

## Low-Temperature Magnetoresistance in Magnesium and Aluminum Containing Small Concentrations of Manganese or Iron\*

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(Received 20 January 1964)

Magnetoresistance measurements in magnetic fields up to 21 kOe have been made on Mg-Mn, Mg-Cd, Mg-Al, Al-Mn, and Al-Fe alloys in the temperature region of liquid helium. Magnesium alloys containing more than 0.1-at. % Mn which exhibit a resistance maximum and minimum in zero field, show a negative magnetoresistance, whereas the more dilute samples (0.001–0.1 at. % Mn) show a positive magnetoresistance, the magnitude of which decreases with decreasing temperature. The magnesium alloys containing non-transition element impurities, as well as the aluminum alloys containing transition metal impurities, are found to obey Kohler's rule. From an analysis of these data it is found that the magnetoresistivity of a dilute alloy of magnesium containing manganese, can be considered as the sum of a normal positive magnetoresistivity (obeying Kohler's rule) and an anomalous term which is negative in sign, does not obey Kohler's rule and is presumably due to a magnetic scattering of the conduction electrons. Using values of the *s-d* exchange integral and the Coulomb scattering integral derived from an analysis of the zero-field resistivity permits an explanation of the magnetoresistivity based on Kasuya's theory, at temperatures near the Néel point.

### 1. INTRODUCTION

NUMEROUS studies made on dilute monovalent and divalent<sup>1,2</sup> metals containing paramagnetic impurities have indicated a negative magnetoresistance at low temperature when the alloy exhibits both a low temperature resistance minimum and maximum. Recent studies on the<sup>3</sup> Cu-Fe and<sup>4</sup> Zn-Mn known to exhibit only a minimum down to the lowest temperatures available indicate the presence of a negative magnetoresistance in the more concentrated samples. A magnesium alloy containing small concentrations of manganese has been shown<sup>5</sup> to exhibit deviations from the Kohler rule, but no conclusive evidence for a negative magnetoresistance was found even at the lowest temperature (1.3°K) and the highest magnetic field available (25 kOe). Magnetoresistance studies on dilute aluminum alloys containing either manganese or iron have been carried out at liquid-helium temperatures at magnetic fields of<sup>6</sup> 1.5 kOe and no anomalies were found. In the present paper we wish to report some magnetoresistance studies on Mg alloys known to exhibit both a resistance minimum and a maximum<sup>7</sup> as well as measurements on normal magnesium alloys exhibiting no resistance anomalies. Also included in the

present work are studies on aluminum-manganese and aluminum-iron alloys where the magnetoresistivity is studied to fields of 21 kOe.

### 2. SPECIMEN PREPARATION AND EXPERIMENTAL METHOD

The dilute Mg-Mn, Al-Mn and Al-Fe alloys used in the present investigation are the same as those used earlier in the studies of the electrical and magnetic properties of these systems.<sup>7-9</sup> The high-concentration Mg-Mn alloys were prepared by quenching from near the melting point after the samples had received a high-temperature homogenizing anneal. The manganese concentration of each Mg alloy was estimated from the

TABLE I. Alloy number, solute concentration, resistance ratio and resistivity at 273°K for all samples studied. Sample number refers to detailed spectroscopic analysis given in Refs. 8 and 12.

Alloy or metal	Sample number	Concentration of solute (at. %)	$\rho_{4.2^\circ\text{K}}/\rho_{273^\circ\text{K}}$	$\rho_{273^\circ\text{K}}$ $\mu\Omega$ cm	
Pure Mg	728	...	0.00351	4.12	
	MgMn	87812	0.001	0.00679	4.25
		87813	0.01	0.0111	4.28
		90911	0.08	0.1231	4.54
		91081 (a)	0.35	0.3188	5.47
MgCd	91081 (b)	0.74	0.5140	6.83	
	396	0.55	0.0955	4.55	
	397	1.01	0.1360	4.82	
	MgAl	400	0.29	0.1242	4.71
		401	0.53	0.2133	5.26
Pure Al	402	0.80	0.2893	5.77	
	GKP	...	0.00187	...	
	AlMn	0.045	0.1209	...	
	AlFe	0.02	0.0045	...	

\* This work was supported by Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio, under Contract AF 33(657)-8744 and the U. S. Office of Naval Research under Contract NONR-3644(00).

† On leave of absence from The Research Institute for Iron, Steel, and other Metals, Tohoku University, Sendai, Japan.

<sup>1</sup> A. N. Gerritsen, *Physica* **25**, 489 (1959) (a tabulation of experimental results up to 1959).

<sup>2</sup> G. J. van den Berg and J. de Nobel, *J. Phys. Radium* **23**, 665 (1962) (a recent review).

<sup>3</sup> Y. Muto, K. Noto and F. T. Hedgcock, *Can. J. Phys.* **42**, 15 (1964).

<sup>4</sup> Y. Muto, *Sci. Rept. Res. Inst. Tohoku Univ. (A)* **13**, 1 (1961).

<sup>5</sup> R. T. Webber, *Phys. Rev.* **105**, 1437 (1957).

