PHYSICAL REVIEW B VOLUME 11, NUMBER 7 1 APRIL 1975

Antiferromagnetic resonance in Mg:Mn alloys*

F. W. Kleinhans,[†] J. P. Long,[‡] and P. E. Wigen
Department of Physics, Ohio State University, Columbus, Ohio 43210

(Received 29 October 1974)

Antiferromagnetic-resonance measurements at 9.3, 23, and 35 GHz of polycrystalline Mg containing 0.49-at.% Mn are found to be in quantitative disagreement with present theories of the antiferromagnetic-resonance line shift. The anisotropy field H_A is also discussed.

I. INTRODUCTION

Local-moment alloys containing Mn^{++} such as Cu:Mn,[1,2] Ag:Mn,[1,2] Mg:Mn,[1,3,4] and[5] Au:Mn have all been observed to undergo an antiferromagnetic transition and to exhibit antiferromagnetic resonance (AFMR) at low temperatures. Following the initial observation and interpretation of manganese AFMR in Cu, Ag, and Mg hosts by Owen *et al.*,[1] it has generally been thought that the AFMR theory of Keffer and Kittel,[6] Nagamiya,[7] and others (developed for insulators) provides a reasonably adequate interpretation of the resonance observed in these types of alloys, although there has generally been some difficulty explaining the source of the anisotropy field H_A.

In this paper, measurements of the AFMR field shift (that is, the shift of the resonance from its paramagnetic value) of a Mg:Mn dilute alloy at 9.3, 23, and 35 GHz are reported and shown to be in very poor agreement with the frequency dependence predicted by the previously mentioned theories. This result is to be compared with measurements of Cu:Mn and Ag:Mn which are in close agreement with the theory. The anisotropy field will also be discussed. Preliminary results on the paramagnetic-resonance data are published elsewhere.[8]

II. EXPERIMENTAL

The Mg:Mn samples had a Mn solid solution concentration of 0.49 at.%, as determined by electron microprobe analysis at Battelle Memorial Institute, and were prepared in a carbon crucible by Dow Chemical Co. using high-purity magnesium and manganese; they were homogenized for $10\frac{1}{2}$ h at 590 °C and quenched in water. Spectroscopic analysis for Al, Ca, Fe, Ni, Pd, Si, Sn, and Zn did not indicate any significant impurity. ESR linewidth and line-shift data indicate a Néel temperature T_N of 9 K.

In comparing the results of this work with previous Mg:Mn investigations, it should be noted that most of the literature report *bulk* Mn concentrations. This invariably overestimates the true Mn solid solution concentration because a significant amount of the Mn is present as a Mn-rich second phase. The alloy used in this work had a bulk Mn concentration of 0.58 at.% (and a residual resistivity ratio of 2.2).

There is no evidence that the second-phase material contributed to the resonance. All of the likely Mn compounds have Néel temperatures much higher than observed in this alloy. Further, the resonance has all the usual characteristics of a dilute alloy resonance, e.g., Dyson line shape with A/B of 2.5 in the paramagnetic region.

The X, K, and K_a band spectrometers were of the conventional reflection cavity type with balanced bridge, diode detection, and magnetic field modulation (145 Hz, 20–40-Oe peak to peak) in conjunction with phase-sensitive detection (P.A.R. HR-8). The usual cavity impurity signal problems were eliminated by making the microwave cavities (TE 101 and 102) out of the Mg:Mn alloy and giving them an ultrasonic acid-etch cleaning before each data run.

Low temperatures were obtained with a stainless-steel variable-temperature helium Dewar and control loop and measured with a Cryo-Cal CR-1000 germanium resistor.

The resonance lines were analyzed using the method of Peter *et al.*,[9] although it should be noted that in the antiferromagnetic (AFM) region the resonance lines appear to be distorted by anisotropy.

