid solution by the oxygen (and carbon?). These, in turn, are assumed constant for alloys made under identical conditions from the same stock material. In the lower concentration alloys, the amount removed must decrease (it is not possible to remove more Mn than is present!) but will become a larger fraction of the total manganese available.

Point (b) above can be handled in two ways. In Chapter V it is shown that the EPR data have the characteristic nature expected of resonances in dilute magnetic alloys, and vary from sample to sample in a way consistent with the electron microprobe determinations of concentration. Of particular note, the EPR data indicate a transition from paramagnetic to antiferromagnetic resonance at temperatures

of 9, 5, and $2\frac{3}{4}$ K in samples #98, #96, and #95, respectively.

In this section the possible second phase materials and their likelihood of contributing to the resonance will be considered. If manganese were present in any of its nonmetallic, paramagnetic forms (e.g. Mn impurity in MgO), the usual hyperfine structure with six lines would be observed. It is not, thus eliminating this possibility. Table 3 lists the Néel temperature of manganese and several of its antiferromagnetic compounds.

TABLE 3

Néel Temperatures of α Mn and Some Mn Compounds.
Data from Kittel [29], Smart [97], and Martin [129].

Material	Néel Temperature T_N
α Mn	100 K
MnO	118 K
MnO ₂	92 K
MnS	160 K
MnS ₂	60 K

EPR has not been observed in α Mn and the Néel temperature is too large to fit the Mg-Mn data. Compounds containing oxygen, sulfur, or carbon seem most likely because it is difficult to exclude oxygen,

129. D.H. Martin, Magnetism in Solids, M.I.T. Press, Cambridge, Massachusetts, 1967.

SO₂ was used for a protective atmosphere during heat treatment, and carbon crucibles were used in making the alloys. The high Néel temperatures in the oxygen and sulfur compounds indicate large internal fields which in turn would require very high frequencies and/or high magnetic fields to observe any resonances present. Only compounds of manganese with the halogens have low T_N comparable with those observed in the Mg-Mn samples, but the halogens are an unlikely impurity in these alloys. Manganese carbide is the only possibility, about which little is known. The reported chemical composition of manganese carbide changes from year to year^{125,130,131} and its magnetic properties are not known.¹³² It is probably an unlikely contributor to the resonance for the same reasons that apply to the other compounds. In considering these impurities, it must be remembered that any single compound would have a fixed transition temperature independent of the bulk alloy, manganese concentration. Finally, it is repeated that the observed resonances are consistent with the results obtained for other alloys and with the electron microprobe determinations of the manganese concentration in the matrix phase.

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130. R.P. Elliott, Constitution of Binary Alloys, First Supplement, McGraw-Hill, New York, 1958.
131. F.A. Shunk, Constitution of Binary Alloys, Second Supplement, McGraw-Hill, New York, 1969.
132. H. J. Goldschmidt, Interstitial Alloys, Plenum Press, New York, 1967.

3. Resistance Ratio Measurements

The resistance ratio is defined here^{29,133} as $R_{RT}/R_{4.2}$, the ratio of the room temperature resistance to the resistance at liquid helium temperature. For high purity metals the resistance ratio will be very high (in the thousands) because in such materials the resistance is primarily due to electron phonon scattering which decreases rapidly as the temperature is lowered (fewer phonons). On the other hand, in alloys the impurity (solute) scattering is roughly temperature independent (Matthiessen's rule). The impurity and phonon contributions are additive with the result that the larger the impurity contribution the smaller the resistance ratio. It has been found in many alloys that impurities not in solid solution, but combined as oxides, for instance, do not contribute appreciably to the resistance.¹²¹ In this case, the resistance ratio will be higher than might be expected on the basis of the net impurity concentration. Thus, resistance ratio measurements can be used as a measure of the true solid solution, impurity concentration.^{18,20,121} The difficulty with this is that initially, for calibration purposes, some independent means must be used to determine the effective impurity concentration.

Gaudet et al.¹⁹ and Hedgcock et al.¹⁸ report resistance ratio versus net impurity concentration data for Mg-Mn which are interesting to compare with the results of this investigation (Figure 8).

133. There are several similar ways of defining the resistance ratio, all being about the same.

FIGURE 8. Resistance ratio in Mg-Mn alloys. It is shown that bulk concentration measurements over estimate the true manganese solid solution concentration.

It is possible to independently calculate the manganese, solid solution concentrations in their alloys using the resistance ratio versus impurity concentration curve calibrated with electron microprobe measurements. When this is done, it is found that their bulk concentration measurements overestimate the amount of manganese in solid solution, as expected. This specific heat data of Martin²⁰ are dependent on the measurements of Gaudet et al. and also need correction.

B. Physical Properties of the Samples

1. Lattice Structure and Density

Pure magnesium crystallizes in the hexagonal close-packed structure (hcp). The unit cell is described by the primitive lattice vectors $\vec{t}_1$, $\vec{t}_2$, and $\vec{t}_3$ where $\vec{t}_3$ is perpendicular to $\vec{t}_1$ and $\vec{t}_2$, and the latter two have an angle of $2\pi/3$ radians between them (Figure 9). The magnitudes are $t_1 = t_2 = a = 3.19 \text{ \AA}$ and $t_3 = c = 5.18 \text{ \AA}$ at 0 K

FIGURE 9. The hexagonal close-packed structure. t_1 , t_2 , and t_3 are the primitive translation vectors. There are two atoms per unit cell centered at the origin and τ .

giving a c/a ratio of 1.62.¹³⁴ There are two atoms per unit cell.

If one is located at the origin, the other is at

$$\vec{r} = (2/3)\vec{t}_1 + (1/3)\vec{t}_2 + (1/2)\vec{t}_3. \quad (\text{III.1})$$

The volume of the unit cell is

$$2\Omega = \vec{t}_1 \cdot \vec{t}_2 \times \vec{t}_3 = a^2 c \sin (2\pi/3), \quad (\text{III.2})$$

and the density is 1.76 gm/cm³ using the value from Ketterson and Stark¹³⁴ extrapolated to absolute zero.