<sup>6</sup> J. G. Thomas and E. Mendoza, *Phil. Mag.* **43**, 900 (1952).

<sup>7</sup> G. Gaudet, F. T. Hedgcock, G. Lamarche, and E. W. Wallingford, *Can. J. Phys.* **38**, 1134 (1960).

<sup>8</sup> F. T. Hedgcock, W. B. Muir, and E. W. Wallingford, *Can. J. Phys.* **38**, 376 (1960).

<sup>9</sup> E. W. Collings and F. T. Hedgcock, *Phys. Rev.* **126**, 1654 (1962).

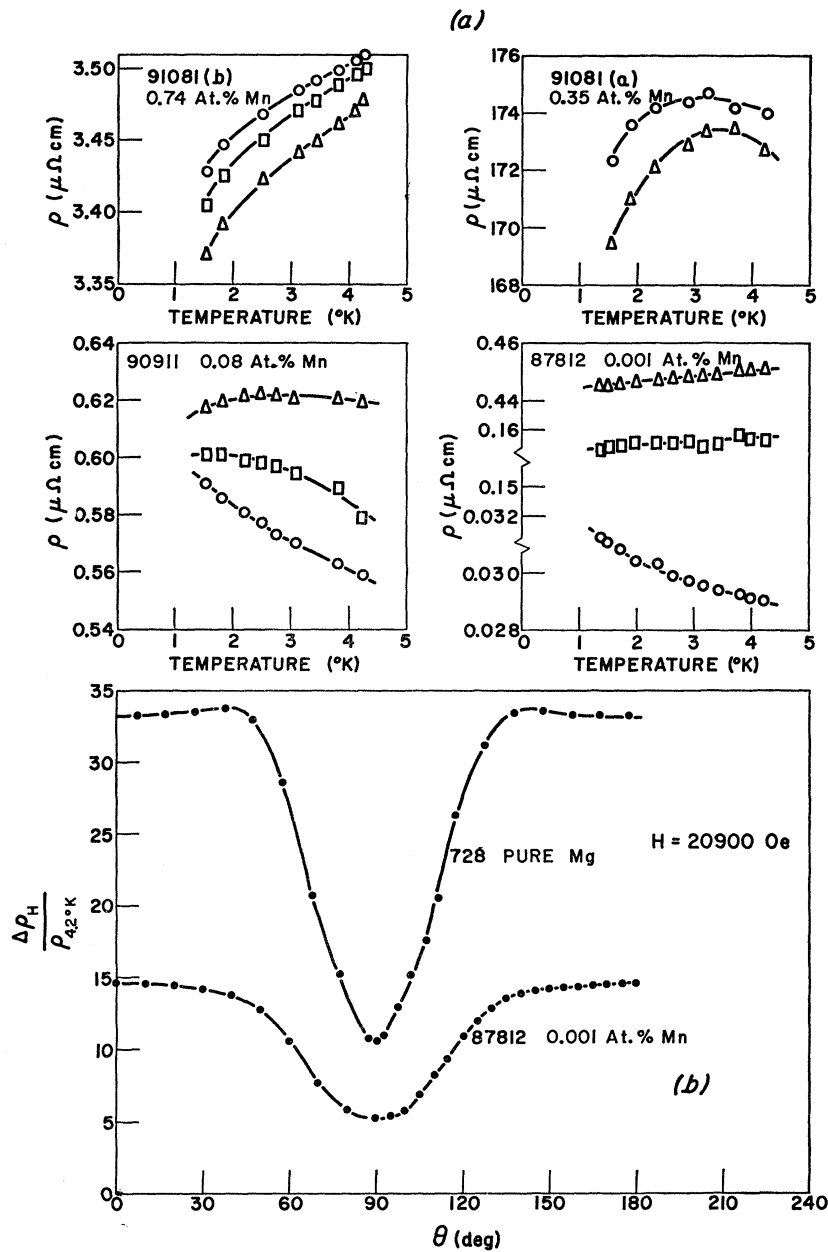


FIG. 1. (a) Resistivity of some Mg-Mn alloys as a function of temperature in a constant magnetic field.  $\circ$ : 0 kOe;  $\square$ : 9.93 kOe;  $\triangle$ : 20.9 kOe. (b) Anisotropy in the magnetoresistivity at 4.2°K for pure Mg and the most dilute Mg-Mn samples. The angle axis was selected to obtain agreement in the minimum value of  $\Delta\rho_{H_{\max}}/\rho_{4.2^\circ\text{K}}$  for both samples.  $\Delta\rho_{H_{\max}}$  means  $\Delta\rho$  at the maximum field studied (20.9 kOe).

smoothed graph of resistance ratio versus nominal composition.<sup>10</sup> The concentration and resistivity of the Mg-Al and Mg-Cd alloys were derived from the earlier data reported by Salkovitz<sup>11</sup> *et al.*<sup>12</sup> The concentration of manganese or iron in the aluminum alloys is derived from the spectroscopic analysis. Table I contains values of the resistance ratio and resistivity for the alloys

<sup>10</sup> E. W. Wallingford, thesis, University of Ottawa, Ottawa, Ontario (unpublished).

