PHYSICAL REVIEW VOLUME 126, NUMBER 5 JUNE 1, 1962

Low-Temperature Magnetic Properties of Dilute Mg-Mn, Al-Mn, Mg-Fe, and Al-Fe Alloys

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(Received April 27, 1961; revised manuscript received March 5, 1962)

Magnetic susceptibility measurements are reported on some dilute alloys of Mg-Mn and Al-Mn in the temperature range, room temperature -1.3°K. Electron spin resonance (ESR) absorption has been observed in the magnesium alloy containing 0.6 at. % manganese and studied as a function of temperature. Room temperature magnetic susceptibility measurements and low temperature ESR experiments are reported for Mg-Fe and Al-Fe alloys. The concentration dependence of the Curie constant at high temperature suggests the presence of four unpaired electrons for the manganese atom dissolved in magnesium. Similar information concerning manganese dissolved in aluminum suggests one unpaired electron if a completely localized d state is formed.

The susceptibility of dilute Mg-Mn alloys shows departures from a Curie law, which could be interpreted as an increase in the spin state of the manganese ion in the region of the resistance minimum. This excess paramagnetism is discussed in terms of the possible mechanisms which could produce a resistance minimum and leads to the conclusion that if there is a ferromagnetic coupling between randomly distributed manganese pairs, the interaction mechanism operates over approximately 10 lattice spacings.

The effective magneton number of Mn in the more dilute Mg-Mn alloys also increases with temperature at high temperatures. The susceptibility of the concentrated Mg-Mn alloy obeys a Curie law except in the region of the resistance maximum where both susceptibility and ESR data indicate an antiferromagnetic transition.

The influence of the low-temperature transition, occurring in the magnesium alloy containing about 0.6 at. % manganese, on the electron spin resonance linewidth and magnetic field value has been measured as a function of temperature giving g values of 2.01 ± 0.01 above 6°K. The shift of the position of resonance field below 6°K is consistent with antiferromagnetic behavior in Mg-Mn. The line shift is proportional to T^{-1} in the antiferromagnetic region which would be consistent with a conduction electron superexchange mechanism for the antiferromagnetic manganese ion interaction. The linewidth is broadened in the region of the resistance minimum and attains a constant value as the temperature is lowered. This behavior is consistent with localized spin interactions, giving rise to larger averaged spin values in the resistance minimum region as suggested from the magnetic susceptibility studies of the more dilute alloys.

1. INTRODUCTION

THE application of magnetic methods to the study of low-temperature resistive anomalies occurring in Cu-Mn,[1,2] Cu-Co,[3] and[4] Cu-Fe has led to some understanding of the influence of internal magnetic fields and the state of the paramagnetic ion on the anomalous resistive behavior of these alloys. The particular system which has received most attention has been Cu-Mn with preliminary reports on the Mg-Mn and Au-Mn systems.[1] The magnetic measurements on the Cu-Mn system indicate a complex magnetic behavior with the following principle features:

(i) At high temperatures the magnetic susceptibility obeys a Curie-Weiss law; the Curie temperature θ is positive and depends strongly on the manganese concentration. For example, Owen *et al.*[1] report θ values of 0°K and 100°K for alloys containing 0.019 and 11.1 at. % manganese, respectively.

(ii) As the temperature is lowered, a gradual antiferromagnetic transition appears to take place at temperatures slightly higher than the Curie temperature determined from the susceptibility measurements.

(iii) In the antiferromagnetic region the magnetic properties exhibit a hysteresis and remanent magnetization which is often referred to as "parasitic ferromagnetism."

Schmitt[5] made the suggestion that a temperature dependent resistivity could occur at low temperatures if the spin degeneracy of the paramagnetic ions was removed. Later Hart[6] and Yosida[7] treated the problem theoretically by considering the magnetic ordering as a short-range phenomenon; the coupling mechanism between the paramagnetic ions was considered as an s-d superexchange mechanism. Yosida[7] found that below the Néel temperature, the resistivity should decrease with decreasing temperature, whereas above the Néel temperature the resistance should be independent of temperature. Therefore, this mechanism would not produce a resistance minimum. Brailsford and Overhauser[8] have suggested a possible mechanism for the resistance minimum by considering local interactions between randomly distributed pairs of paramagnetic ions. Both Overhauser[9] and Marshall[10] have recently developed models for producing a cooperative magnetic

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

[2] R. W. Schmitt and I. S. Jacobs, J. Phys. Chem. Solids **3**, 324 (1957).

[3] I. S. Jacobs and R. W. Schmitt, Phys. Rev. **113**, 459 (1959).

[4] F. T. Hedgcock, Phys. Rev. **104**, 1564 (1956).

[5] R. W. Schmitt, Phys. Rev. **103**, 83 (1956).

[6] E. W. Hart, Phys. Rev. **106**, 467 (1957).

[7] K. Yosida, Phys. Rev. **106**, 893 (1957); **107**, 396 (1957).

[8] A. D. Brailsford and A. W. Overhauser, J. Phys. Chem. Solids **15**, 140 (1960).

[9] A. W. Overhauser, Phys. Rev. Letters **3**, 414 (1959).

[10] W. Marshall, Phys. Rev. **118**, 1519 (1960).

transition to antiferromagnetism in a dilute alloy which would allow the occurrence of a resistance maximum.

The influence of impurities on the resistive properties of magnesium and of aluminum have been reported by numerous authors.[11] Recently experimental data have been reported on the influence of the concentration of manganese on the low-temperature electrical properties of magnesium[11,12] and aluminum.[11] No anomalies have been observed in Al-Mn system, whereas both a resistance minimum and maximum have been observed in Mg-Mn.