Addition of manganese in the amount of 1/2 atomic percent or less decreases the lattice constants by much less than one percent¹³⁵ as is predicted by the approximate relationship (Vegard's law)¹³⁶

$$d_a = nd_{\text{Mn}} + (1-n)d_{\text{Mg}}, \quad (\text{III.3})$$

where n is the atomic fraction of manganese, and d_a , d_{Mn} , and d_{Mg} are the mean interatomic distances of the alloy, manganese, and magnesium, respectively. Because the changes are small, and for convenience, the pure magnesium lattice parameters are used in this investigation and provide ample accuracy. For the same reasons, the $T = 0$ K parameters are used at all temperatures (in the range $T = 2$ to 100 K). At room temperature, thermal expansion has only increased the lattice constants by 1/3 of a percent.¹³⁷

134. J.B. Ketterson and R.W. Stark, Phys. Rev. 156, 748 (1967).

135. Raynor, p. 85.

136. Raynor, p. 67.

137. Raynor, p. 10.

Using these approximations, the number of atoms per unit volume is

$$N_0 = 1/\Omega = 4.37 \times 10^{22} \text{ atoms/cm}^3.$$

Magnesium has the electronic configuration $[\text{Ne}] 3s^2$ and manganese the configuration $[\text{Ar}] 3d^5 4s^2$. Both give up their outer two, s electrons to the conduction band and therefore the free electron per atom ratio is not changed on alloying with manganese. The number of conduction electrons per unit volume is

$$n = 2N_0 = 8.74 \times 10^{22} \text{ conduction electrons/cm}^3.$$

2. Free Electron Model Properties

The parameters $\eta(E_f)$, E_f , and v_f are needed to evaluate several of the expressions in Chapter II. $\eta(E_f)$ is the density of states per unit volume and spin direction at the Fermi surface, E_f is the Fermi energy, and v_f is the velocity of an electron at the Fermi surface. These are calculated in the free electron gas model.²⁹ This is a good approximation for magnesium if an effective mass $m^* = 1.33 m$ is used, where m is the electron mass.^{134,138,139}

The usual expressions for E_f and $\eta(E_f)$ are²⁹

$$E_f = \frac{\hbar^2}{2m^*} (3\pi^2 n)^{\frac{2}{3}} \quad (\text{III.4})$$

and

$$\eta(E) = \frac{1}{4\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2}. \quad (\text{III.5})$$

138. I. Estermann, S.A. Friedberg, and J.E. Goldman, Phys. Rev. 87, 582 (1952).

139. Discussion with D.A. Zych, The Ohio State University.

Solving (III.4) for m^* and substituting in (III.5) with $E = E_f$ gives

$$\eta(E_f) = 3n/4E_f . \quad (\text{III.6})$$

The Fermi velocity v_f is

$$v_f = \hbar k_f / m^* \quad (\text{III.7})$$

where k_f is the Fermi wave number

$$k_f = (3\pi^2 n)^{\frac{1}{3}} . \quad (\text{III.8})$$

The values of all these parameters for magnesium at $T = 0$ K are given in Table 4.

3. Antiferromagnetic Properties

This section presents additional evidence for the antiferromagnetic character of Mg-Mn at low temperatures and thus strengthens the AFMR interpretation of the microwave data.

Magnetic susceptibility measurements have been made by Owen et al.^{4,5} and Collings and Hedgcock.²³ A transition to AFM is indicated by a leveling off in magnetic susceptibility as the temperature is decreased. Owen et al. report a value of $T_N = 0$ to 4 K in Mg-Mn (0.67%) and the data of Collings and Hedgcock indicate a T_N of 8 K in Mg-Mn (0.59%). These measurements do not agree too well with each other or with the EPR determined Néel temperatures of this work. However, the reported concentrations are bulk values and do not necessarily represent the amount of manganese in solid solution. The absolute value of the magnetic susceptibility can be used to

TABLE 4

Physical Parameters of Mg at $T = 0$ K.
 These are nominally correct for dilute Mg-Mn alloys.

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	$\rho = 1.76 \text{ gm cm}^{-3}$
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	$v_f = 1.20 \times 10^8 \text{ cm sec}^{-1}$
Energy	$E_f = 5.4 \text{ ev}$
Density of states	$\eta(E_f) = 1.21 \times 10^{22} \text{ states ev}^{-1} \text{ spin}^{-1} \text{ cm}^{-3}$
Fermi temperature, E_f/k_B	$T_f = 6.67 \times 10^4 \text{ K}$

determine the amount of manganese in solid solution if the manganese ion is assumed to be in a pure Mn^{++} , $S = 5/2$ state with magnetic moment²⁹

$$\mu = p\beta = g \sqrt{S(S+1)} \beta = 5.92 \beta \quad (\text{III.9})$$

where p is the size of the moment in units of Bohr magnetons β , g is the spectroscopic splitting factor, and S is the net angular momentum ($L = 0$). Owen et al. and Collings and Hedgcock report p_{eff} values of 3.55 and 4.75 respectively, using

$$p_{\text{eff}} = (3 k C/N_0 C_I \beta^2)^{\frac{1}{2}} \quad (\text{III.10})$$

where N_0 is the number of atoms per unit volume, C_I is the atomic fraction impurity concentration, and C is the measured Curie constant, $C = \chi(T-\theta)$. Using (III.10), an adjusted value of C_I can be computed:

$$C_I(\text{adjusted}) = \frac{p^2(\text{measured})}{p^2(\text{theoretical})} C_I(\text{bulk}). \quad (\text{III.11})$$

With this correction to the concentrations, the Néel temperatures determined from susceptibility measurements are in reasonable agreement with the EPR determined Néel temperatures. (Table 5)

The resistivity data of Gaudet et al.¹⁹ also indicate a transition to the antiferromagnetic state in these alloys.¹⁴⁰ They observed a resistivity curve of the form shown in Figure 10.

140. They did not offer this interpretation because resistivity anomalies in dilute alloys were not understood at that time (1960).

Néel Temperatures of Mg-Mn Alloys.

Reference		T_N (EPR)	T_N (Susceptibility)
	(at.%)	(K)	(K)
This work ^a	0.02	$2\frac{3}{4}$	-
This work ^a	0.11	5	-
Owen et al. ^b	0.24	$\sim 4^c$	0 to 4
Collings and Hedgcock ^b	0.38	6	8^c
This work ^a	0.49	9	-

a. Electron microprobe values of C_I .

b. C_I calculated from measured susceptibility (see text).

c. Estimated by this investigator using their data.

FIGURE 10. Typical resistivity curve of Mg-Mn. The low temperature anomalies are exaggerated.

Such data are now given the following interpretation.^{54,55} At temperatures below the local minimum the resistivity begins to rise because of the Kondo $\ln T$ term, but when antiferromagnetic ordering occurs at even lower temperatures the $\ln T$ term is suppressed and the resistivity exhibits a local maximum. The temperature of the local maximum occurs in the range from 1.2 K to 6.7 K in Mg-Mn alloys with bulk manganese concentrations of 0.16 to 0.60 atomic percent. Thus the AFM character of Mg-Mn alloys at low temperatures is well established.

IV. EXPERIMENTAL PROCEDURE

A. Microwave Spectrometer

Microwave measurements were made at ~ 9.4 GHz (X band) and ~ 23.5 GHz (K band) using reflection cavity spectrometers. A block diagram of the X band spectrometer appears in Figure 11. The K band unit was essentially the same except for the substitution of a magic T in place of the circulator. The spectrometer configurations are of the balanced bridge form. With the cavity perfectly coupled to the wave guide, no power is reflected back to the diode detector. Then when the magnetic field is adjusted for resonance, the sample absorbs power, "loading" the cavity and changing its Q. The resultant impedance mismatch between cavity and wave guide reflects power back to the detector, allowing the resonance to be observed. In actual operation the bridge is unbalanced slightly in order to bias the detector diode. Additionally, conventional "lock-in" detection methods were used to substantially improve the signal to noise ratio. This is achieved by the "trick" of shifting the demodulated microwave resonance signal from approximately DC to audio frequencies. This allows high gain, low noise, narrow band amplifiers to be used; in this case, a Princeton Applied Research (PAR) HR-8 lock-in amplifier. The audio frequency resonance signal is obtained by modulating the magnetic field with a pair of Helmholtz coils on the magnet pole faces. The driving frequency is

FIGURE 11. Spectrometer block diagram.

obtained from the PAR reference oscillator and is a compromise between high frequencies to reduce $1/f$ noise in the detector and low frequencies to pass through the stainless steel dewar walls and the microwave cavity walls without severe attenuation. A frequency of 145 Hz with peak to peak amplitudes on the order of 20 to 40 gauss was used.