<sup>11</sup> We would like to thank Dr. Salkovitz for his generosity in supplying these samples.

<sup>12</sup> E. I. Salkovitz, A. I. Schindler, and E. W. Kammar, *Phys. Rev.* **105**, 887 (1957).

studied. The resistance samples were in the form of rolled strips (approximately  $10 \times 0.3 \times 0.03$  cm); the contacts in the form of knife edges were pressed into place on a bakelite former containing the sample. A current-potential method was used for the resistance measurements with a galvanometer amplifier to read the voltages. The sensitivity of the amplifier was better than  $3 \times 10^{-9}$  V/mm deflection. The galvanometer and current stability did not result in more than a 2% change in calibration during any one magnetoresistance run. Since the magnetoresistance of the more highly concentrated samples was small while the zero-field

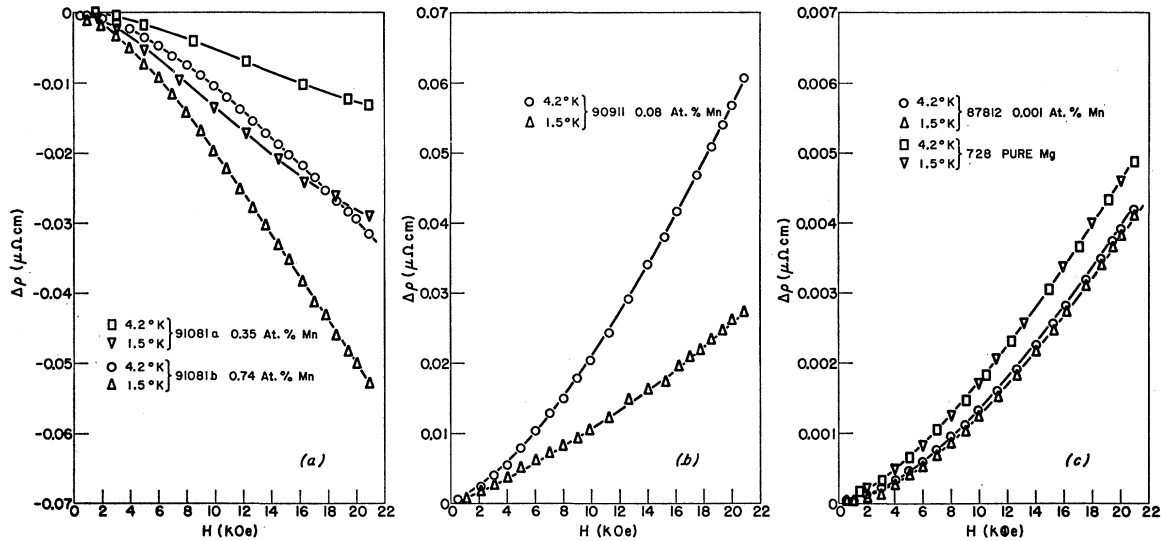


FIG. 2.  $\Delta\rho$  as a function of the magnetic field strength for a number of Mg-Mn alloys: (a) for samples 91081(a) and (b); (b) for the sample 90911; (c) for samples 87812 and 728 (pure Mg).

resistance was comparatively high, the magneto-resistance measurements on these samples was accomplished by suppressing the zero-field sample voltage with the aid of a Leeds and Northrup Type K-2 potentiometer. A Harvey Wells Corporation electromagnet was used which produced fields of approximately 21 kOe in a gap of 1.25 in. with a stability of magnet current of one part in  $10^5$  at midcurrent values. All measurements were made at 4.2°K or lower by pumping on liquid helium. The vapor pressure of the bath was controlled by a Cartesian manostat.

### 3. EXPERIMENTAL RESULTS

Figure 1(a) shows the resistivity of some of the Mg-Mn alloys as a function of temperature in a constant magnetic field and it can be noticed that all of the samples exhibit anomalies in the temperature-dependent resistivity. At the maximum field available samples 87812 and 90911 exhibit a positive magneto-resistance, while both samples exhibit a resistance minimum. Samples 91081(a) and (b) exhibit an absolute decrease in the resistivity on the application of a magnetic field, the magnitude of the decrease increasing with magnetic field strength in the temperature region studied. These samples exhibit resistance maxima (and minima) in agreement with earlier reports.<sup>7</sup>

There is a marked anisotropy in the magneto-resistivity for Mg samples which is presumably due to preferred orientation induced by cold working the samples. The magnitude of the anisotropy can be seen for samples 728 and 87812 shown in Fig. 1(b). The maximum magneto-resistance values were used, and at this value very little angular dependence could be noted in the relative magneto-resistivity. For more concentrated samples, the anisotropy is so small that no

significant difference appears for any chosen direction.