If it is assumed that alloys containing a paramagnetic ion are sufficiently dilute when the atom is put into solid solution with a weakly diamagnetic or paramagnetic solvent, then it should be possible to consider the paramagnetic ion as in the same state as an isolated atom with the valence or *s* electrons joining the common conduction band of the solvent. On such an assumption the magnetic susceptibility should obey a simple Curie law for noninteracting particles. However, most dilute alloys containing paramagnetic ions show deviations from the simple Curie behavior. Attempts have been made to interpret the magnetic properties of dilute alloys containing paramagnetic ions in the following ways:

(i) A thermal activation of electrons or holes into the *d* shell of the paramagnetic ion by allowing a *d* level to lie near the Fermi level of the conduction band.[13]

(ii) A localized coupling between the paramagnetic ions, the number of such systems depending on the statistical distribution of ions in the solvent.[14]

(iii) A change in the density of states of the conduction electrons in the temperature range of the resistance anomaly.[4]

(iv) An *s-s* electron interaction between Mott-Friedel bound *s* states and electrons in the conduction band.[4]

(v) A mechanism which would require the formation of a *d* band by the Friedel resonance broadening mechanism.[15]

(vi) Owen *et al.*[1] have assumed a coupling of the manganese ion and the conduction electrons and interpreted the paramagnetic resonance observed in the dilute Cu-Mn alloys as a result of spin flipping of the conduction electron which is magnetized by the *s-d* interaction. This mechanism requires that the manganese ion be in an *S* state.

In the hope that measurements on dilute magnetic systems will further the understanding of resistance anomalies, it is the purpose of the present paper to present measurements on the magnetic susceptibility and ESR in dilute magnesium and aluminum alloys containing small concentrations of manganese or iron. These results will be discussed in the light of the preceding interpretations of the magnetic behavior of dilute alloys containing paramagnetic impurities.

2. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

2.1 Sample Preparation

The dilute magnesium and aluminum alloys used in these investigations were the same as those used in the earlier studies of the electrical properties of these alloys.[11,12] The high-concentration Al-Mn and Mg-Mn alloys were prepared in this laboratory by melting 99.99% pure solvent with the desired additive in high-purity graphite crucibles and quenching from the melt. The ingots were then given a homogenizing anneal and tested for alloy uniformity by measuring the residual resistances of samples cut from various sections of the ingot. Electrical resistance and magnetic susceptibility measurements were made on the low-concentration Mg-Mn samples which were given strain-relieving anneals after fabrication. Only the highest concentration alloy (~0.6 at.% Mn) was used in the ESR measurements. A small piece of rod for susceptibility measurements, a wide rolled strip for ESR and a narrow rolled strip for resistance were all prepared from the same piece of nominal 0.6% Mn alloy. The samples were quenched in ice water after being heated together in a helium atmosphere for 2 hr at 600°C, thus ensuring that the specimens used in all three measurements had the same concentration of Mn in solution.

2.2 Method of Measuring the Magnetic Susceptibility

The low-temperature susceptibilities were measured using the Curie method employing a servo-balance especially designed for measurements on materials of low resistivity.[16] The absolute susceptibility of the samples were determined at room temperature on a Bunge microbalance which was fitted into a vacuum case. All of the susceptibility samples were studied as a function of field ($H_{\max}=8500$ oe) and, whether the Curie method or Gouy method was used to determine the susceptibility, ferromagnetic corrections were made for each sample. When the Curie method was used and ferromagnetic impurity corrections made, the magnetic field gradients were determined using zone refined germanium as a standard with the value of 0.103×10^{-6} emu/g for the susceptibility. Magnetic field strengths were determined using a Rawson rotating-coil fluxmeter. The temperature dependence of the susceptibility was normally measured relative to the room temperature

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[11] See F. T. Hedgcock, W. B. Muir, and E. E. Wallingford, Can. J. Phys. **38**, 376 (1960) for a review of previous work.

[12] G. Gaudet, F. T. Hedgcock, G. Lamarche, and E. E. Wallingford, Can. J. Phys. **38**, 1134 (1960).

[13] E. W. Pugh, B. R. Coles, A. Arrott, and J. E. Goldman, Phys. Rev. **105**, 814 (1957).

[14] A. J. Dekker, Physica **24**, 697 (1958).

[15] J. Friedel, Suppl. Nuovo cimento **12**, 286 (1958).

[16] F. T. Hedgcock and W. B. Muir, Rev. Sci. Instr. **31**, 390 (1960).

value. After it had been shown that the ferromagnetic correction was not a function of temperature, the relative susceptibility was reduced to an absolute value using the room temperature susceptibility value. Further details of the experimental method can be found in an earlier publication.[16]

2.3 Method of ESR Measurement

Electron spin resonance measurements were made with a conventional double-modulation spectrometer which employed a reflection-type cavity, 'magic-*T*' bridge, and operated at a frequency of 9400 Mc/sec. A microwave power of 8 mw was absorbed in the cavity and sample, and the 1-kc/sec magnetic field modulation was 3 oe peak-to-peak or less when examining the Mg-Mn alloy. The cavity, operating in the TE_{102} mode with a circular coupling hole of 17/64-in. diameter, was of silver-plated stainless steel. The Varian X13 klystron was immersed in an oil bath, the reflector supplied from dry cells, the accelerator from a well-stabilized (1 in 10^5) 280-v power supply, and the filament supplied from a 6 v accumulator. Its frequency of operation was locked to that of the resonant cavity (by circuitry similar to that of the signal detecting circuit) by frequency-modulating the klystron with 0.2 to 0.4 v rms at 25 kc/sec and re-applying the phase-detected dc to the klystron repellor.

