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Magnetoresistances of Dilute Alloys of Manganese in Copper, Manganese in Zinc and Chromium in Zinc at Liquid Helium Temperatures*

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Synopsis

Magnetoresistances of alloys of Mn in Cu (5.4 atomic per cent Mn), Mn in Zn (0.12 atomic per cent Mn) and Cr in Zn (0.10 atomic per cent Cr) are measured in the magnetic field up to about 76 KOe at liquid helium temperature. The magnetoresistance of CuMn alloy decreases with increasing field and shows a reproducible hysteresis. The ratio of the decrease of resistance for the strongest magnetic field applied here to the field-free resistance at 0°K is about 7 per cent, while the ratio of the decrease of resistance for an infinite magnetic filed at 4.24°K to the field-free value at 0°K is estimated to be 38 per cent, using our experimental results and the method proposed by K. Yosida. Magnetoresistances of ZnMn and ZnCr alloys are also measured under the same experimental conditions as that for CuMn alloy.

I. Introduction

Dilute alloys of transition metals in monovalent and divalent metals are known to show some interesting electrical and magnetic properties at low temperatures. The most extensive experimental and theoretical works have been done on CuMn alloys. The electrical properties of the CuMn alloys are characterized by an anomalous temperature-dependent electrical resistance and a negative magnetoresistance at low temperatures.(1),(2),(3) The magnetic behaviour at low temperatures shows an antiferromagnetic transition.(3),(4) The specific heat,(3),(5) thermoelectric power,(3) Hall coefficient,(3) and electron and nuclear resonance(4),(6) have also been studied.

The most striking feature observed in the magnetoresistance of CuMn alloys is that the resistance decreases on applying either a transverse or a longitudinal magnetic field at liquid helium and hydrogen temperatures. This is an effect discovered by Gerritsen and Linde(1) who also observed that the size of the transverse

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* The 1008th report of the Research Institute for Iron, Steel and Other Metals.

(1) A. N. Gerritsen and J. O. Linde, Physica, **18** (1952), 877.

(2) R. W. Schmitt and I. S. Jacobs, J. Phys. Chem. Solids, **3** (1957), 324.
I. S. Jacobs and R. W. Schmitt, Phys. Rev., **113** (1959), 459.

(3) Y. Shibuya, Y. Tawara, S. Tanuma, Y. Saito, Y. Muto and T. Fukuroi, Kamerlingh Onnes Conference, Leiden, June (1958) [Suppl. Physica, **24** (1958), S 175].
S. Tanuma, J. Phys. Soc. Japan, **14** (1959), 541.

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

(5) J. de Nobel and F. J. du Chatenier, Physica, **25** (1959), 969.

(6) T. Sugawara, J. Phys. Soc. Japan, **14** (1959), 643.

and longitudinal effect is a comparable order. They also showed that the resistance can be made to decrease by 10 per cent in some cases for the magnetic field up to 20 KOe, whereas the field-free resistance anomaly amounts to only a few per cent of the residual resistance.

Theoretically, the behaviour of CuMn alloys was investigated by K. Yosida.(7) On the basis of the exchange interaction between the conduction electrons and the manganese ions, he explained the magnetic properties, anomalous electrical resistivity and negative magnetoresistance of CuMn alloys. However, his theory does not give an explanation of the resistance minimum and maximum which have been found in the resistance-temperature curves of the alloys with less than one atomic per cent Mn.

The resistance minimum of dilute alloys of divalent metals has been observed with Mg alloys.(8) We also found the resistance minimum in the case of dilute alloys of Mn and Cr in Zn.(9) But we could not find out any anomalous electrical behaviour with ZnSn alloy(9).

We report here experiments on the magnetoresistance of an alloy of 5.4 atomic per cent Mn in Cu for the field up to 76 KOe. The 5.4 atomic per cent CuMn alloy was selected as we know that it shows no resistance minimum. Magnetoresistances of more dilute CuMn alloys will be reported later. We also studied the magnetoresistance of alloys of 0.12 atomic per cent Mn in Zn and 0.10 atomic per cent Cr in Zn up to the above-mentioned magnetic field. All measurements were performed on the transverse effect of the magnetoresistance at 4.24°K. The resistivities of these specimens are considerably larger than that of pure Cu or Zn metal, so that it seems that there is no need of considering the effect of quantization of the electron orbit in an applied magnetic field up to 76 KOe.