Figure 2 shows the magneto-resistance as a function of magnetic field strength for a number of specimens. As seen in Fig. 2(a) there is presumably sufficient magnetic scattering in the alloys to make the sign of the magneto-resistivity totally negative for samples 91081(a) and (b). Samples 90911 in Fig. 2(b) and sample 87812 in Fig. 2(c) show that  $\Delta\rho$  is smaller at the lower temperature, while no such temperature dependence is observed for a pure magnesium sample exhibiting no anomalous behavior in the zero field resistivity. [See sample 728, Fig. 2(c).] It can therefore be suggested that there is a negative magneto-resistivity component in the more dilute Mg-Mn samples. Figures 3(a) and 3(b) show  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  as a function of magnetic field strength for a sample of Mg-Cd and Mg-Al, respectively. As would be expected,  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  increases with increase in magnetic field, and the magnitude of the change at fixed field decreases with impurity concentration increase (i.e., normal impurity scattering). Figures 4(a) and 4(b) show  $\Delta\rho/\rho_T$  as a function of magnetic field for an Al-Fe and Al-Mn sample, where it can be seen that there is no temperature dependence to the magneto-resistance in these alloys.

### 4. DISCUSSION

The change in resistivity  $\Delta\rho$  in a magnetic field  $H$  is given by the Kohler rule as

$$\Delta\rho/\rho_T = F(H\rho_\theta/\rho_T), \quad (1)$$

where<sup>13</sup>  $\rho_\theta$  is the resistivity at the Debye temperature  $\theta$

<sup>13</sup> As there is some uncertainty in the value of  $\theta$  to be used in alloys, most workers approximate by using the value of resistivity at the ice point and we will follow the same approximation.

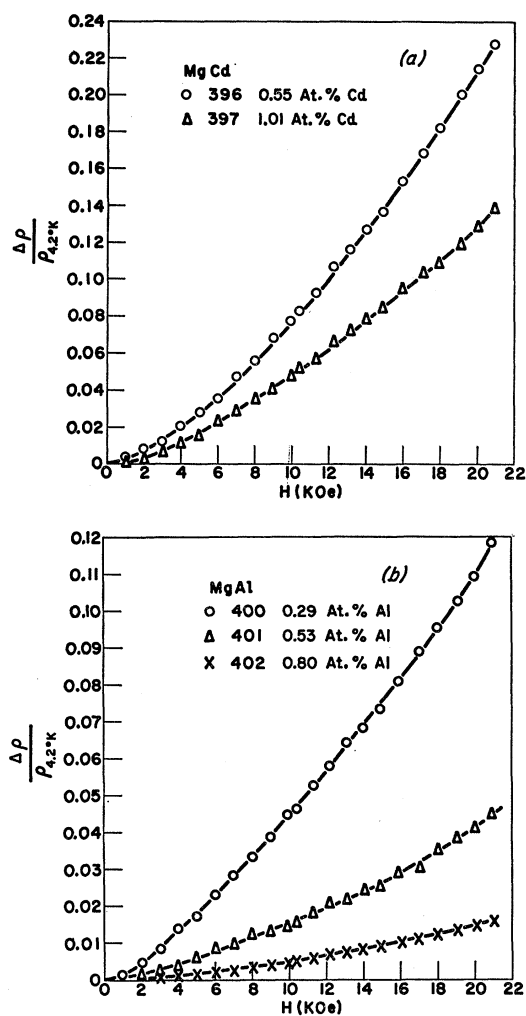


FIG. 3.  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  as a function of magnetic field strength: (a) Mg-Cd and (b) Mg-Al alloys.

and  $\rho_T$  the resistivity at temperature  $T$ , the functional form of  $F$  being unspecified. Kohler's graph for some of the Mg and Al alloys is shown in Figs. 5 and 6, where it can be seen that all of the alloys presented obey the Kohler's rule. It can be noticed that the deviation from Kohler's rule is larger for the Mg-Al alloys than for the Mg-Cd alloys, and it could be speculated that this is a result of the difference in valence between solute and solvent in the case of the Mg-Al alloys. In Fig. 5 is the magneto-resistivity data at 4.2°K for the more dilute Mg-Mn alloys. It can be seen that Kohler's rule is obeyed which is in agreement with the previous conclusions of Webber,<sup>5</sup> Yntema,<sup>14</sup> and Thomas and Mendoza.<sup>6</sup> As we will see later this Kohler behavior is a result of the fact that although there is a negative component in the magneto-resistivity of these alloys it is much smaller than the normal positive magneto-resistivity of these

<sup>14</sup> G. B. Yntema, Phys. Rev. **91**, 1388 (1953).

alloys. The magneto-resistivity data for sample 90911 is shown as an insert in Fig. 5, where it can be seen that Kohler's rule is not obeyed. The present studies on Al alloys are in agreement with the conclusions of Thomas *et al.*,<sup>6</sup> and Hedgcock *et al.*,<sup>8</sup> that the transition metals Mn and Fe do not induce a resistive anomaly in aluminum.