Samples were glued to the vertical, narrow cavity walls and were thus normal to the field of the magnet. Mounted in this way, four pieces could be placed in the cavity without the need for any supporting structure with its accompanying dielectric loss and occasional spurious signals. With Mg-Mn it was found that two pieces were sufficient for good signal-to-noise ratio and these were both mounted in the lower half of the cavity. Temperature was measured with a calibrated carbon resistor attached to the cavity wall. Measurements below 4.2°K were done while pumping on a liquid helium bath, while temperatures above 4.2°K were attained using the cold gas from boiling liquid helium.[16]

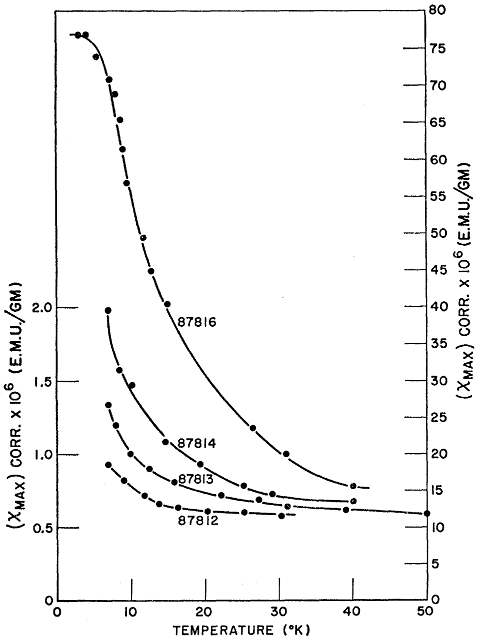

FIG. 1. Magnetic susceptibility of some dilute alloys of Mg-Mn as a function of temperature. The right-hand scale refers to sample No. 87816.

The magnetic field was produced by a 4-in. Newport electromagnet supplied from a separately excited dc generator. The current was stabilized to 1 in 4000 by controlling the field current with an error voltage developed across a 2-ohm resistor in series with the magnet coils. A 10-turn helipot incorporated in the stabilizing amplifier, and driven by a 1-rpm motor, enabled the magnetic field to be swept within the range 600 to 4500 oe, usually at a rate of about 7 oe/sec

The field was measured with a Rawson rotating-coil fluxmeter, the $\frac{1}{4}$-in. probe of which fitted into an aluminum socket glued to the center of one of the magnet pole faces. The fluxmeter was calibrated at 100-oe intervals using proton resonance, and allowance was made for the small difference between the magnetic field at the center of a pole face and that at the sample site. As a check on experimental accuracy, when an alloy sample happened to corrode in the cavity and the familiar hyperfine spectrum of Mn^{++} in a dielectric crystal appeared, the magnetic field (H) at the center of this spectrum was compared with the field (H_c) calculated from the known average g value of Mn^{++} (viz., 2.0018). The result of a set of 16 observations is $(H-H_c)=1$ oe± 4 (standard deviation). The error can be accounted for as uncertainty in reading the fluxmeter dial which would be about ±5 oe. Other measurements with carefully positioned substances having lines of known g values (such as DPPH and an n-type silicon semiconductor) confirmed the above conclusion as to magnetic field accuracy.

3. EXPERIMENTAL RESULTS

3.1 Magnetic Susceptibility

Figure 1 shows the magnetic susceptibility of more dilute alloys of Mg-Mn as a function of temperature. The susceptibilities have been calculated at maximum magnetic field and corrected for ferromagnetic impurity (see Table I). The susceptibilities have not been corrected for the temperature-independent paramagnetism of the solvent. In these curves an excess paramagnetism at low temperature is apparent. Table I contains a listing of the effective magneton numbers P_{eff} calculated from the room-temperature susceptibility from the relation

$$(\chi_{\text{alloy}}-\chi_{\text{Mg}})=\Delta\chi=C/T,$$

and $P_{\text{eff}}=3kC/N\alpha\beta^2$, where k = Boltzmann's constant,

TABLE I. Values of the room temperature susceptibility and effective magneton numbers for dilute magnesium and aluminum alloys. Absolute values of susceptibility measured relative to zone-refined germanium ($\chi = 0.103 \times 10^{-6} \pm 0.001$ emu/g).

Sample	Wt.% Mn	Wt.% Fe	$\chi(27°C) \times 10^6$ emu/g	$(F_{Fe}/\text{total force})_{H_{max}}$	P_{eff} (27°C)
		Magnesium alloys			
728	0.001		0.498	0.5%	...
87812	0.005		0.517	1%	7 ±1
87813	0.019		0.534	2%	5.0±0.5
87814	0.038		0.564	3%	4.8±0.5
87815	0.046		0.564	2%	5.5±0.5
87816	1.34		2.64	3%	4.8±0.1 4.7±0.2
727-1		0.0023	0.502	20%	4.7±1.5
727-2		0.0027	0.502	15%	4.7±1.5
		Aluminum alloys			
GKP	0.001		0.603	0.5%	...
GKM	0.011		0.604	1.5%	1.4±0.1
GKN	0.053		0.612	1%	1.6±0.1
GKO	0.092		0.624	2%	1.7±0.1
GKK		0.025[a]	0.605	1%	1.2±0.4
GKL		0.025[a]	0.605	3%	1.2±0.5

[a] The maximum solid solubility of Fe in Al at 600°C is approximately 0.25%. The remaining Fe is presumably in the form of Al_3Fe and owing to the small concentration involved gives a negligible contribution to the susceptibility.

N = number of Mg atoms/g, α = atom fraction of Mn, and β = Bohr magneton.

In the case of sample No. 87816 the second of the two values of P_{eff} is derived from the slope of the inverse susceptibility curve above room temperature [Fig. 2(c)]. The values of the solvent susceptibilities were measured to be 0.498×10^{-6} emu/g and 0.603×10^{-6} emu/g for magnesium and aluminum, respectively, and these values are both lower than those listed elsewhere.[17] Since the ferromagnetic corrections are small in these pure materials and since the susceptibility temperature coefficient produces a change of less than 1% in the susceptibility at liquid helium temperatures, it is thought the observed values are a result of samples of higher purity than those previously measured. P_{eff} for the alloy was calculated at room temperature assuming the Weiss constant to be negligible at room temperature and using the atom fraction α of the transition element, as determined from spectroscopic analysis. The error in α represents the largest contribution to the error in the determination of P_{eff}. It will be noticed that none of the values for P_{eff} in Table I correspond to the effective magneton number expected for Mn^{++} in an S state (i.e., 5.9); the effective magneton number being much lower in aluminum than in magnesium. A smoothed value of P_{eff} can be obtained for Mn in Mg by plotting $\Delta\chi$ vs concentration. This is shown in Fig. 2(a), the slope of the line yielding an average value of 5.2±0.2 for P_{eff}. This value is again considerably lower than 5.9 expected for Mn^{++} in an S state. An effective magneton number for sample 87816 was determined from the susceptibility above room temperature as shown in Fig. 2(c) and listed in Table I. The effective magneton number from the high temperature Curie constant agrees quite well with the values determined at room temperature. Figure 2(b) shows the inverse susceptibility of an Al-Mn alloy as a function of T and it can be seen that a Curie law is not obeyed. In Fig. 2(d) the plot of $\Delta\chi^{-1}$ vs T for sample No. 87816 shows a leveling off at the low temperature end. This could be considered as evidence for antiferromagnetism. From the linear