After amplification and demodulation by the PAR, the signal is directed to the X-Y recorder. The PAR demodulator is a full wave rectifier driven at the reference oscillator frequency and with phase adjustable to that of the returning diode detector signal. Hence, the name "phase sensitive detector". This method of detection results in the complete rejection of all noise 90° out of phase with the input signal. Because the modulation field "samples" the slope of the resonance, the final PAR output signal is the derivative of the absorption, dP/dH . A more complete description of this can be found in Assenheim.¹⁴¹

Microwave power was generated by Varian V-58 and EM-1188 reflex klystrons at X and K band, respectively. The microwave power was limited to approximately 10 milliwatts because of several factors, including the need to minimize sample heating at low temperatures.

The magnetic field was provided by a Varian V-3400, 15 inch electromagnet, controlled by a Mark II Fieldial unit which allowed the magnetic field to be swept slowly through the resonance (5 to

141. H.M. Assenheim, Introduction to Electron Spin Resonance, Monographs on Electron Spin Resonance, Plenum Press, New York, 1966.

10 minute sweeps). The Fieldial senses the magnetic field (with a Hall probe) rather than the magnet current, and is thus able to provide accurate and stable sweeps without hysteresis.

Because the resonance linewidths are so broad (200 to 600 gauss), only moderate accuracy is needed for the magnetic field and microwave frequency measurements. At X band the frequency was measured with a Hewlett-Packard X532B wavemeter. It was found to be accurate to 1 part in 5000 via an "in system" calibration using an EIP 360A frequency counter with autoheterodyne converter (time base accuracy 1 part in 10^7 overall). The K band frequency measurements were made using a Hewlett-Packard K532A wavemeter with a stated accuracy of 1 part in 1000. The magnetic field was determined to 1 part in 500 by calibration of the Fieldial using a Ventron nuclear magnetic resonance gaussmeter ("Pound box") and the EIP frequency counter.¹⁴² This last error corresponds to less than 1/33 of the linewidth at X band, and less than 1/20 of the linewidth at K band. The g values of #98-K, #98-X, and #96-X were determined using a DPPH calibration signal obtained by placing a minute quantity of DPPH in the Mg-Mn cavities ($g_{\text{DPPH}} = 2.0036$).⁶⁴

The klystron is "locked" to the cavity resonance frequency with an automatic frequency control (AFC). This device frequency modulates¹⁴³ the klystron by applying a low voltage 10 kHz signal

142. Much higher accuracies are attainable using this method if needed.

143. This modulation must be much less than the equivalent frequency linewidth $\gamma\Delta H$ of the resonance signal.

to the klystron reflector. The resultant variation in spectrometer output signal is detected by a phase sensitive amplifier similar in principle to the PAR. The rectified AFC output is applied to the klystron reflector and always has the correct polarity necessary to reduce the frequency deviation between klystron and cavity resonance frequency.

B. Samples

Rectangular TE 101 and TE 102 cavities were used at X and K band, respectively. These were machined (with a vertical mill) out of single pieces of the Mg-Mn samples, making it possible to eliminate the impurity signals generally found in copper, brass, or plated cavities. After construction, the interiors of the cavities were "sand blasted" with glass beads to eliminate any preferential surface structure resulting from the milling operation. Despite the rounded corners and "sand blasted" surfaces, Q's exceeding 1000 were obtained. Only those interior cavity surfaces bordering on regions of large rf magnetic field contribute to the resonance.

As a final step before each data run, the cavities were cleaned in an ultrasonic cleaner with reagent grade chemicals in the sequence, benzene, acetone, acid etch, and acetone. Concentrated sulfuric acid was found to give the cleanest surface. A clean cavity is crucial. Impurity signals and not spectrometer sensitivity are generally the limiting factor in the observation of very weak resonances.

C. Cryostat

Low temperatures were achieved with a stainless steel Andonian variable temperature dewar. Starting outside and working toward the center, the dewar has the following construction; vacuum space, liquid nitrogen (LN_2) jacket, vacuum space, liquid helium (LHe) reservoir, vacuum space, and central tube for experimental apparatus.¹⁴⁴ The central tube containing the waveguide and cavity is cooled by the flow of cold helium gas through it. The cooling is regulated by a throttle valve which allows a small flow of LHe from the helium reservoir into the bottom of the central tube where it vaporizes. The cavity is thermally isolated from the rest of the spectrometer with a section of stainless steel waveguide. Below 10 K small fluctuations in the He gas density, and therefore dielectric constant, produced fluctuations in the cavity resonance frequency which were too rapid for the AFC to follow.¹⁴⁵ This difficulty was eliminated by reducing the pressure in the central tube to a few torr using a vacuum pump. As an added advantage, pumping allows temperatures below 4.2 K to be reached. In practice, temperatures as low as 2.3 K could be obtained by these means.

144. The three vacuum spaces are innerconnected. Because of the usual space restrictions, the tail section fitting between the magnet pole faces does not have an LN_2 jacket, but instead has a metal shield thermally anchored to the LN_2 reservoir.

145. At higher temperatures flow instabilities produced fluctuations of a similar nature but were easily eliminated by creating a slight back pressure (of a few inches of water) at the He gas exhaust port.

Slightly lower temperatures were obtained by flooding the central tube (and cavity) with LHe and pumping on it until it became superfluid below the λ point (2.3 K).¹⁴⁶ Then with the microwave power and magnetic field modulation reduced to a minimum, temperatures in the range 2.1 to 2.3 K were obtained.¹⁴⁷

The temperature of the cavity was controlled and stabilized with a Leeds & Northrup Electromax temperature controller. This unit compares the voltage of an (Au-Fe)-Chromel thermocouple, attached to the cavity; with an internal, variable, reference voltage. Deviation between the two indicates a deviation from the set temperature (reference voltage) and if the cavity is too cold, heat is supplied by a manganin heater wire wrapped around the cavity. At the set temperature the controller is able to maintain just the right amount of heating necessary to oppose cooling, rather than cycling on and off. Below 7 K the controller was not used as the natural stability and speed of response of the system was greater than that obtainable with the control loop. In this mode of operation the temperature was changed by varying the throttle valve setting.

Two Cryo Cal, Inc., CR-1000 Germanium Resistance Thermometers were used to measure the cavity temperatures, one each for the X

146. The spectrometer will not operate with "normal" helium in the cavity because of frequency fluctuations caused by bubbles in the boiling LHe.