III. THEORY

The AFMR theory as developed by Keffer and Kittel is followed here. They assume a two-sublattice antiferromagnetic crystal with cubic or uniaxial symmetry and solve a pair of coupled Bloch equations of the form

$$\frac{dM}{dt} = \gamma \vec{M} \times \vec{H}_{\mathrm{eff}} \ , \qquad (1)$$

where $\vec{M}$ is the sublattice magnetization, γ is the spectroscopic splitting factor of the sublattice, and $\vec{H}_{\mathrm{eff}}$ is the net effective magnetic field. Further, we have

$$\vec{H}_{\mathrm{eff}} = \vec{H}_a + \vec{H}_E + \vec{H}_A + \vec{H}_{\mathrm{rf}} \ ,$$

where $\vec{H}_a$, $\vec{H}_E$, $\vec{H}_A$, and $\vec{H}_{\mathrm{rf}}$ are the applied, exchange, anisotropy, and rf fields, respectively. With the applied field perpendicular to the symmetry axis (anisotropy axis), Eq. (1) yields a resonance at an applied field

$$H_a \approx + (2H_E H_A + H_0^2)^{1/2} , \qquad (2)$$

where H_0 is the *paramagnetic* resonance field of the specimen. The low Néel temperatures of the Mn local moment alloys and the small AFMR field shifts imply[10] $2H_E H_A \ll H_0^2$, and Eq. (3) reduces to

$$\delta H = H_a - H_0 = - H_E H_A / H_0 \; . \qquad (3)$$

For H_0 parallel to the symmetry axis there are two cases depending on whether or not the applied field H_a exceeds the critical field for spin flop, $H_c = [2H_E H_A/(1-\alpha)]^{1/2}$, where α is $\chi_{\parallel}/\chi_{\perp}$. Because of the low $H_E H_A$ in these alloys, H_a almost certainly exceeds H_c at X band and higher (except possibly just below the Néel temperature). For $H_a > H_c$ the antiferromagnetic sublattices "spin flop" perpendicular to the applied field and the resonance condition becomes

$$H_0 \approx (2H_E H_A + H_a^2)^{1/2} , \qquad (4)$$

which simplifies to

$$\delta H = H_a - H_0 = H_E H_A / H_a \qquad (5)$$

for $2H_E H_A < H_a^2$. Equation (5) predicts a positive field shift, and such a shift has never been reported for Mn alloys, either in single crystal or polycrystalline investigations.[1] In polycrystalline samples the line might be smeared out. However, the absence of a positive field shift in the single-crystal work is one of the factors which suggest that the anisotropy field may not be tied to a crystalline symmetry axis, but it is of an unconventional nature in these dilute alloys. That a resonance line can be seen at all in polycrystalline samples implies a very weak (less than a few Oe) crystalline anisotropy field. Otherwise the angular dependence of the resonance would completely smear it out.

The resonance actually observed in both single-crystal and polycrystalline work exhibits a downfield shift in the AFM region and is attributed to the resonance condition described by Eq. (3). The anisotropy field has been explained as follows[1,2]: Because of the very weak *crystalline* anisotropy fields, the antiferromagnetic sublattices spin flop perpendicular to the applied field. The magnetic sublattices in turn polarize the conduction electrons and/or local moment nuclei,[11] creating an effective anisotropy field perpendicular to the applied field. If correct, this explains why the resonance in polycrystalline materials is not significantly broader than in single crystals.

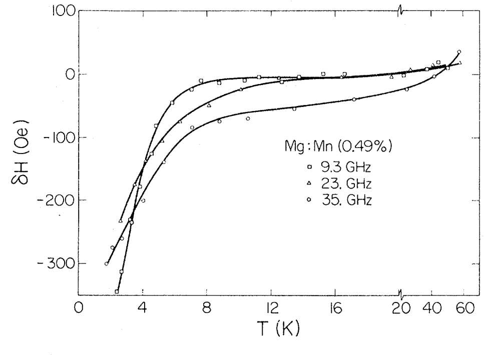

FIG. 1. Resonance field shift vs temperature in polycrystalline Mg:Mn(0.49 at.%) at X, K, and K_a band. Zero shift corresponds to $g = 2.002$. Each datum point is the average of several measurements.