As discussed in an earlier publication by the authors<sup>8</sup> for the Cu-Fe system, the magneto-resistivity of a dilute alloy containing paramagnetic impurities can be considered as the sum of a normal magneto-resistivity term which is temperature independent ( $\rho_n$ ) and an anomalous term which is negative and decreases with decreasing temperature ( $\rho_s$ ) at liquid helium temperatures. This last term is presumably a result of the presence of paramagnetic impurities since it usually appears only near and below the magnetic ordering temperature for the alloy system. Yosida<sup>15</sup> and Kasuya<sup>16</sup> have both considered the theoretical problem of the magnetic interaction between conduction electrons and localized magnetic ions where an  $s$ - $d$  exchange interaction is assumed to produce a molecular field. Below a magnetic ordering temperature (usually antiferromagnetic in nature) theory predicts a monotonic decrease of resis-

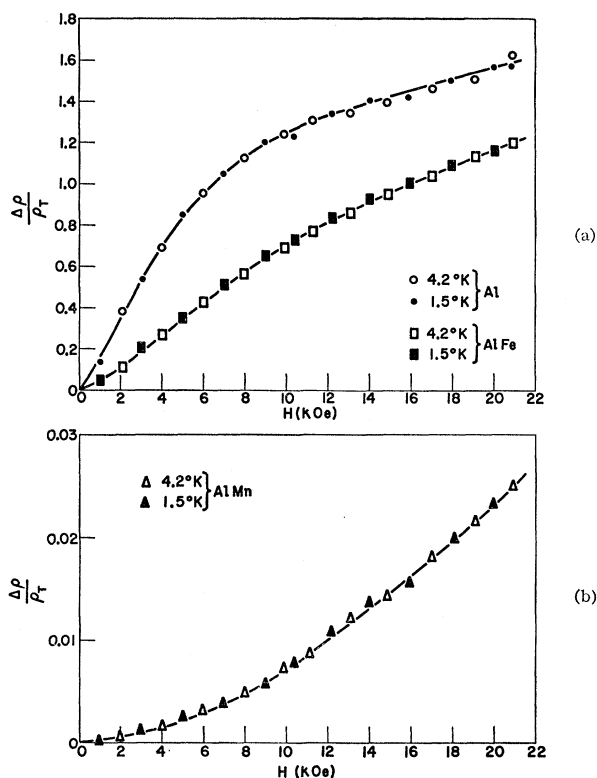


FIG. 4.  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  as a function of the magnetic field strength at 4.2 and 1.5°K: (a) for pure Al and an Al-Fe alloy; (b) the Al-Mn alloy.

<sup>15</sup> K. Yosida, Phys. Rev. **107**, 396 (1957).

<sup>16</sup> T. Kasuya, Progr. Theoret. Phys. (Kyoto) **22**, 227 (1959).

tance as the temperature is lowered. Both theories predict a negative magnetoresistance which is proportional to the square of the magnetization at low magnetic field strengths. Neglecting a small term in Kasuya's expressions for the magnetoresistivity under various field and temperature conditions, we can write

$$H=0, T=0 \quad \rho_0 = \frac{3\pi m^* C}{2 \hbar \zeta N e^2} [A^2 + (g-1)^2 j^2 J^2], \quad (2)$$

$$H=0, T \geq T_N \quad \rho_{TN} = \frac{3\pi m^* C}{2 \hbar \zeta N e^2} \times [A^2 + (g-1)^2 j(j+1)J^2], \quad (3)$$

$$H \neq 0, T \neq 0 \quad \rho = \frac{3\pi m^* C}{2 \hbar \zeta N e^2} \frac{[A^2 + \langle j^2 \rangle_{av} J^2]}{A^2 + \left( \langle j^2 \rangle_{av} - \bar{j}_z \frac{2xe^x}{(e^x-1)^2} \right) J^2}, \quad (4)$$

where  $m^*$  and  $e$  are the electron effective mass and charge, respectively,  $\zeta$  is the Fermi energy,  $C$  is the concentration of paramagnetic ions,  $N$  is the number of atoms/cm<sup>3</sup>,  $J$  is the  $s$ - $d$  exchange interaction constant,  $A$  is the Coulomb interaction constant,  $x = g\mu_B H/kT$ ,  $\bar{j}_z$  is the average  $z$  component of the angular momentum  $j$  of the paramagnetic ion, and  $\langle j^2 \rangle_{av}$  is the average of the square of the angular momentum of the paramag-