II. Preparation of specimens

(1) CuMn alloy. First, the mother CuMn alloy (19.32 weight per cent Mn) was made by melting the oxygen free Cu (99.997 per cent in purity) and electrolytic Mn (99.99 per cent in purity) under high vacuum in a high-frequency induction furnace. Then the ingot was forged and heat-treated at 750°C for 5 hours. Next, the alloy of 5.4 atomic per cent Mn in Cu was made by melting Cu from the same origin and the mother alloy under similar conditions. Then this alloy was forged and cold-drawn to the wire of 0.3 mm in diameter. It was annealed at 750°C for 5 hours and, as described later, at 450°C for an hour after making a specimen.

(2) ZnMn and ZnCr alloys. First, an alloy of 4.25 weight per cent Mn in Zn and an alloy of 1.20 weight per cent Cr in Zn were made by melting Zn (99.999 per cent in purity) and Mn (99.999 per cent in purity) or Cr (99.999 per cent in purity) under an atmosphere of argon in a high-frequency induction furnace. Then an

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

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

(9) Y. Muto, Y. Tawara, Y. Shibuya and T. Fukuroi, J. Phys. Soc. Japan, **14** (1959), 380; Y. Muto, ibid., **15** (1960), 2119.

alloy of 0.12 atomic per cent Mn in Zn was made by melting Zn and ZnMn mother alloy under similar conditions, except for using a S.B. glass crucible in place of an alumina one which was contaminated with very small amounts of Fe included. An alloy of 0.10 atomic per cent Cr in Zn was also prepared similarly. These alloys were also forged and cold-drawn to the wire of 0.3 mm in diameter.

The ZnMn and ZnCr alloys are expected to have the same structure as Zn metal, which have a close packed hexagonal structure. According to Schramm,(10) the solid solubility of Mn in Zn was found to be 0.58 atomic per cent at the eutectic temperature and less than 0.02 atomic per cent at 200°C. As the ZnMn alloy containing 0.12 atomic per cent Mn, there remains some doubt as to whether all the Mn is really in solid solution. Thus the specimen sealed in an evacuated S.B. glass tube was heated at 330°C for an hour, and then quenched rapidly into ice water. Therefore, we believe that it is within the solubility limit.

The solid solubility of Cr in Zn is known to be 0.04 atomic per cent Cr at the eutectic temperature and 0.013 atomic per cent Cr at 350°C according to Heumann.(11) As to the ZnCr alloy containing 0.10 atomic per cent Cr, whether all the Cr is really in solid solution is very doubtful. We were obliged to fabricate this alloy with the similar method to the ZnMn alloy. The specimen sealed in an evacuated S.B. glass tube was heated at 350°C for about 2 hours and then quenched rapidly into ice water. In the previous note,(9) we showed that the electrical resistance of ZnCr alloy with 0.10 atomic per cent Cr, which is taken from the same origin as the present one, and with 0.01 atomic per cent Cr increases both with decreasing temperature. As the electrical behaviours of these two alloys are similar and it is presumable that the alloy containing 0.01 atomic per cent Cr enters within the solubility range, we expect that the alloy containing 0.10 atomic per cent Cr is also within the solubility limit.

III. Experimental procedures

The resistance of a specimen was measured using the standard potentiometric technique. Measurements were made with the current flowing in each direction through the specimen so that the influence of the thermal e.m.f. in the potential leads could be eliminated. The thermal e.m.f. in other parts of the measuring circuit was usually negligible. The accuracy of measuring resistance is estimated to be about ±0.1 per cent owing to errors of constancy of the magnetic field. And the uncertainty of the specific resistance itself attains about 3 per cent owing to errors in measuring dimensions of specimens.

A specimen of CuMn alloy was a wire of approximately 0.3 mm diameter by about 8 mm long and fixed on a lucite plate. Specimens of ZnMn and ZnCr alloys were wires of similar diameter by about 8 cm long and fixed on lucite plates in form of snake. In the case of the CuMn alloy, potential leads of the same material were spot-welded and then the specimen was annealed at 450°C for an hour in

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(10) J. Schramm, Z. Metallkunde, 32 (1940), 399.

(11) T. Heumann, Z. Metallkunde, 39 (1948), 45.

vacuo. In the case of ZnMn and ZnCr alloys, potential leads of the respective material were soldered by using $Bi_{60}Cd_{40}$ solder which melts at about 150°C and does not become superconductive down to 1°K.