TABLE I. Frequency dependence of the AFMR line shift δH.[a]

Alloy	ν_l/ν_u [b]	$\delta H_u/\delta H_l$
Mg:Mn (0.49 at.%)	0.41	0.84
Mg:Mn (0.49 at.%)	0.27	0.92 (0.73)[c]
Cu:Mn (1.4 at.%)[d]	0.39	0.41
Cu:Mn (1.4 at.%)[e]	0.27	0.25
Cu:Mn (5.6 at.%)[d]	0.39	0.35
Cu:Mn (4.0 at.%)[e]	0.27	0.25
Ag:Mn (4.2 at.%)[d]	0.39	0.32

[a] The shift δH is measured between the high-temperature paramagnetic resonance and the resonance field at 2–4 K.

[b] The subscripts l and u refer to the lower and upper frequency of a pair of measurements. In all cases, the lower frequency is at X band.

[c] The shift is measured between 2 and 12 K. See Fig. 1.

[d] Reference 1.

[e] Reference 2.

IV. RESULTS AND DISCUSSION

Figure 1 shows the AMFR field shifts observed for Mg:Mn at X, K, and K_a band. There is a marked contrast between the sharp paramagnetic to antiferromagnetic transition at 9.3 GHz and the less distinct transition at 35 GHz. This may be associated with the fact that at 35 GHz the 12.5-kOe applied field is about $\frac{1}{5}$ of the estimated saturation exchange field of this alloy.[12] Another feature to be noted is the apparent lack of any saturation of the field shift at temperatures well below T_N, as might be expected if the exchange and anisotropy fields follow a Brillouin temperature dependence.

The most interesting feature is the less than expected frequency dependence of the field shifts. Equation (3) predicts a downfield shift inversely proportional to the spectrometer frequency since $H_0 = \omega/\gamma$. In Table I the ratios of the field shifts and frequencies are presented for this as well as prior investigations of Mn alloys. The field shift scales as predicted for the cubic alloys, but a substantial discrepancy exists for the hexagonal Mg:Mn alloy. Whether this breakdown is related to the hexagonal symmetry of Mg:Mn is difficult to judge. All of these materials are disordered alloys with a magnetic structure more complex than the simple two-sublattice molecular field model used to derive the resonance equations.[1,13] As first noted by Owen *et al.*, the distortion of the line shape in the AFM region suggests that crystal-field effects are more important in hexagonal Mg:Mn than in cubic alloys. The AMFR linewidth in Mg:Mn may also be indicative of this. As the temperature is lowered it monotonically increases to ≈375 Oe from 200, 280, and 360 Oe at the Néel temperature for *X*, *K*, and K_a band, respectively. By comparison, the linewidth in cubic Cu:Mn and Ag:Mn is essentially constant below T_N.

It is clear that further theoretical work is needed to develop an adequate theory of AFMR in Mg:Mn alloys and perhaps for all noncubic alloys. Such a theory should also provide a more adequate explanation of the anisotropy field in local-moment alloys. If polarization of the conduction electrons is responsible, quantitative details of the mechanism are needed. In particular, it will be necessary to understand in greater detail the AFM region dynamics of the conduction electron to lattice relaxation bottleneck[14-16] which occurs in Cu:Mn, Ag:Mn, and Mg:Mn alloys. As a result of this bottleneck the conduction electrons are more nearly in spin equilibrium with the local moments than with the lattice. Thus the anisotropy field will be ineffective in the limiting case when the conduction electrons and local moment spins remain parallel under the dynamic conditions of resonance. This is because in the Bloch equations the cross terms $\vec{M}\times\vec{H}_A$ go to zero.