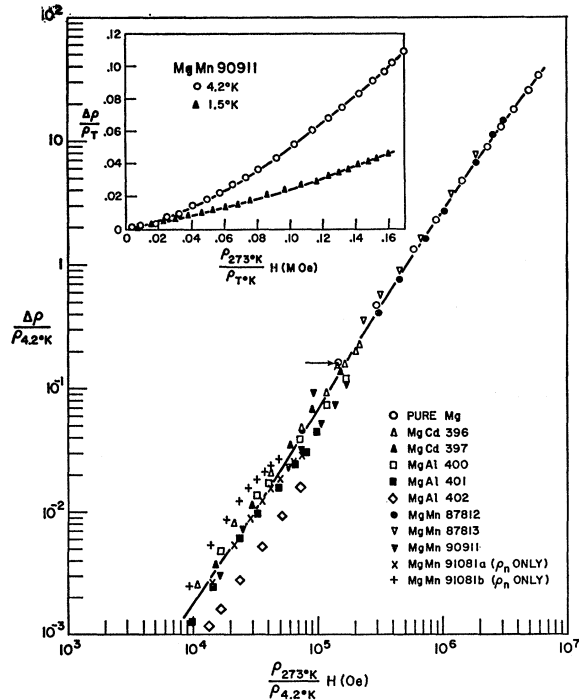


FIG. 5.  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  as a function of  $(\rho_{273^\circ\text{K}}/\rho_{4.2^\circ\text{K}}) \cdot H$  for Mg samples. In insert is shown  $\Delta\rho/\rho_T$  as a function of  $(\rho_{273^\circ\text{K}}/\rho_T) \cdot H$  for the sample 90911 at 4.2 and 1.5°K.

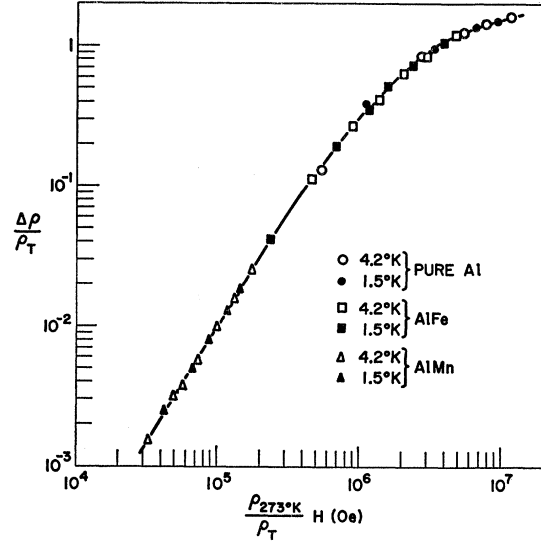


FIG. 6.  $\Delta\rho/\rho_T$  as a function of  $(\rho_{273^\circ\text{K}}/\rho_T) \cdot H$  for Al samples.

netic ion. For the method of finding these averages, the reader is referred to the original publication of Kasuya.<sup>16</sup> Using a simple molecular-field model,  $H=H_0$  when  $H_{\text{app}}=0$ , and if  $H_0$  is zero, then it has the value  $H_{\text{app}}$  in the presence of an external field. Collings and Hedgcock<sup>9</sup> have shown through electron spin resonance and susceptibility studies that an antiferromagnetic transition occurs in the Mg-Mn system in the region of the resistance maximum. If one neglects the presence of the resistance minimum in these alloys and assumes the temperature of the maximum to be the Néel temperature,<sup>17</sup> we can use Eqs. (2) and (3) to calculate  $A$  and

TABLE II.  $J$ : the  $s$ - $d$  exchange integral;  $A$ : Coulomb interaction constant; and  $A/J$  values of some MgMn alloys. The most reliable values for  $A$  and  $J$  are estimated from the data of Gaudet *et al.* (Ref. 7), where the resistivity was measured below 1°K.

Concentration (at. %)	$J$ ( $10^{-12}$ erg)	$A$ ( $10^{-12}$ erg)	$A/J$	
0.35	0.491	2.87	5.85	Present investigation
0.80	0.466	2.77	5.95	Wallingford's thesis
0.72	0.498	2.76	5.55	Wallingford's thesis
0.46	0.478	2.78	5.82	Wallingford's thesis
0.16	0.473	2.74	5.80	Gaudet <i>et al.</i>
average	0.48	2.78	5.80	

<sup>17</sup> Magnetic studies on these alloys (Ref. 9) have shown that only in the most concentrated sample is there any evidence for a Néel temperature but there are deviations from Curie's law in the region of the resistance anomaly for all of the Mg-Mn sample studies. Whether the temperature of the resistance maximum occurs at what one normally considers the Néel temperature is certainly still an open question theoretically. [See M. Baiyln, Westinghouse Research Report 029-B000-P1, 1961 (unpublished).]