The magnet used is a coreless conducting sheet type solenoid of Bitter type installed recently in our institute. The magnetic field up to 76 KOe was generated in the cylindrical space of 3 cm in diameter and 4 cm high in the inside of the coreless solenoid by flowing a strong direct current up to 8,500 Amps. The details of the equipment will be published elsewhere.

IV. Experimental results

The magnetoresistance of the CuMn alloy at 4.24°K is shown in Fig. 1 as a function of the magnetic field strength. We can see two features. The first feature is that the resistance decreases with increasing the magnetic field. The second one is that a hysteresis of the magnetoresistance is observed.

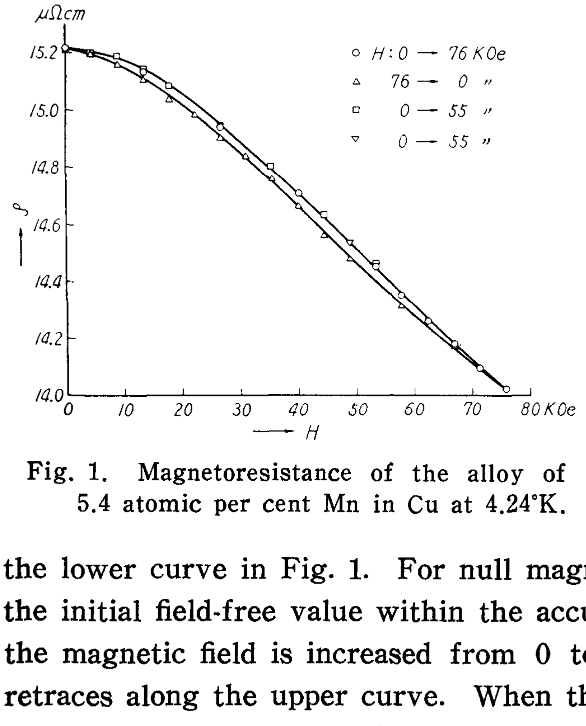

Fig. 1. Magnetoresistance of the alloy of 5.4 atomic per cent Mn in Cu at 4.24°K.

Let us touch upon the hysteresis phenomenon first, leaving the dependency of the magnetoresistance on the field till later on. In order to try the reproducibility of the hysteresis, we carried out the following experiment. As the magnetic field increases from 0 to 76 KOe, the resistance diminishes as along the upper curve in Fig. 1. Then as the magnetic field decreases from 76 to 0 KOe, the resistance increases as the lower curve in Fig. 1. For null magnetic field, the resistance coincides with the initial field-free value within the accuracy of the experimental error. When the magnetic field is increased from 0 to 55 KOe again, the magnetoresistance retraces along the upper curve. When the magnetic field is annulled once more, the resistance returns to the initial value. Thus the behaviour of the resistance against the field traces the same process over again. Therefore, the hysteresis of the magnetoresistance is reproducible within the experimental error.

Next, we take up the field-dependency of the resistance. Since the difference between the upper and lower curves in Fig. 1 being slight as a whole, we shall discuss the magnetoresistance which corresponds to the upper curve. In Fig. 2, we have plotted the $\log(\Delta\rho_H/\rho_{4.2})$ against $\log H$, where $\Delta\rho_H = \rho_{4.2} - \rho_H$, and $\rho_{4.2}$ is the resistance at 4.24°K. It seems that $\Delta\rho_H/\rho_{4.2}$ increases approximately proportional to H^2 for the range below 20 KOe and becomes roughly proportional to H on approaching the highest field attained. $\Delta\rho_H/\rho_{4.2}$ for $H = 75.7$ KOe is about 7.8 per cent.

The electrical resistance versus temperature curve is shown in Fig. 3, in which

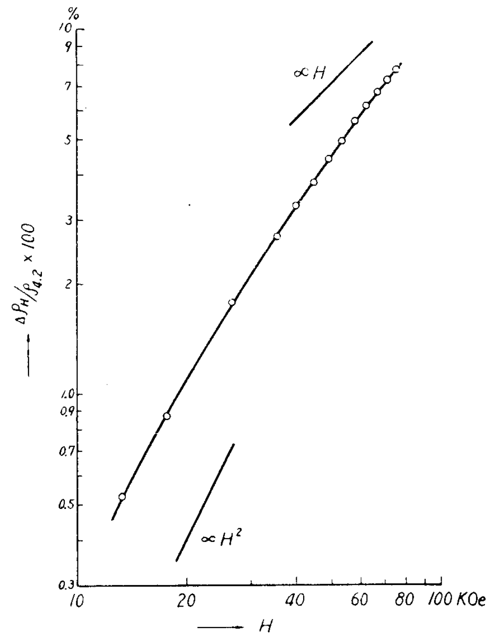

Fig. 2. $\log\Delta\rho_H/\rho_{4.2}$ vs. $\log H$ for CuMn alloy at 4.24°K.