In this regard, there are some resonance data of Okuda and Date[17] which bear directly on the bottleneck and effectiveness of the conduction electron polarization as an anisotropy field. In Cu:Mn (2 at.%) they found that the addition of 0.3-at.% Ni quadrupled the shift δH from 350 to 1400 Oe and the linewidth ΔH from 80 to 320 Oe (measured at 1.5 K). Similar effects were observed by them[2] upon the addition of Co, Fe, Pd, and Ti, whereas Al and Zn were not found to significantly affect either δH or ΔH. We feel this result clearly points to the conduction electrons as the principal source of the anisotropy field in Mn local-moment alloys. The addition of a third element opens up the relaxation bottleneck via spin-flip scattering[15,18] off the impurities and thereby enhances the effectiveness of the anisotropy field by uncoupling the conduction electrons from the local moments.

In summary, no quantitative theory exists for calculating the anisotropy field in Mn local-moment alloys, and existing AFMR theories are only qualitatively correct for Mg:Mn and possibly all noncubic moment alloys. Single-crystal investigations of Mg:Mn or other hexagonal alloys would provide valuable additional information in helping to resolve these matters.

ACKNOWLEDGMENTS

The first author (F.W.K.) would like to thank A. C. Gossard, A. Narath, and F. C. Thatcher for helpful discussions.

---

*Work supported in part by the National Science Foundation.

†Present address: Indiana University–Purdue University Indianapolis, Indiana 46205.

‡Present address: Department of Physics, University of Illinois.

[1] J. Owen, M. Browne, W. D. Knight, and C. Kittel, Phys. Rev. 102, 1501 (1956); J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids 2, 85 (1957).

[2] K. Okuda and M. Date, J. Phys. Soc. Jpn. 27, 839 (1969).

[3] E. W. Collings and F. T. Hedgcock, Phys. Rev. 126, 1654 (1962).

[4] F. W. Kleinhans, dissertation (The Ohio State University, 1971) (unpublished).

[5] D. Shaltiel and J. H. Wernick, Phys. Rev. 136, A245 (1964).

[6] F. Keffer and C. Kittel, Phys. Rev. 85, 329 (1952).

[7] T. Nagamiya, Prog. Theor. Phys. 6, 342 (1951).

[8] F. W. Kleinhans and P. E. Wigen, AIP Conf. Proc. 5, 1204 (1971).

[9] M. Peter, D. Shaltiel, J. H. Wernick, H. J. Williams, J. B. Mock, and R. C. Sherwood, Phys. Rev. 126, 1396 (1962).

[10] It is difficult to obtain a reliable estimate for H_EH_A. The values of H_EH_A determined by using Eq. (3) are consistent with the assumption used to derive Eq. (3) for *X* band and higher frequencies.

[11] K. Okuda and M. Date (Ref. 2) have made electron-nuclear-double-resonance measurements in Ag:Mn which support the contention that a nuclear polarization field is partially responsible for the anisotropy field. However, this field by itself is almost an order of magnitude too small to explain the observed shifts (see Ref. 4 for details).

[12] Using a simple two-sublattice molecular-field model the exchange field can be estimated from the Néel temperature by using $H_E = 3kT_N B_{5/2}(x)/g\mu_B(\frac{5}{2}+1)$, yielding $H_E = 58$ kOe at $T = 0$. See J. Samuel Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, 1966).

[13] J. S. Kouvel, J. Phys. Chem. Solids 21, 57 (1961); 24, 795 (1963).

[14] H. Hasegawa, Prog. Theor. Phys. 21, 483 (1959).

[15] A. C. Gossard, A. J. Heeger, and J. H. Wernick, J.

Appl. Phys. 38, 1251 (1967).

[16] Several recent theoretical papers discuss this problem in the paramagnetic region, e.g., David C. Langreth and John W. Wilkins, Phys. Rev. B 6, 3189 (1972); S. E. Barnes and J. Zitkova-Wilcox, Phys. Rev. B 7, 2163 (1973); and M. B. Walker, Phys. Rev. B 7, 2920 (1973).

[17] K. Okuda and M. Date, J. Phys. Soc. Jpn. 22, 1512 (1967).

[18] Y. Yafet, J. Appl. Phys. 39, 853 (1968).