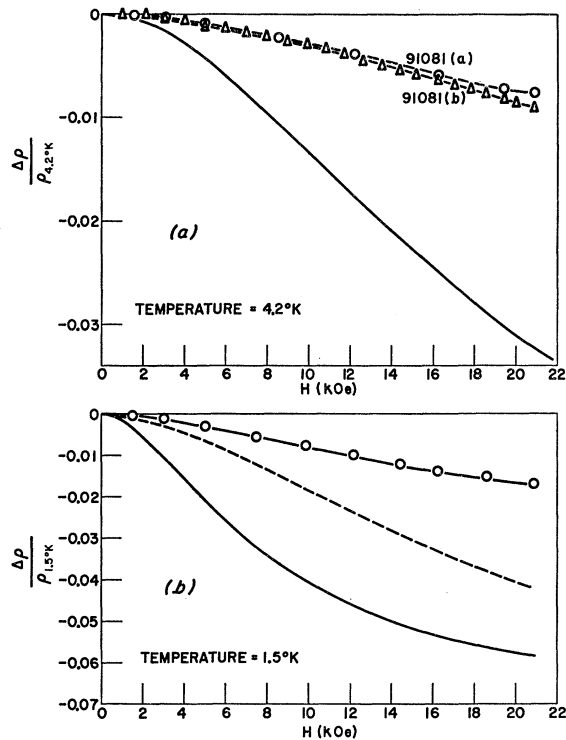


FIG. 7. (a)  $\Delta\rho/\rho_{4.2^\circ\text{K}}$  as a function of the magnetic field.  $\circ$ : experimental results for the sample 91081(a).  $\Delta$ : experimental results for the sample 91081(b), and — the calculated curve ( $\rho_s$ ) based on expression (4). (b)  $\Delta\rho/\rho_{1.5^\circ\text{K}}$  as a function of the magnetic field.  $\circ$ : experimental results for the sample 91081(a). —: the calculated curve ( $\rho_s$ ) based on expression (4). - - -: the corrected curve ( $\rho$ ) after allowance has been made for  $\rho_n$ .

$J$ . This has been done for a number of alloys and the resulting values of  $A$  and  $J$  are listed in Table II. It can be seen that the values so derived for the various alloys are independent of concentration and result in an average value of  $0.48 \times 10^{-12}$  erg for  $J$  and  $2.78 \times 10^{-12}$  erg for  $A$ . The manganese ion is assumed to be in an  $S$  state with the value of the effective magneton number as derived from susceptibility studies ( $S=2$ ). The free ion value of  $J$  derived for the  $\text{Mn}^{2+}$  ion would yield a value of  $0.35 \times 10^{-12}$  erg, whereas a value of  $J$  for the Cu-Mn system derived from the experimental results is  $0.67 \times 10^{-12}$  erg.

Using the values of  $A$  and  $J$  derived from the zero-field results and expression (4) of Kasuya, it is possible to calculate the magnetoresistance as a function of magnetic field. Shown in Fig. 7(a) is the result of such a calculation for a sample 91081(a) and (b) at the temperature of  $4.2^\circ\text{K}$ . The difference between the calculated and experimental curves can be assumed due to the positive normal magnetoresistance component  $\rho_n$ . If the difference between the theoretical and experimental curves is in fact equal to  $\rho_n$ , then the difference should obey the Kohler rule. This difference is shown in Fig. 5 where as good a fit to the Kohler rule is found as

for alloys containing nontransition metal impurities. Figure 7(b) shows the same calculation done at  $1.5^\circ\text{K}$ . The solid curve corresponds to that calculated from Eq. (4) and the dashed curve after allowance has been made for  $\rho_n$ , the normal impurity scattering discussed above. As can be seen, the agreement between experiment and theory at this temperature is not good. If one suggests a cooperative magnetic interaction and a resulting internal field,  $H_0$  will shift the zero on the field axis but will not alter the magnitude of the magnetoresistance. Only by altering  $A/J$  could agreement with experiment for a particular magnetic field be found, but it is unlikely that these constants should be a function of temperature or magnetic field—certainly no theoretical treatment suggests that they should be.<sup>18</sup> It therefore seems that some essential feature is lacking in the Kasuya theory for the temperature dependence of the magnetoresistance in metal alloys containing transition metal impurities.

Although there is no adequate theory to explain the resistance minimum, it is interesting to apply Kasuya's expression for the magnetoresistivity in those alloys exhibiting a resistance minimum only [Eq. (4)]. For example, by assuming the same value of  $J$  and  $A$  as for the more concentrated alloys exhibiting a maximum, an estimate of  $\Delta\rho$  at maximum magnetic field for sample 90911 yields  $\Delta\rho_s = -2.4 \times 10^{-8} \Omega\text{-cm}$  at  $4.2^\circ\text{K}$ . This can be compared with the experimentally observed value of  $\Delta\rho = 6.1 \times 10^{-8} \Omega\text{-cm}$ . Therefore, the normal magnetoresistivity term, the difference of these two values, equals  $8.5 \times 10^{-8} \Omega\text{-cm}$ . Then  $\Delta\rho_n/\rho_{4.2^\circ\text{K}} = 0.152$  for  $H\rho_{273}/\rho_{4.2^\circ\text{K}} = 149$  kOe. This point is shown as A in Fig. 5, giving better agreement to the initial Kohler curve plotted for this alloy. If this improvement in the fit is a result of the influence of  $\Delta\rho_s$ , then it could be speculated that the magnetoresistance of alloys exhibiting a minimum will be negative<sup>19</sup> when  $A/J$  is small and the concentration relatively large and becomes positive when  $A/J$  is large and the concentration of paramagnetic ions is smaller.

## 5. CONCLUSIONS

(1) From the temperature dependence of the electrical resistivity of concentrated Mg-Mn alloys in zero magnetic field a value of the  $s$ - $d$  exchange integral  $J$  and the Coulomb integral  $Q$  of  $0.48 \times 10^{-12}$  erg and  $2.78 \times 10^{-12}$  erg, respectively, are found which are independent of manganese concentration up to the solid solubility limit.