147. The magnetic modulation field generates eddy currents in the walls of the dewar and cavity which leads to Joule heating.

and K band spectrometers, respectively.¹⁴⁸ They were calibrated at LHe and LN₂ temperature, but it is difficult to determine their absolute accuracy over the entire temperature range. The absolute error may be as large as 1 or 2 K at some temperatures. Equally important are the internal consistency and repeatability of the temperature measurements. The major source of uncertainty in the measured temperature is the observed drift during the time required for magnetic field sweeps through the resonance line. The temperature was measured immediately before and after each field sweep and the mean value used in plotting the data. Drift was on the order of 0.1, 0.3, and 0.5 K in the temperature ranges 2 to 7 K, 7 to 25 K, and 25 to 100 K, respectively. Difficulties associated with temperature differences between the cavity and powder samples mounted in wax or thin sheet samples mounted along the cavity wall are avoided here, because the cavity is the sample and has the heater and temperature sensors mounted directly on it.

D. Data Recording and Reduction

Data were recorded on a Varian F80, X-Y recorder. Field sweeps of 2.5 or 5 kG were generally used, giving a scale of 6½ or 13 gauss per millimeter, respectively; and measurements were made to 1/2 mm accuracy. At least two field sweeps were made at each

148. The CR-1000 model is doped for optional use in the 1.5 to 100 K range.

temperature, one with increasing field and one with decreasing field. This was done in order to determine the hysteresis resulting from the combined effects of electronic lag due to long PAR time constants, recorder hysteresis, and magnetic field hysteresis in the samples and/or magnet control loops. Hysteresis in the recorder and PAR filter circuits was readily identifiable and corrections made for it. When separately measured, no hysteresis was found (nor expected for the sweep ranges used) in the magnet control circuits. Any magnetic hysteresis in the samples is less than 10 gauss.

The method of Peter et al.⁷⁴ (Figure 2) is very suitable for measuring experimental spectra and was used in both the paramagnetic and the antiferromagnetic region. With this method the linewidth and resonance field are essentially determined by the measurement of the low field peak which, being much larger than the high field peak, is less susceptible to distortion by noise or base line drift.¹⁴⁹ Only $y = y_1/y_2$ depends on the high field peak and neither the linewidth nor resonance field are sensitive to small variations in y . The determination of y is discussed further in Chapter V.

149. The major source of base line shift is an interaction between the magnetic, modulation field induced eddy currents in the cavity walls and the main magnetic field [G. Feher, Bell System Tech. J. 36, 449 (1957)]. Specifically, the cavity walls are distorted by magnetic forces on the eddy currents and as the main field slowly sweeps through the resonance the distortion changes. This in turn alters the cavity coupling and shows up as a change in the detector current. The PAR could easily filter out these effects were it not for the fact that they are oscillating at the modulation field frequency which is precisely the frequency to which the PAR is tuned.

Because the resonance field depends on the spectrometer frequency, it is necessary to normalize the data for each sample to a specific frequency. Frequency changes occur when the cavity is filled with liquid helium ($\Delta f/f \cong 0.03$) or as a result of acid cleaning the cavity. In both cases the cavity resonance frequency is lowered; in the former case because the microwaves have a shorter wavelength in liquid helium causing the cavity to appear larger; and in the latter case because the cavity actually is slightly larger (on the inside). These frequency induced field shifts are compensated with the formula

$$\delta H = \left(\frac{h}{g\beta} \right) \delta f$$

or

$$\delta H \text{ (Gauss)} = 0.357 \delta f \text{ (MHz)}.$$

In sample #98, χ is large enough to require a consideration of demagnetization corrections. For paramagnetic samples, a resonance field shift of $\delta H = -2\pi\chi H_0$ or $\delta H = +4\pi\chi H_0$ is expected when H_0 is parallel or perpendicular to the sample surface, respectively.⁵ For a hollow rectangular cavity the field shifts for adjacent walls tend to oppose each other and primarily lead to a slight line broadening of no more than a few ten's of gauss. The demagnetization corrections are somewhat different in the antiferromagnetic state⁸¹ but again are expected to be negligible. If demagnetization corrections are important, the resonance field will shift as the cavity is rotated relative to the field. Such an effect was

looked for but not definitely observed and therefore no demagnetization corrections were made.

E. Resistance Ratio Measurements

The room temperature and liquid helium temperature resistances of samples #94, #95, #96, and #98 were obtained using the standard four terminal method (two leads for current and two for voltage) with screw type contacts. The results are estimated to have an uncertainty of ten percent and appear in Figure 8.

V. RESULTS AND DISCUSSION

A. Paramagnetic Resonance Results

In Section 1 below, the linewidths and various relaxation processes are discussed. It is shown that the Mg-Mn system is bottlenecked and that no hyperfine structure is expected. A lower limit is obtained for $|J_{sd}|$. Section 2 discusses the measured g values and in Section 3 the theoretical line shapes of Peter et al.⁷⁴ are shown to fit the observed line shapes.

The samples investigated are designated as #98-K, #98-X, #96-X, and #95-X; where "X" refers to X band measurements and "K" refers to K band measurements.

1. Linewidths and Relaxation Rates

Equation (II.27)

$$\gamma\Delta H = \delta_{sL} \left(\frac{3 \eta(E_f) k T}{2 N_0 S(S+1)C_I} \right) \quad (\text{II.27})$$

appropriate for a bottlenecked resonance, predicts a linewidth ΔH increasing linearly with T. The dependence of ΔH on C_I is complicated by the dependence of δ_{sL} on C_I , but it is generally observed (Cu-Mn, Ag-Mn) that the linewidths become narrower for higher concentrations of the paramagnetic impurity. The temperature and concentration dependence of the observed Mg-Mn linewidths are shown in Figures 12 through 15, and they exhibit the characteristics just described.

FIGURE 12. The temperature dependence of the linewidth, ΔH , in Mg-Mn(0.49%) at K band.

FIGURE 13. The temperature dependence of the linewidth, ΔH , in Mg-Mn(0.49%) at X band.

FIGURE 14. The temperature dependence of the linewidth, ΔH , in Mg-Mn(0.11%) at X band.

FIGURE 15. The temperature dependence of the linewidth, ΔH , in Mg-Mn(0.02%) at X band.

At the lower temperatures the linewidths are observed to level off or to start increasing with decreasing T , and this is attributed to a transition to antiferromagnetic resonance. The apparent, less than linear increase of ΔH with T at the higher temperatures is primarily attributed to the difficulty of measuring the very broad, weak lines observed at these higher temperatures; and it is not believed to be a real effect. For this reason the higher temperature data are given less weight in determining the rate of change of linewidth with temperature. This slope, $d(\Delta H)/dT$, can be used to find the effective spin-lattice relaxation rate δ_{sL} given by (II.28),

$$\frac{d(\Delta H)}{dT} = \delta_{sL} \left(\frac{3 \eta (E_f) k}{2 N_0 \gamma S(S+1) C_I} \right). \quad (\text{II.28})$$

The values so obtained are listed in Table 6. For comparison, the lone value of Collings and Hedgcock²³ is also given. As expected, the spin-lattice relaxation rate is dominated by relaxation through the manganese ion cores (Sec. II-B-3).