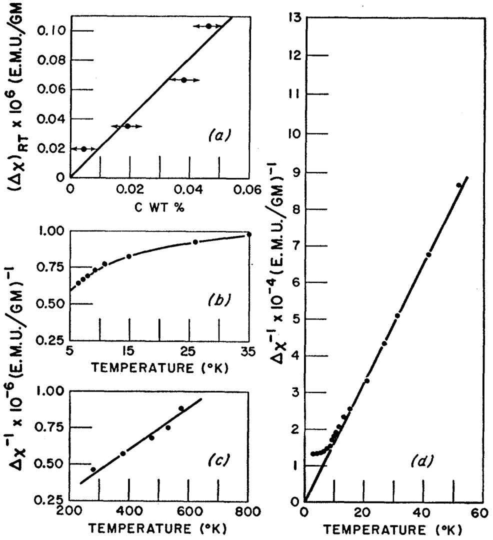

FIG. 2. Inset (a) is a graph of the paramagnetic susceptibility of manganese in magnesium as a function of manganese content. (b) Inverse susceptibility of Al+1% Mn alloy as a function of temperature. (c) Inverse susceptibility of Mg-Mn alloy No. 87816 at high temperatures. (d) Inverse susceptibility of Mg-Mn alloy No. 87816 at low temperatures. The inverse susceptibility has been corrected for the paramagnetism of the solvent.

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[17] *Constantes Selectionnees* (Masson and Cie, 1957), Vol. 7.

portion of this curve a value of 4.1±0.1 is found for P_{eff}. This is lower than the values of 4.8±0.1 calculated from the room temperature susceptibility and 4.7±0.2 calculated from the slope of Fig. 2(c).

In Fig. 3 the normalized susceptibility, $\Delta\chi/\Delta\chi_{\mathrm{R.T.}}$, for the Mg-Mn alloys is shown as a function of T^{-1}. It will be noticed that the Mg-Mn alloys all show deviations from a Curie law and in fact there is an excess paramagnetism in the region of the resistance minimum as has been previously reported in dilute copper alloys.[4] This excess paramagnetism is shown in the inset of Fig. 3 and it can be seen to vary inversely with temperature. Excess specific heats in the Cu-Fe,[18] Cu-Mn,[19] Cu-Co [20] systems have also been observed to vary inversely with temperature in the region of the resistive minimum. Calculations of P_{eff} from the slopes of the two sections of straight lines yield values of 3.6 and 4.1 in the temperature region between 50°K and 20°K, and 20°K and 7°K, respectively, as compared with the average room temperature value of 5.2. Alternatively one can assume the average room temperature value of 5.2 for P_{eff} and calculate the percent alignment of spins from the low-temperature susceptibility results. This calculation yields a 50% alignment between 20°K and 50°K and a 70% alignment between 7°K and 20°K. This spin alignment deficit (as compared to the Curie prediction) is in qualitative agreement with specific heat measurements on the alloys[21] where it appears that considerable entropy is available if complete ordering is to occur at lower temperatures.

It has been previously reported[11] that iron in magnesium produces a resistance minimum while iron in aluminum does not. Included in Table I are values for P_{eff} of iron in aluminum and magnesium. The errors are large since the ferromagnetic correction is quite large and because of the limited solid solubility of iron in these materials, there is a large error in the concentration of iron in solid solution. Because of the uncertainties in these samples, no experiments on the temperature dependence of the magnetic susceptibility were attempted.

3.2 Electron Spin Resonance

Figure 4 shows a typical resonance curve for magnesium sample No. 87816 containing a nominal concentration of 0.6 at.% Mn measured at 4.2°K.

(a) *Amplitude of the Resonance Derivative*

Figure 5 shows the variation of height of the absorption derivative with temperature. The measurements were made relative to the heights of DPPH signals, to compensate for changes in cavity Q with temperature. The alloy used showed a resistance maximum in the region 6°K to 7°K, a phenomenon which would be accompanied by an increase in skin depth and an exposure of a larger number of paramagnetic ions to the rf field. But the increase in resistance is only 6% between 6°K and 30°K, so that the corresponding percentage increase in skin depth will be about half this amount and therefore not sufficient to explain the maximum in the resonance derivative curve. The area under the absorption curve is proportional to the magnetization of the manganese ions and hence at constant field to the magnetic susceptibility of these ions. Since the linewidth is constant in the region under consideration (see below) the height of the absorption curve and consequently that of its derivative must also be a function of susceptibility. Figure 5, therefore, shows that a maximum in the susceptibility would be expected. However, the measured values of $1/\chi$ show only a leveling off in this region (Fig. 3). In either case an antiferromagnetic transition is indicated in the vicinity of 6°K.