(2) For Mg-Mn alloys exhibiting both a resistance

<sup>18</sup> Yosida pointed out that experimental agreement with his theory worsened as the temperature was lowered below the Néel point. Kasuya remarked on the discrepancy and suggested the magnetically ordered states should be represented by some sort of collective spin mode at sufficiently low temperatures.

<sup>19</sup> A total negative magnetoresistivity has been observed in Cu-Fe, Cu-Mn and Zn-Mn alloys exhibiting only a resistive minimum. (See Refs. 3 and 4.)

minimum and maximum the total magnetoresistance is negative. This magnetoresistance can be separated into a negative ( $\rho_s$ ) and positive ( $\rho_n$ ) component. The spin component  $\rho_s$  can be explained using the same  $J$  and  $A$  values as derived above at temperatures near the Néel temperature. The normal component ( $\rho_n$ ) is found to obey Kohler's rule. The observed temperature dependence of the negative component ( $\rho_s$ ) does not follow from the existing theory.

(3) For the more dilute Mg-Mn alloys exhibiting only a resistance minimum, there appears to be a negative magnetoresistivity component again requiring the

same  $A$  and  $J$  values as above. The positive magnetoresistance component obeys Kohler's rule.

(4) Magnesium containing nontransition impurities follow Kohler's rule as do the alloys of aluminum containing transition metal impurities.

#### ACKNOWLEDGMENTS

The authors would like to acknowledge the technical assistance of Mrs. H. Hohnke and G. Mark, and to thank Dr. E. W. Collings, Dr. W. B. Muir, and D. Mathur for their suggestions and numerous discussions during the course of these experiments.

### $F$ -Band Shape in the CsCl Structure Under Pressure\*†

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(Received 24 January 1964)

Color centers have been formed by x irradiation of RbCl above the polymorphic transition pressure, and the shape of the new  $F$  band at 509  $m\mu$  in this CsCl-type structure has been examined under a pressure of 6200 atm at liquid-helium temperature. The band shows no evidence of the multiplet structure observed in the cesium halides, thus indicating that the lattice structure is not responsible for this effect. The  $F$  band in CsCl has also been formed and studied under pressure at helium temperature, and the triplet components show the usual relative intensity and the characteristic  $F$ -band shift. No evidence of  $K'$  bands was observed for these hydrostatic pressures.

#### INTRODUCTION

RECENT studies of color centers in CsCl and CsBr<sup>1-3</sup> revealed structure on the principal absorption band, in contrast to the usual  $F$  band in alkali halides with the NaCl-type lattice. This structure, which Rabin and Schulman<sup>2</sup> decomposed into three components at liquid-helium temperature, appears to be identical for centers formed by x irradiation or additive coloring, is unaffected by bleaching or heat treatment, and is not sensitive to sample purity. It therefore seems reasonable to associate these multiplets with a single electron-excess center, presumably an  $F$  center composed of an electron bound to a negative-ion vacancy. Rabin and Schulman<sup>2</sup> first proposed that if these components are all due to one center, then they must represent a splitting of the excited  $F$  state by a

crystal-field effect peculiar to the CsCl-type lattice, or a splitting caused by the cesium ion itself.

The present work was undertaken to determine the influence of crystal structure by studying the  $F$  band formed in the pressure-induced simple cubic phase of a normally face-centered cubic alkali halide. RbCl transforms from the NaCl lattice structure to the CsCl lattice structure at about 5000–6000 atm. On the basis of a Mollwo relation between peak position and lattice constant for other CsCl-type crystals, one expects the  $F$  center to appear at about 520  $m\mu$  in the high-pressure form. Jacobs<sup>4</sup> looked for this peak in RbCl crystals x rayed or additively colored at atmospheric pressure prior to the structure transformation, but was unable to detect any new center. Drickamer *et al.*<sup>5,6</sup> found a new band, which they called the  $K'$  band, which replaced the  $F$  band in simple cubic phases at very high pressures and room temperature.

With the apparatus described below, it is possible to transform the crystal first and then form the CsCl-type centers by x raying under pressure at room or low temperatures. In particular it is possible to form

\* This work was supported in part by the U. S. Atomic Energy Commission.

† Based on part of a thesis submitted to the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree (1962). A preliminary report of this aspect of the work was given by D. Lazarus at the Conference on Crystal Lattice Defects, Kyoto, Japan, September 1962.

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<sup>1</sup> P. Avakian and A. Smakula, *Phys. Rev.* **120**, 2007 (1960).

<sup>2</sup> H. Rabin and J. H. Schulman, *Phys. Rev. Letters* **4**, 280 (1960); *Phys. Rev.* **125**, 1584 (1962).

<sup>3</sup> D. W. Lynch, *Phys. Rev.* **127**, 1537 (1962).

<sup>4</sup> I. S. Jacobs, *Phys. Rev.* **93**, 993 (1954).

<sup>5</sup> W. G. Maisch and H. G. Drickamer, *Phys. Chem. Solids* **5**, 328 (1958).

<sup>6</sup> R. A. Eppler and H. G. Drickamer, *J. Chem. Phys.* **32**, 1418 (1960).