A lower limit for the magnitude of J_{sd} can be obtained if the very reasonable assumption is made that δ_{sL} is proportional to C_I . The argument is as follows: The general linewidth expression is

$$\gamma \Delta H = \left(\frac{\delta_{sL}}{\delta_{sL} + \delta_{sd}} \right) \delta_{ds} + \gamma \Delta H (T = 0) \quad (\text{II.20})$$

where an extra term, $\Delta H(T = 0)$, has been added for the residual linewidth at $T = 0$ K. Solving for δ_{sL} , eliminating δ_{sd} and δ_{ds} with (II.25) and (II.26), respectively; and using appropriate

TABLE 6
Spin Lattice Relaxation Rates in Mg-Mn^a

Sample	Mn Concentration (at.%)	δ_{sL} (10^{10} sec^{-1})
#98-K	0.49	11. +2-1
#98-X	0.49	11.4 $\pm$ 0.6
Collings & Hedgcock	0.38 ^b	7.8 +4-2 ^c
#96-X	0.11	4.7 $\pm$ 0.5
#95-X	0.02	3.1 $\pm$ 0.8

- a. Calculated using (II.28).
b. Adjusted value. See Section III-B-2.
c. Values calculated from their published linewidth data, Fig. 6, Ref. [23]. ΔH_{PTP} has been converted to ΔH using (II.36).

parameters for Mg-Mn (Table 4) yields finally,

$$\delta_{sL} = \left[\frac{0.233 T}{C_I \% [\Delta H(T) - \Delta H(0)]} - \frac{0.0000324}{C_I \% J_{sd}^2} \right]^{-1} \times 10^{10} \text{ sec}^{-1} \quad (\text{II.20}')$$

where the linewidth is in gauss, T in Kelvin, J_{sd} in electron volts, and $C_I\%$ is the manganese concentration in atomic percent. The first term on the right corresponds to the bottleneck limit and the second term contributes when the bottleneck is broken ($\delta_{sL} \gg \delta_{sd} \sim J_{sd}^2$). For J_{sd}^2 large, (II.20') yields the values of δ_{sL} given in Table 6. The effect of decreasing $|J_{sd}|$ is shown in Figure 16. Only the more accurate results (for samples #98-X, #96-X, and #95-X) are included.

FIGURE 16. The effect on δ_{sl} of changing J_{sd} , calculated with (II.20'). Data for sample # 98-X, # 96-X, and # 95-X.

It will be noticed that as $|J_{sd}|$ becomes smaller, the relationship between δ_{sL} and $C_I\%$ is no longer linear. Indeed, for $|J_{sd}| = 0.1$ eV, (II-20') predicts δ_{sL} to be 40% greater in the more dilute 0.02% sample than it is in the 0.11% sample; which is a most unlikely result. The lowest reasonable value of $|J_{sd}|$ is estimated to be 0.12 eV if the errors in the measured slopes, $d(\Delta H)/dT$, are considered. This is comparable with the estimate of $J_{sd} \cong 0.1$ eV in Cu-Mn given by Heeger.³ Calculations of J_{sd} using susceptibility, specific heat, and optical data yield a value of $J_{sd} \cong -0.5$ eV for Mn^{++} in metallic hosts.¹⁵⁰ However, it is generally found that EPR determinations of J_{sd} yield smaller values than other types of measurements because of the wavevector dependence of the exchange integral.^{3,113,151} Thus, the result, $|J_{sd}| \geq 0.12$ eV, is consistent with other estimates of J_{sd} .

The concentration dependence of the spin-lattice relaxation rate, $d(\delta_{sL})/d(C_I\%)$ is $16.7 \pm 4 \times 10^{10} \text{ sec}^{-1} (C_I\%)^{-1}$; taking into account the uncertainty in J_{sd} , the determination of $C_I\%$, and the linewidth data. This value can be expressed as a spin-flip scattering cross section using (II.29). The result is $\sigma_{Mn} = 2 \times 10^{-18} \text{ cm}^2$.

Extrapolation of the δ_{sL} versus $C_I\%$ curve to $C_I\% = 0$ yields a residual spin-lattice relaxation rate of $3 \times 10^{10} \text{ sec}^{-1}$. An

150. D.A. Smith and G.B. Smith, Phys. Rev. B 4, 191 (1971).

151. EPR measurements depend on $J_k(q = 0)$ while other properties depend on $J_k(q \sim 2k_f)$, Ref. [3] and [113].

estimate of the intrinsic spin-lattice relaxation rate, δ_{sL}^I , can be determined from resistivity data in high purity magnesium.¹⁵² Using the simple approximation²⁹

$$\delta_{sL}^I (4.2 \text{ K}) \cong \tau^{-1} = (ne^2 \rho_{4.2})/m^* \quad (\text{V.1})$$

where τ is the mean free time between collisions yields

$\delta_{sL}^I = 0.08 \times 10^{10} \text{ sec}^{-1}$.¹⁵² This latter result, as well as the temperature independent nature of the observed δ_{sL} , demonstrates that the residual spin-lattice relaxation rate is almost wholly due to residual impurities, lattice defects, and surface relaxation rather than intrinsic spin-lattice relaxation. These data are collected and compared with the available data for Cu-Mn and Ag-Mn in Table 7.¹⁵³

The relaxation rates δ_{ds} , δ_{sd} , δ_{sL} , and δ_{eff} are listed in Table 8. Comparison of δ_{sd} and δ_{sL} indicates the extent to which the relaxation bottleneck exists. The values in Table 8 may also be used to test the criteria for the suppression of hyperfine splitting,

$$\delta_{sL} \ll \delta_{sd}$$

and

$$\omega_{\text{hf}} \ll \delta_{ds} .$$

(II.31)

152. Suggested by D.A. Zych, The Ohio State University.

$\rho_{4.2} = 8.9 \times 10^{-13} \Omega\text{m}$ using $\rho_{293} = 4.45 \times 10^{-8} \Omega\text{m}$ and a resistance ratio of 100,000 for high purity single crystals, as found by Zych.

153. EPR resonance has also been observed in Au-Mn and Pd-Mn [D. Shaltiel and J.H. Wernick, Phys. Rev. 136, A245 (1964)] but data of a different nature than contained in Table 7 is reported.

TABLE 7

Comparison of Mg-Mn, Cu-Mn, and Ag-Mn

Alloy	$d(\delta_{sL}/d(C_I\%))$	σ_{Mn}	J_{sd}	Residual δ_{sL}
	$(10^{10} \text{ sec}^{-1} C_I\%^{-1})$	(10^{-18} cm^2)	(eV)	$(10^{10} \text{ sec}^{-1})$
Mg-Mn	16.7 ± 4	2	$\geq 0.12 $	3
Cu-Mn ^a	6	0.4	~ 0.1	21
Ag-Mn ^b	<21	<2.6	?	17

a. Data from Gossard et al. [9], except J_{sd} which is given by Heeger [3].

b. Data from Gossard et al. [10].