It was found impossible to detect a resonance in an Al-Mn alloy containing 1 at.% manganese in solid solution. To compare the relative intensities of the Mg-Mn ESR signal with that of one from Al-Mn, the following

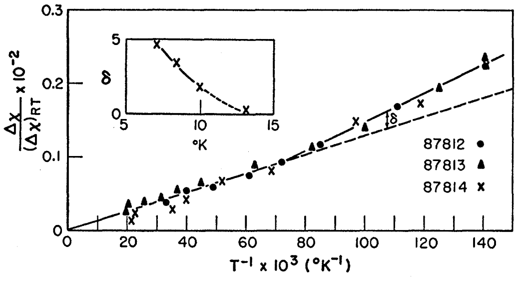

FIG. 3. The reduced susceptibility $\Delta\chi/\Delta\chi_{\mathrm{R.T.}}$ plotted as a function of reciprocal temperature. The inset in the figure is the excess paramagnetism δ plotted as a function of temperature.

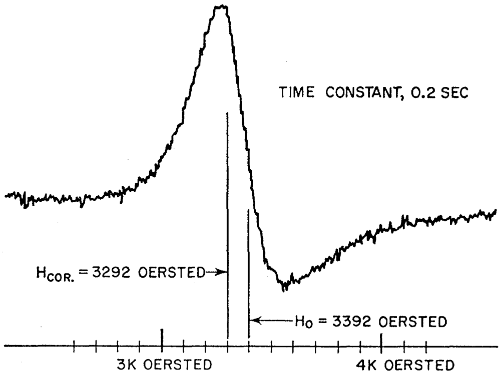

FIG. 4. A typical resonance curve observed in the concentrated Mg-Mn alloy No. 87816 (~0.6 atomic percent manganese) at 4.2°K.

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[18] D. L. Martin and J. P. Franck, *Proceedings of the Seventh International Conference on Low Temperature Physics, Toronto, 1960* (University of Toronto Press, Toronto, 1960), p. 262.

[19] J. E. Zimmerman and F. E. Hoare, J. Phys. Chem. Solids **17**, 52 (1960).

[20] L. T. Crane and J. E. Zimmerman, Phys. Rev. **123**, 113 (1961).

[21] D. L. Martin, Can. J. Phys. **39**, 1385 (1961).

experiment was performed. Two pieces of 0.6% Mg-Mn were placed in a resonance cavity together with a sample of DPPH and the relative heights of the resonance signal were measured. The experiment was repeated with two Al-Mn samples in the cavity, but no resonance could be detected even at 4.2°K. If a barely detectable signal had been observed from Al-Mn (i.e., with a signal-to-noise ratio 1:1) the relative height of the absorption derivatives of Mg-Mn and Al-Mn of equivalent concentrations and skin depth would have been 30:1 provided of course that the linewidths were equal. It seems therefore that the spectroscopic state of manganese in aluminum is different from that in magnesium.

No ESR signal could be detected from the Mg-Fe, Al-Fe alloys.

(*b*) *Linewidth*

Table II shows the average linewidth in several temperature groupings. Tests for statistically significant differences were applied and it was concluded that the linewidth was independent of temperature below 18°K and equal to 313±25 oe. This linewidth corresponds to a relaxation time of 2.2×10^{-10} sec and is in good agreement with the values observed by Owen *et al.*[1] The linewidth in the region above 18°K yields a relaxation time of 1.2×10^{-10} sec. Between 6°K and 18°K the resistance minimum in this alloy occurs and, as can be seen in Fig. 6, the linewidth is in excess of a simple T proportionality, indicating an additional broadening mechanism is operative in this region.

TABLE II. Width of electron spin resonance (ESR) line.

Temperature range (°K)	Linewidth (oe)
1.9 - 2.4	298±25
2.5 - 3.0	318±20
3.03- 3.5	296±17
3.56- 4.2	329±23
5.0 - 7.0	311±22
8.8 -10.4	292±19
14.8 -17.6	305±15
17.9 -19.9	337±22
26.0	381±22
25.0 -45	440±51

(*c*) *Position of the Electron Spin Resonance Line*

The theory of spin resonance of conduction electrons in a metal has been worked out by Dyson[22] and applied by Feher and Kip[23] to measurements on alkali and other metals. The line shape and magnetic field value at the center of the absorption derivative depended (for a particular specimen shape, say, thick compared to the skin depth) on the quotient T_D/T_2, where T_D is the time conduction electrons take to diffuse through the microwave skin under the action of the microwave field and T_2 is the normal electron-spin relaxation time. For paramagnetic solutes in alloys, the theory of conduction electron resonance is taken over for the special case $T_D=\infty$. It is then found that the absorption derivative has a characteristic asymmetric shape, the amplitudes of the "positive" and "negative" portions being in the ratio 2.55/1. As can be seen in the resonance curve in Fig. 4 this is borne out by experiment in the Mg-Mn alloy. The line is also shifted in such a way that if H_{corr} is the field required to satisfy the resonance equation for the paramagnetic ion, and H is the apparent resonance field (where the derivative has maximum slope): $H_{\text{corr}}=H-\Delta H/3$, where ΔH is the usual linewidth.

To check the present apparatus this relation was first verified for dilute Cu-Mn at 80°K, at which temperature it was known to be paramagnetic. The relation was then applied to determine the behavior of the Mg-Mn resonance line in the temperature range 1.9°K to 64°K. The corrected resonance magnetic field for insertion in the equation $h\nu=g\beta H_{\text{corr}}$, in order to determine the g value, is $H_{\text{corr}}=H-\Delta H/3$ for paramagnetic ions in a metallic conductor. For Mg-Mn, this equation gives a practically constant $g=2.00$ for temperatures down to 6.5°K. Below 6.5°K, the resonance line started to move to a lower magnetic field in a manner characteristic of transition to an antiferromagnetic state.[24] In this state

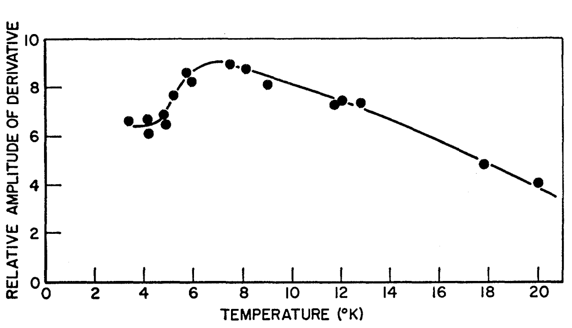

FIG. 5. Amplitude of the derivative of absorption versus temperature for magnesium sample No. 87816.