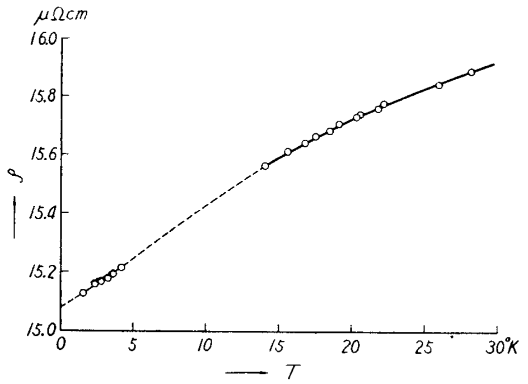

Fig. 3. Specific resistance vs. temperature of CuMn alloy.

an anomalous decrease of resistance with decreasing temperature is visualized.

In Fig. 4, the magnetoresistance of ZnMn alloy at 4.24°K is plotted as a function of the field strength. Alike the magnetoresistance of CuMn alloy, the resistance decreases with increasing the field in the low field range. But it stops to decrease at about 30 KOe, then begins to increase with increasing the field. At about 60 KOe, it regains to the field-free value and then continues to increase up to 76 KOe.

The specific resistance of ZnMn alloy below 4.24°K is presented in Fig. 5. The resistance increases with decreasing temperature, which tendency suggests that ZnMn alloy should display a resistance minimum above 4.2°K. It is also noticeable that $d\rho/dT$ decreases with decreasing temperature, which fact implies that a resistance maximum would also

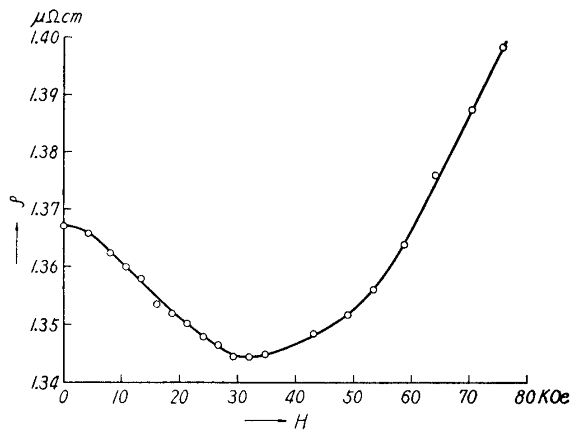

Fig. 4. Magnetoresistance of ZnMn alloy at 4.24°K.

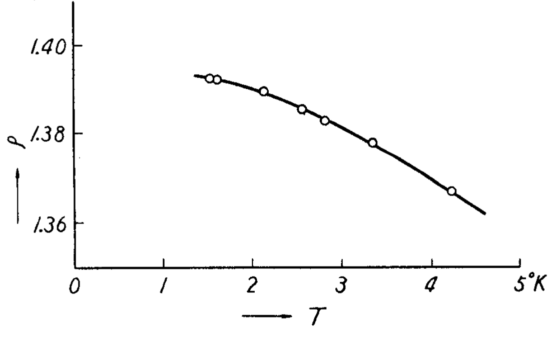

Fig. 5. Specific resistance vs. temperature of ZnMn alloy.

appear at a lower temperature.

The magnetoresistance of ZnCr alloy at 4.24°K is shown in Fig. 6 as a function of the field strength. At first sight, the behaviour of the magnetoresistance of the ZnCr alloy is very different from the above-mentioned alloys. Namely, the resistance increases with increasing field, showing a small hump at the low field range. Notwithstanding the hump disappears above 20 KOe, the resistance continues to increase up to 76 KOe.