TABLE 8

Relaxation Rates:

 δ_{ds} , δ_{sd} , δ_{sL} , and δ_{eff}

	#98-X (0.49%Mn)	#96-X (0.11%Mn)	#95-X (0.02%Mn)
$\delta_{eff} (10^{10} \text{ sec}^{-1})^a$	. . . 200 to 600 gauss $\rightarrow$ 0.35 to 1.1		
$\delta_{ds} (10^{10} \text{ sec}^{-1})^b$		3.2(.18)T	
$\delta_{sd} (10^{10} \text{ sec}^{-1})^c$	3780(218)	857(49)	139(8)
$\delta_{sL} (10^{10} \text{ sec}^{-1})^d$	11.5(12.1)	4.8(5.2)	3.2(5.2)
Calculated using $J_{sd} = 0.5(0.12) \text{ eV}$			

a. $\gamma\Delta H = \delta_{eff}$ b. computed using (II.26) c. computed using (II.25)
d. computed using (II.20')

For Mn in metals, $^{105}\omega_{\text{hf}} \cong 0.083 \times 10^{10} \text{ sec}^{-1}$ and thus no hyperfine splitting is expected nor observed in any of the samples at any temperature. Physically, the lack of hyperfine structure results from the rapid hopping of the local moment spin from site to site via the conduction electrons; ($\delta_{\text{sL}} \ll \delta_{\text{sd}}$ means the conduction electrons are strongly coupled to the local moments). The hyperfine fields will be averaged out if the hopping rate, primarily determined by the slower of δ_{ds} and δ_{sd} , is faster than ω_{hf} .

Extrapolation of the linewidths to $T = 0 \text{ K}$ yields the values presented in Table 9.

TABLE 9

Residual $T = 0 \text{ K}$ Linewidths

Mg-Mn #98-K	(0.49%Mn)	235 gauss
Mg-Mn #98-X	(0.49%Mn)	160 gauss
Collings & Hedgcock	(0.38%Mn) ^a	150 gauss ^b
Mg-Mn #96-X	(0.11%Mn)	190 gauss
Mg-Mn #95-X	(0.02%Mn)	100 gauss

a. Adjusted value. See Section III-B-2.

b. Obtained from Fig. 6, Ref. [23]. ΔH_{PTP} has been converted to ΔH using (II.36).

In comparison, the residual $T = 0$ linewidths in Cu-Mn are on the order of 0 to 60 gauss.^{10,16,63} Direct local moment to lattice relaxation⁶³ and unresolved fine structure (II.30) are probably the

main contributors to the residual linewidth in Mg-Mn.

The fine structure contribution depends on the magnitude of D which is not known for Mn in Mg. Tao et al.⁶⁷ obtain a fine structure constant, D , of 155 gauss for Gd^{+++} in a single crystal of Mg-Gd using measurements of the shift in the center of gravity of the unresolved fine structure multiplets at low temperature. Manganese should have a larger D because the 3d levels are less localized than the 4f levels, and therefore are influenced more by the crystalline field. However, even if D is only 155 gauss, the residual linewidth in polycrystalline samples would be more than 300 or 400 gauss which is not observed in Mg-Mn. Indeed, even for the Mg-Gd single crystal studies, the linewidth only varies between 110 and 250 gauss when the angle between the symmetry axis and applied field is varied. Tao et al. invoke exchange relaxation narrowing of the fine structure to resolve this discrepancy. Whether or not this is occurring in Mg-Mn is not known. Thus it is difficult to make a quantitative estimate of the unresolved fine structure contribution to the linewidth.

The apparent variation in residual linewidth with concentration and frequency may or may not be real. The relaxation processes discussed do not have any strong frequency dependence.

2. g Shifts

The relaxation bottleneck, present in Mg-Mn, greatly diminishes any g shifts resulting from the s-d exchange interaction where

$$\delta g_0 = 3n J_{sd}(0)/2N_0gE_f \quad (11.10)$$

is the full shift and

$$\delta g = \frac{(\delta_{sL})^2}{(\delta_{sL} + \delta_{sd})^2 + (\gamma \lambda M_d^0)^2} \delta g_0 \quad (\text{II.21})$$

is the bottlenecked shift. The measured g values and g shifts are listed in Table 10 along with theoretical g shifts computed using (II.21) with $J_{sd} = -0.12$ eV. A larger value of J_{sd} actually results in a smaller g shift because of the J^2 dependence of δ_{sd} . The values of g obtained in this investigation equal the Mn^{++} free ion value, 2.002,¹⁵⁴ to within the experimental error, although there is a tendency toward values somewhat lower than the free ion value. This implies that J_{sd} is negative. In comparison, other EPR investigations (Table 11), have found slightly positive g shifts implying

TABLE 10

Mn^{++} g values in Mg-Mn

Sample	g	$\delta g(\text{Expt.})^a$	$\delta g(\text{Theor.})^b$
#98-K	1.998 ± 0.01	-0.004	-0.0001
#98-X	2.001 ± 0.005	-0.001	-0.0001
#96-X	1.991 ± 0.01	-0.011	-0.003
#95-X	1.98 ± 0.02	-0.02	-0.005

a. Assuming $g_0 = 2.002$, Ref. [154].

b. Using (II.21) and $J_{sd} = -0.12$ eV.

154. A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, The International Series of Monographs on Physics, Clarendon Press, Oxford, 1970. Table 7.17.

positive J_{sd} .¹⁵⁵ Susceptibility, specific heat, and optical data for Mn^{++} in metallic hosts yield $J_{sd} \cong -0.5$ eV as mentioned earlier;¹⁵⁰ but because of the wavevector dependence of J_{sd} , there could be a sign change between $J_{sd}(q = 0)$ and $J_{sd}(q = 2 k_f)$.¹⁵¹ The broad

TABLE 11
 Mn^{++} g Values in Metallic Hosts

Alloy	Reference	Frequency (GHz)	g
Mg-Mn(0.38%) ^a	Collings & Hedgcock	9.4	2.01 ± 0.01
Mg-Mn(0.24%) ^a	Owen et al.	9.1	2.02 ± 0.01
Cu-Mn(1-10%)	Owen et al.	9.1	2.01 ± 0.01
Cu-Mn(2%)	Shaltiel & Wernick	50.	2.010 ± 0.005
Cu-Mn(2%)	Okuda & Date	34.4	2.012 ± 0.002
Ag-Mn(4.2%)	Owen et al.	9.1	1.99 ± 0.01
Ag-Mn(2%)	Shaltiel & Wernick	50.	2.010 ± 0.005
Au-Mn(2%)	Shaltiel & Wernick	50.	2.005 ± 0.005
Pd-Mn(2%)	Shaltiel & Wernick	50.	2.09

a. Adjusted value of the concentration. See Section III-B-3.