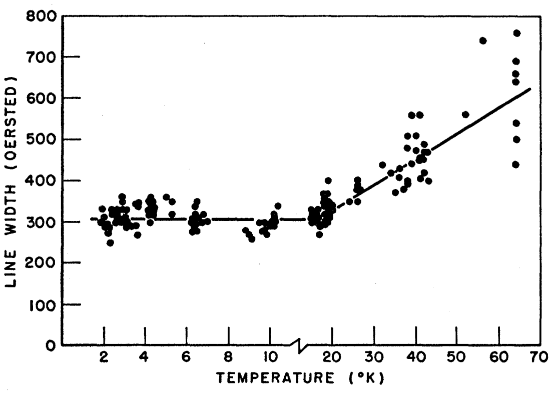

FIG. 6. Line width of manganese resonance in magnesium alloy No. 87816 as a function of temperature.

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[22] I. J. Dyson, Phys. Rev. **98**, 349 (1955).

[23] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[24] For a useful review of the effects and full references see F. Keffer, H. Kaplan, and Y. Yafet, Am. J. Phys. **21**, 250 (1953).

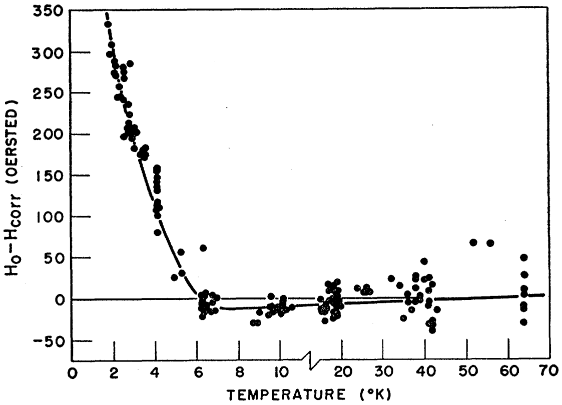

FIG. 7. Apparent shift of the resonance field in the concentrated Mg-Mn alloy No. 87816 as a function of temperature.

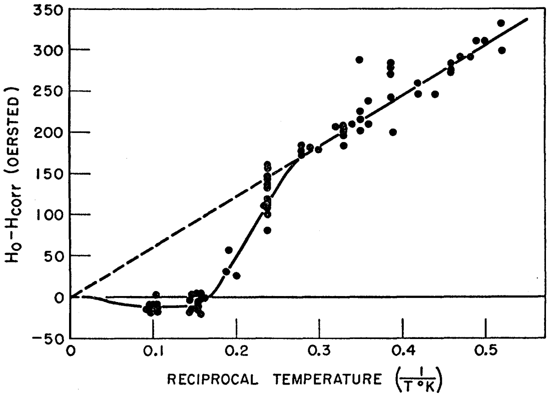

FIG. 8. Shift of the resonance field in magnesium alloy No. 87816 as a function of T^{-1}. The position of the electrical resistance maximum in this alloy is approximately 6°K.

it has not been proved that the resonant field is given correctly by $H-\Delta H/3$, so that H_0-H_{corr} may not be a valid measure of the internal field change (where H_0 satisfies the resonance condition when $g=2.00$). Instead in general, one would be better to plot simply H_0-H to show the change in line position with respect to its position in the paramagnetic state. In the present case, the linewidth is constant so that no difficulty arises since the relative line shift is the same by either method, however, a plot of H_0-H_{corr} is preferable since it more readily shows the transition from the paramagnetic state. Figure 7 shows the line shift (H_0-H_{corr}) as a function of temperature. The shift in position of the resonance line is of particular interest since the resistance-temperature plot has a maximum between 6°K and 7°K. Plotting the line shift against reciprocal temperature expands the low temperature region and shows that below 3.5°K the line shift is inversely proportional to the temperature. This is shown in Fig. 8.

In determining the resonance field, because of the sometimes large paramagnetic susceptibility of alloys with paramagnetic solutes, a demagnetizing correction is sometimes required. If the plane of the sample is parallel to the applied field H, the line is shifted to a lower field by an amount $2\pi\chi H$, where χ is the volume susceptibility; while if the plane of the sample is perpendicular to H as in these experiments, the line is shifted to a higher field by amount $4\pi\chi H$. For temperatures below 10°K the correction was 2 oe, and above 10°K was only 1 oe. Although these corrections were applied as a matter of course they were actually less than the experimental error.

(*d*) *Accuracy of Measurement*

The accuracy of the quantity H/ν is limited only by the accuracy with which the fluxmeter dial can be read since the frequency ν is known to 1 part in 10^4. It is estimated that the field can be measured to ±5 oe on the 4-koe range; and for the Mg-Mn alloy the position of maximum absorption can be measured almost as accurately as this, but the corrected position of resonance involves the linewidth ΔH which is the separation of the turning points of the derivative curve. Because of the lack of sharpness of these points the g value has an error of ±0.01. The position of the resonance line in relation to the free-spin value H_0 ($g=2.002$) was determined from the calculated value of H_0. A marker such as DPPH was not used as a reference as it was found to interfere with the shape of the resonance line and made accurate determination of line position difficult.

4. TEST FOR POSSIBLE PERMANENT MAGNETIZATION OF THE SAMPLE

Owen *et al.*[1] observed that Cu-Mn alloys containing 1.4 and 5.6 at.% manganese exhibited a small spontaneous magnetization at 4°K. Measurements of the remanence as exhibited by the magnetization of these alloys have been continued by a number of workers.[2,3] The magnetization measurements can be summarized as follows:

(i) A soft component of magnetization which resulted when the specimen was cooled in zero field. The zero-field magnetization could be reversed by applying an external field of 5000 oe.