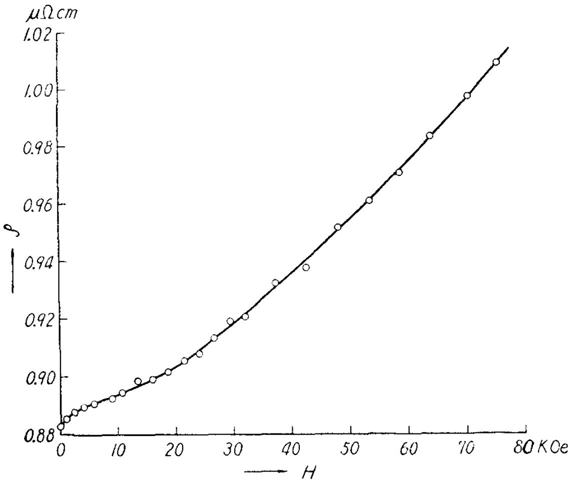

Fig. 6. Magnetoresistance of ZnCr alloy at 4.24°K.

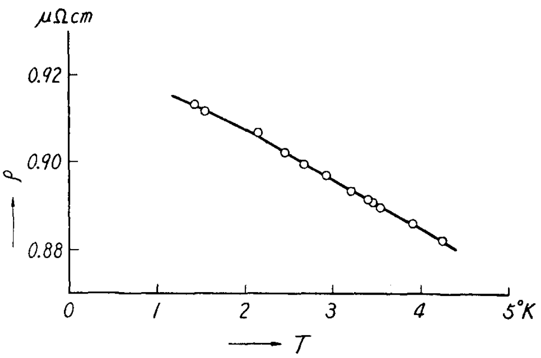

Fig. 7. Specific resistance vs. temperature of ZnCr alloy.

In Fig. 7, it is seen that the specific resistance of ZnCr alloy increases with decreasing temperature, the tendency also suggesting the existence of a resistance minimum above 4.2°K.

V. Discussion

The appearance of the hysteresis in the magnetoresistance of CuMn alloy was already reported by Schmitt and Jacobs.⁽²⁾ They also found that the magnetization of CuMn alloy shows the hysteresis. Thus they showed that the magnetoresistance depends not only on the magnetic field but also on the magnetization. According to their analysis, the relation between the magnetoresistance and the magnetization is a quadratic one. But as their experiment was only performed below 8 KOe, we do not know whether the above-mentioned relation holds or not for a stronger field. As we are planning the measurement of the magnetization up to 80 KOe, this problem will soon be solved experimentally.

K. Yosida⁽⁷⁾ tried to explain the magnetic and electrical properties of CuMn alloys from the view-point of the molecular-field using the *s-d* exchange interaction between the conduction electrons and the manganese ions. The magnetoresistance calculated is approximately proportional to the square of the magnetization for the low field range in agreement with the experimental results by Schmitt and Jacobs.

Y. Saito and T. Fukuroi⁽³⁾ measured the magnetic properties of CuMn alloy

(5.4 atomic per cent Mn) of the same origin as the present specimen and reported that the alloy shows an antiferromagnetic behaviour. Their result agrees well with that of Owen et al.(4) We know that the spin is smaller than 5/2 and is approximately assessed at 2. It is also estimated that the Néel temperature, T_N, is 28 ±10°K. Using the magnetic data, the field-free resistance at T_N and 0°K and by means of Yosida's method for analysis, we can calculate the resistivity for an infinite value of magnetic field at any finite temperature, ρ_∞. Thus ρ_∞ is estimated to be about 9.29 $\mu\Omega$ cm and this corresponds to the decrease of 38 per cent of ρ_0, where ρ_0 is the resistivity at 0°K. Nevertheless, $\Delta\rho_H/\rho_0$ in this experiment is only about 7 per cent.

The decrease of the magnetoresistance of ZnMn alloy for low magnetic field may also be explained by the *s*-*d* interaction mechanism in a similar way to the CuMn alloy. The decrease of the magnetoresistance is very small, because the ZnMn alloy contains only 0.12 atomic per cent Mn. Therefore, it seems that the magnetoresistance begins to increase as the normal metals and alloys. But we cannot elucidate the details in the resistance-field curve.

The magnetoresistance of ZnCr alloy follows apparently similar behaviour to normal alloys except for the hump in the low field range, but its details are not evident now.

Summary

(1) The measurements of the magnetoresistance of CuMn (5.4 atomic per cent Mn), ZnMn (0.12 atomic per cent) and ZnCr (0.10 atomic per cent) alloys were performed at 4.24°K as the function of the magnetic field strength up to 76KOe.

(2) The magnetoresistance of the CuMn alloy decreases with increasing field and a reproducible hysteresis phenomenon is observed.

(3) The magnetorestance of the ZnMn alloy decreases up to 30 KOe and then turns to increase with increasing field.

(4) The magnetoresistance of the ZnCr increases with increasing field.

Acknowledgment

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