155. Whether J_{sd} is positive or negative depends on the relative magnitudes of the various contributions to the exchange integral. Direct exchange is always positive while covalent admixing of the s and d wavefunctions yields a negative contribution. A further discussion of this point may be found in Ref. [113] and [M. Peter, S. Koide, and B. Giovannini, Proc. Int. Conf. Magnetism, Nottingham (1964), published by the Inst. of Phys. and the Phys. Soc. London, p 154].

linewidths, and the bottleneck, in these alloys make a more precise determination of δg difficult. However, the linewidth is approximately frequency independent, and thus measurements at higher spectrometer frequencies may resolve the differences between the various EPR measurements.

3. Line Shapes and Intensities

Figure 17 represents a typical experimental resonance curve for sample #98-X. This is compared with the theoretical line shape of Peter et al.⁷⁴ (open circles) calculated as follows: the parameters W , y , and the midpoint of W are measured on the experimental curve and these unambiguously determine x and c (Eq. II.37) needed to compute the theoretical line shape. Only the amplitude is adjusted to optimize the fit, which is very good. The A/B ratio is 2.5 in agreement with Dyson's theory^{57,72} ($A/B = 2.55 \rightarrow y = 0.72 \rightarrow c = 1.0$).

A slight broadening of the wings of the resonance is noticeable and this could result from exchange relaxation narrowing of the central portion of the line. In this case the central part of the line will have a Lorentzian shape but the wings will fall off exponentially.^{154,156,157}

156. J.H. Van Vleck, Phys. Rev. 74, 1168 (1948).

157. P.W. Anderson and P.R. Weiss, Rev. Mod. Phys. 25, 269 (1953).

FIGURE 17. Experimental curve (solid line) for Mg-Mn(0.49%) at X band and 34 K. The open circles are the theoretically calculated line shape, $f(x) = (1 - 2cx - x^2)/(1 + x^2)^2$, with $c = 0.94$ (see text).

Noise, base line drift,¹⁴⁹ and the ever present $g = 2$ impurity signal¹⁵⁸ caused some distortion in the line shapes of the lower concentration samples and for the K band sample.¹⁵⁹ This distortion is a major source of uncertainty in the quoted g values of these samples (Table 10).

The same effects causing distortion of the line shapes produced some variation in y . Therefore, an average value $\bar{y}$ was determined for each sample and used in the line shape analysis. The values used were $\bar{y} = 0.64, 0.72, 0.74$, and 0.75 in samples #98-K, #98-X, #96-X, and #95-X, respectively. Only sample #98-X showed a definitely discernible variation of $\bar{y}$ with temperature (See Section V-B-3).

No absolute determinations of the line intensities were made. The intensity is expected to scale with the manganese concentration and qualitatively this effect was observed at X band.

-
158. It is an unavoidable fact of life that every cavity has an impurity signal at $g = 2$ if the spectrometer sensitivity is high enough. In sample #95-X the impurity signal was comparable in amplitude, but much narrower (80 gauss) than the Mn^{++} signal. The symmetrical shape observed, indicates a surface impurity rather than a bulk impurity. Because of its narrow, symmetrical shape it was relatively straight forward to separate the impurity signal from the Mn^{++} resonance.
159. There is an inherent loss in sensitivity at higher frequencies because of the smaller sample (cavity) area and shallower skin depth.

B. AFMR Results

AFMR in dilute magnetic alloys is not fully understood, and in particular, the use of polycrystalline samples increases the difficulty of determining the source of the anisotropy field H_A . This and other points are discussed at length in Chapter II and will only be briefly reviewed in this chapter.

1. Néel Temperatures

In the EPR results for these alloys, the onset of antiferromagnetism is most clearly shown by the rapid shift of the resonance to smaller magnetic fields as the temperature is lowered in the region below a "critical" temperature, Figures 18 to 21. This critical temperature depends on the manganese concentration and is equated with the Néel temperature, T_N , of these alloys. This association is established by considering the resonance field equations

$$\delta H = -2 H_E H_A / H_a \quad (\text{II.46})$$

or

$$\delta H = -H_E H_A / H_a \quad (\text{II.48})$$

and the temperature dependence of H_E and H_A . The exchange and anisotropy fields, H_E and H_A , are zero above the Néel temperature and increase rapidly below it. Thus the resonance field begins shifting at the Néel temperature. However, this transition is not expected to be as abrupt as that in AFM compounds, because of the dilute, structurally disordered character of these alloys.

FIGURE 18. The temperature dependence of the resonance field in Mg-Mn(0.49%) at K band.

FIGURE 19. The temperature dependence of the resonance field in Mg-Mn(0.49%) at X band.

FIGURE 20. The temperature dependence of the resonance field in Mg-Mn(0.11%) at X band.

FIGURE 21. The temperature dependence of the resonance field in Mg-Mn(0.02%) at X band.

At almost the same "critical" temperatures, the resonance linewidths (Fig. 12 to 15) stop decreasing with decreasing temperature, and this effect is assumed to be associated with the onset of antiferromagnetism. Considering both the linewidth and resonance field shift data, Néel temperatures of 9 ± 1 , 5 ± 1 , and $2\frac{3}{4} \pm \frac{1}{2}$ K are obtained for the Mg-Mn alloys with manganese concentrations of 0.49%, 0.11%, and 0.02%, respectively. The concentration dependence of the Néel temperature is qualitatively what would be expected. In the more concentrated alloys the manganese local moments are closer together, resulting in stronger RKKY exchange interactions between them. As a result of these stronger interactions, higher temperatures are required to break up the magnetic ordering. It is not known what the exact concentration dependence of T_N should be.

2. Resonance Field Shifts: Temperature and Frequency Dependence

Two equations were presented in Chapter II which predict resonance field shifts to smaller fields:

$$\begin{aligned} \delta H &= H_a - H_0 = -2 H_E H_A / H_a \\ \text{if } \vec{H}_a \parallel \vec{c}, H_a < H_c ; \end{aligned} \quad (\text{II.46})$$

and

$$\begin{aligned} \delta H &= H_a - H_0 = -H_E H_A / H_a \\ \text{if } \vec{H}_a \perp \vec{c} \end{aligned} \quad (\text{II.48})$$

where $\vec{c}$ is the anisotropy axis. Owen et al.⁵ argue that (II.48) is the correct equation to use for Cu-Mn because crystalline anisotropy is negligible. In this case, when the alloy goes AFM, the manganese

sublattices immediately "spin flop" into a direction perpendicular to $\vec{H}_a$ which is the state of lowest energy in the absence of crystalline anisotropy. The anisotropy fields needed for AFMR then result from polarization of the nuclear and conduction electron spins, half of which will be parallel to the average direction of $\vec{M}_1$ and half parallel to the average direction of $\vec{M}_2$. The net result is $\vec{H}_{AN}$ and $\vec{H}_{AE} \perp \vec{H}_A$ and case (II.48) applies. However, in hexagonal Mg-Mn alloys, crystalline field effects are thought to be more important than in cubic Cu-Mn. Then, with polycrystalline samples, the resonance shift is described by an appropriate average of (II.46) and (II.48):

$$\delta H = -C H_E H_A / H_a \quad (V.2)$$

where C varies between 1 and 2 depending on the relative contributions of H_{AN} , H_{AE} , and H_{AC} to the anisotropy field.