(ii) A hard component of magnetization which re. sulted when the specimen was cooled in a field of 5000 oe-

(iii) The remanent magnetization decreased rapidly as the temperature was raised and is approximately zero at the Néel temperature.

(iv) The hard component of magnetization, when induced in the sample, shifted the position of the resonance line by as much as 250 oe.

Table I includes values of the percentage contribution to the total susceptibility due to the ferromangetic contribution. This value was derived at room temperature by assuming an exponential saturation of the ferrous impurity magnetization. Measurements of the ferromagnetic correction as a function of temperature showed it to be independent of temperature. No detectable remanence was observed in these alloys so that the ferrous component can be described as soft.

The following ESR experiment was performed to check if the soft component of magnetization would influence the position of the resonance field. The sample was cooled to 4.2°K in zero field and the field was swept to 4 koe several times. The sample was then cooled to 2.6°K in a field of 3 koe and a series of resonance runs was made with the field sweep, in opposite directions in alternate runs. There was no detectable line shift to within ± 1 oe. Hence both the susceptibility and ESR data indicate that the observed soft magnetization is due to the presence of very small quantities of ferromagnetic impurities and not associated with the manganese magnetization.

5. DISCUSSION OF RESULTS

5.1 Excess Paramagnetism in the Temperature Region of the Resistance Minimum

Brailsford and Overhauser[8] have postulated a mechanism for the appearance of resistive anomalies in paramagnetic alloys on the assumption that statistically distributed nearest-neighbor pairs of paramagnetic ions are coupled ferromagnetically. Dekker,[14] Sato *et al.*,[25] and Smart[26] have discussed the influence of the statistical nature of the distribution of paramagnetic ions on the magnetic properties of dilute systems. The general result is that ferromagnetic interactions will give rise to an excess paramagnetism with too high a value of P_{eff} derived from the low-temperature data. The susceptibility of a system containing isolated spin systems (χ_s) and ferromagnetically coupled pairs (χ_f) can be written as

$$\Delta\chi = \chi_s + \chi_f = (c/T)[1 + (\Delta c/c)],$$

where $c = N_s P_{\text{eff}}^2 \beta^2 / 3k$, N_s = number of isolated spin systems, Δc = the excess paramagnetic Curie constant due to ferromagnetically coupled spins of number N_f, and the other symbols have the same meaning as previously. Using a spin value of 2 for the manganese ion at high temperatures and a maximum spin value of 4 per coupled pair yields a value of Δc equal to 3.33 N_f/N_s. To account for the observed excess paramagnetism in sample No. 87814 (say, at 7°K) would require 1.8×10^{17} ferromagnetically coupled pairs per gram. Assuming a random distribution of manganese ions the statistical probability of finding this number of pairs would be less than 0.002. If then, a ferromagnetic coupling mechanism is used to interpret the magnetic susceptibility results, the range of the ferromagnetic interaction would have to be of the order of 10 interatomic distances.

Further experimental evidence that there is some interaction occurring between the paramagnetic ions can be seen from the ESR data previously presented in Fig. 6, where an excess line broadening is observed between 6°K and 18°K. This could be taken as evidence for spin interactions resulting in an additional line broadening as the temperature is lowered. Since both ferromagnetic and antiferromagnetic interactions lead to line broadening, it is impossible to decide which type of interaction is responsible for the additional linewidth observed. The fact that the $\Delta\chi$ values for all of the alloys lie on the same normalized curve indicates that the excess paramagnetism varies linearly with concentration. The "size" of the resistance anomaly has also been observed to vary linearly with concentration in the low concentration region.[11] Both these observations and the conclusion from the previous calculation in this section would lead one to believe that it is unlikely that pair or higher order coupling between spin systems would produce these low temperature anomalies. It is rather interesting to note that δ (the excess paramagnetism, Fig. 3) varies linearly with T^{-1} moreover, within the accuracy of the measurement the temperature at which δ appears is independent of paramagnetic ion concentration.

5.2 Antiferromagnetism

Both the ESR results and the magnetic susceptibility indicate an antiferromagnetic transition occurring in the high concentration Mg-Mn alloy No. 87816 at approximately 6°K. No obvious excess paramagnetism is exhibited in the magnetic susceptibility in the region of the resistance minimum (approximately 12°K). However, this is probably due to the opposing influence of the excess paramagnetism discussed in Sec. 5.1 and the antiferromagnetic transition, the effects acting to linearize the Curie plot. It should perhaps be pointed out that the value of the Curie temperature is zero within the accuracy of the measurement indicating no *average* internal field for the most concentrated alloy.

If it is assumed that the antiferromagnetic structure can be considered as two interpenetrating sublattices with ferromagnetic interactions in each sublattice, the temperature dependence of the resonance field ($H_0 - H_{\text{corr}}$) can be discussed following the treatment of Owen *et al.*[1] The resonance condition for such a structure is given by

$$\omega = \gamma[H^2 + 2H_E H_A]^{\frac{1}{2}},$$

where H is the applied static magnetic field perpendicular to the preferred axis, H_E is the molecular field for each sublattice and will be proportional to the magnetization (M_s) of each sublattice, H_A is the anisotropy field, and $\gamma = ge/2$ mc. For resonance in the paramag-

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[25] H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids **10**, 19 (1959).

[26] J. S. Smart, J. Phys. Chem. Solids **16**, 169 (1960).

netic region we can write

$$\omega = \gamma H_0,$$

so that near the transition temperature

$$2H_E H_A = H_0^2 - H_{\text{corr}}^2,$$

and for small line shift

$$(H_0 - H_{\text{corr}}) = H_E H_A / H_0.$$

If we write $H_E = \lambda M_s$, where λ is an *s-d* interaction constant relating the conduction electron and paramagnetic ion magnetization, then

$$(H_0 - H_{\text{corr}}) = (\lambda H_A / H_0) M_s.$$

Further, if the anisotropy field H_A is temperature independent and the magnetization of the paramagnetic ions M_s obeys a Curie law, then $(H_0 - H_{\text{corr}})$ should be proportional to T^{-1}. As can be seen in Fig. 8 this behavior is observed at temperatures well into the transition region, i.e., less than 5.5°K. It seems reasonable, therefore, to suggest that the exchange mechanism responsible for the antiferromagnetic transition is some type of *s-d* superexchange mechanism; with the premise, of course, that the spin system can be considered as two interpenetrating sublattices with a normal antiferromagnetic exchange and anisotropy field.