If H_{AC} is important, the use of polycrystalline samples will produce line broadening. Such broadening in the AFM regime has not been observed in Cu-Mn, but is clearly apparent in the Mg-Mn data, Fig. 12, 13, and perhaps 14. Of course, there are other possible sources of this broadening, such as magnetic inhomogeneities in the alloys.

The temperature dependence of the field shifts indicate that H_{AC} is not the only important source of anisotropy field. If it were, the shift δH would attain a limiting value at temperatures below $T/T_N \sim 0.5$ unless H_E and H_{AC} increase much less rapidly than the Brillouin function as T is decreased. Experimentally, none of

the shifts show evidence of saturating as the temperature is decreased. (In #95-X the Néel temperature is too low to test this point with the available data.) The field shifts δH are only roughly described by $\delta H \propto 1/T$; whereas Collings and Hedgcock found a reasonably good fit to $\delta H \propto 1/T$ below $T/T_N = 0.6$. Table 12 lists the Néel temperatures, field shifts, and approximate exchange and anisotropy fields for the alloys used in this investigation and in those of Owen et al.⁵ and Collings and Hedgcock.²³ The limitations of the molecular field model must be kept in mind when considering the calculated exchange and anisotropy fields.

In trying to determine the relative importance of H_{AC} on the one hand, and H_{AE} and H_{AN} on the other, it should be remembered that these latter two produce large shifts in cubic alloys and there is no reason to think that they would not be of similar magnitude in hexagonal alloys. The use of single crystal specimens would be the best way to investigate H_{AC} further.

In addition to the temperature dependence, (II.46) and (II.48) predict a frequency dependence of the shift δH . At higher spectrometer frequencies, H_a is larger and the shift δH should be smaller. Table 13 indicates the observed frequency dependence of the shift δH in Mg-Mn(0.49%) and in Cu-Mn and Ag-Mn. The data for Cu-Mn and Ag-Mn fit the theory quite well, but the shift in Mg-Mn has a substantially smaller frequency dependence than predicted. The source of this discrepancy is not known. Perhaps the simple molecular field model of AFMR is less applicable to hexagonal Mg-Mn, than it

TABLE 12
AFMR Parameters of Mg-Mn

Sample	At.%Mn	ν	T_N	$H_E^0(T=0\text{ K})^a$	$\delta H(T=2.5\text{ K})$	$H_A(T=2.5\text{ K})^b$
		(Ghz)	(K)	(Gauss)	(Gauss)	(Gauss)
#98-K	0.49	23.5	9	58,000	278	27
#98-X	0.49	9.4	9	58,000	330	12
#96-X	0.11	9.4	5	32,000	118	9
#95-X	0.02	9.2	$2\frac{3}{4}$	18,000	28	7
Collings & Hedgcock	0.38 ^c	9.4	6 ^d	38,000	245	14
Owen et al.	0.24 ^c	9.1	4	26,000	155 ^e	15 ^e

a. Calculated using (II.52).

b. Calculated using (V.2) with $C \approx 1.5$.

c. Adjusted value, see Section III-B-3.

d. Determined from the line shift data. The linewidth stops decreasing at 18 K ($\Delta H = 300$ gauss); evidently as a result of some line broadening mechanism unrelated to the onset of AFM.

e. Measured at 2 K.

is to the cubic systems Cu-Mn and Ag-Mn. Measurement of the field shift in Mg-Mn at higher frequencies than K band would provide interesting additional data.

TABLE 13
Frequency Dependence of δH

Alloy	Reference	ν_l/ν_u^a	$\delta H_u/\delta H_l^a$
Mg-Mn(0.49%)	This work	0.40	0.84
Cu-Mn(5.6%)	Owen et al.	0.39	0.35
Cu-Mn(1.4%)	Owen et al.	0.39	0.41
Cu-Mn(1.5-4%)	Okuda & Date	0.27	0.27
Ag-Mn(4.2%)	Owen et al.	0.39	0.32

a. The subscripts l and u refer to a pair of measurements. l is the one made at the lower frequency, and u the one made at the upper frequency.

3. Linewidths, Shapes, and Intensities

Figures 12, 13, and 14 include the linewidth data in the AFM state for samples #98-K, #98-X, and #96-X, respectively. The Néel temperature in #95-X was too low to obtain any useful AFMR linewidth data. As discussed previously (Chapt. II and V), the increase in linewidth as the temperature is lowered, clearly seen in Figures 12 and 13, may result from an angular dependence of the field shift that would tend to broaden the linewidth in polycrystalline samples.

However, there may be other equally plausible explanations. At present the theory of AFMR relaxation is too inadequate to draw any definite conclusions.

The apparent scatter in the linewidth data of #98-X (Fig. 13) at temperatures below T_N is the result of some type of sample hysteresis. For any given data run, the linewidths fall on a smooth curve, but the curves do not coincide for different runs. This is presumably related to differences in thermal and magnetic treatment received by the sample in any given data run. It is interesting that no corresponding hysteresis is observed in the field shift data, Figure 19. Only by deliberately cooling the sample from high temperatures and in high magnetic fields (15kG) was it possible to induce thermoremanent magnetization effects similar to those observed in Cu-Mn^{5,96} and in Mg-Mn.²³ With this pretreatment the resonance field was observed to shift a few tens of gauss at 3 K depending on whether the resonance was swept through from low to high fields, high to low fields, or with the field direction reversed.

Sample #98-X was also observed to have a temperature dependent lineshape in the AFM state. This is reflected in the variation of γ with respect to T , Figure 22. Owen et al. also noticed a change in the line shape of Mg-Mn(0.24%)²¹ in the AFM state but not in Cu-Mn. Again, this may reflect a difference between the hexagonal and cubic alloys.

These effects observed in sample #98-X may be present in the other samples, but if so, were not observed because of the greater data scatter and lower Néel temperatures (in #95-X and #96-X).

FIGURE 22. The temperature dependence of the line shape parameter y in Mg-Mn(0.49%) at X band (see Fig. 2).

Collings and Hedgcock found that the amplitude of the absorption of $\text{Mg-Mn}(0.38)^{24}$ decreased about 30% below the Néel temperature. Exact measurements were not made in this investigation, but qualitatively a similar reduction was observed.

C. Summary

In the paramagnetic state the linewidths and lack of hyperfine structure or large g shifts are found to be well explained by the relaxation bottleneck theory of Hasegawa and others. The spin-orbit induced spin-flip scattering cross section of manganese, and a lower limit for the exchange integral $|J_{sd}|$ are determined using the linewidth data.

In the antiferromagnetic state the results are qualitatively explained by the antiferromagnetic resonance equations of Nagamiya and Keffer and Kittel which are derived using a two sublattice molecular field model. Three sources of anisotropy field are considered but of these, the important electronic contribution is poorly understood. Investigations with single crystals are needed to determine the relative importance of crystalline anisotropy which appears to be larger in hexagonal alloys than in cubic alloys. The observed frequency dependence of the shift is less than expected. Measurements at higher frequencies would provide additional information concerning this point and would also allow more accurate g values to be determined.

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