A change in line position which varies inversely with temperature could be interpreted as a kind of electronic Knight shift. This situation has been considered by Owen *et al.*[1] who show that such a shift, if it is occurring, should be observable in the paramagnetic region. Since no such movement in position occurs for Mg-Mn in this region, it is concluded that the sudden change at 6°K is indeed due to a magnetic transition.

5.3 Spectroscopic State of the Paramagnetic Ion

If manganese and iron contribute 2 electrons per atom to the conduction band of magnesium and aluminum, respectively, then the ions Mn^{++} and Fe^{++} should result. Mn^{++} should be in a $(3d)^5$ configuration corresponding to a $^6S_{\frac{5}{2}}$ ground state. The Fe^{++} ion should be in a $(3d)^6$ configuration with a ground state of $^5D_2$. Using the spin-only equation an effective magneton number of 5.9 would be expected for Mn^{++} and 4.9 for Fe^{++}. As can be seen in Table I the observed effective magneton numbers correspond to 5.2 ± 0.2 for Mn in Mg and 4.7 ± 1.5 for Fe in Mg. It can be seen that the error in P_{eff} for Mn in Mg permits one to say that the manganese ion is not in a $^6S_{\frac{5}{2}}$ state. This has also been observed in the Cu-Mn system[1,2] and would lead one to suggest an $S=2$ state for Mn in both solvents. The temperature dependence of the susceptibility for Al-Mn does not obey a Curie law. This effect has been discussed by Friedel[15] as evidence of *d*-band formation in this system. Presumably similar arguments could be given for the Al-Fe system in order to explain the low effective magneton number observed.

As has already been discussed in Sec. 3.1 the effective magneton number for Mn in Mg varies with temperature. Perhaps the simplest suggestion to interpret this, and the fact that the effective magneton number does not correspond to the one expected, is to assume that all of the manganese ions are not in an *S* state. The splitting of a *d* state by a cubic field in a metal has been discussed by Callaway and Edwards[27] and results in a lowering of the triply degenerate *d* state with respect to the doubly degenerate state. If the upper states lie sufficiently close to the conduction-band Fermi level of the solvent, a population of the upper levels would result from electrons in the conduction band. The scheme suggested would result in a mixture of Mn ions in Mg existing in $(3d)^5$ and $(3d)^3$ states. Occupied lower levels would give rise to a *g* value of approximately 2.00 and the mixture of the two states would result in an effective magneton number of approximately 5.2.

If we say that the ionizing energy for a *3d* electron is too great to allow the above process to take place, then there is the possibility of the formation of ions in a $(3d)^6$ state. Assuming that the exchange energy[28] could place the ground level of a $(3d)^6$ state near the Fermi level, the number of ions in $(3d)^5$ and $(3d)^6$ electron configurations would vary with the position of the Fermi level. This could produce a lowering of P_{eff} as the Fermi level is raised. Also the attractive possibility exists that with the Mn ion in a $(3d)^6$ state, there is the possibility that by the action of a crystalline field together with spin orbit interaction, the ground state degeneracy of the ion is removed providing levels[26] which might permit an inelastic scattering to take place at low temperatures and hence result in the Elliot Schmitt[2] resistivity mechanism. However, it is intended to determine the susceptibility tensor of single crystals of Mg-Mn and also the anisotropy in the *g* factor as determined by ESR. It is hoped that the combination of these two measurements will give some indication as to the order of magnitude of the splitting of the *d* state of Mn in Mg.

6. CONCLUSIONS

(1) There is an apparent excess paramagnetism in the dilute magnesium-manganese alloys which could be interpreted as a ferromagnetic coupling of the manganese ions. However, the range of the interaction found does not allow the effects to be interpreted as nearest neighbor interactions. The ESR results also indicate an

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[27] J. Callaway and D. M. Edwards, Phys. Rev. **118**, 923 (1960).

[28] In recent theoretical work P. W. Anderson [Phys. Rev. **124**, 41 (1961)] and P. A. Wolff [*ibid.* **124**, 1030 (1961)] consider mechanisms for the formation of magnetic levels in metals. In the Anderson picture the magnetic states are split by so-called exchange self-energy rather than the true exchange energy mentioned above.

additional line broadening in the region of the resistance minimum which is presumably due to an interaction similar to that observed in the susceptibility results.

(2) The ESR and magnetic susceptibility results indicate an antiferromagnetic transition is taking place in the most concentrated Mg-Mn alloy in the region of the resistance maximum. All of the Mg-Mn alloys have a zero Curie temperature and there is no evidence of "parasitic ferromagnetism" as shown in the Cu-Mn alloys.[1]

(3) The susceptibility data indicate that the manganese ion in magnesium has an effective magneton number of 5.2±0.2 at high temperatures and 3.6±0.2 at low temperatures. The iron ion in aluminum has an effective magneton number of 4.7±1.5 in magnesium and 1.2±0.4 in aluminum.

(4) The effective magneton number for Mn in Mg depends on temperature; the fact that it does not correspond to an S state suggests that the d state of the ions is split by the crystalline field of the metal. A mixture of ionic states could lead to the observed results and also yield a g value of 2.00 for ESR. The most useful ion formed by the activation process would be one in a $(3d)^6$ configuration.

ACKNOWLEDGMENTS

The authors would like to acknowledge the interest and aid of Dr. J. S. Dugdale and Dr. M. Bailyn in this work. We would also like to thank Miss M. Treuil for the determination of the room temperature susceptibility of the alloys and G. Mark for his technical assistance while carrying out the experiments. The National Research Council of Canada supported this work through a grant in aid.