Low-Temperature Electrical and Magnetic Behavior of Dilute Alloys: Mn in Cu and Co in Cu†

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Measurements are reported of the remanent magnetization in a 1.8 atom percent Mn in Cu alloy at 4.2°K and of the low-temperature resistance, magnetoresistance, and magnetization of solid solution alloys of 0.5, 1.0, and 2.0 atom percent Co in Cu. The isothermal remanence of the Cu(Mn) alloy saturates at about 3×10^{-2} (μ_B/Mn atom) after application of a field of about 14 kilo-oersteds, and does not increase after application of pulsed fields up to 140 koe. It is equal to the saturation thermoremanence obtained after cooling in fields $\geq$1.5 koe. Both remanences reverse in relatively low fields of about 2 koe. The magnetoresistance and magnetization of the Cu(Co) alloys obey the relation, $\Delta\rho=-b\sigma^2$, found previously for Cu(Mn) alloys, with b temperature-independent in contrast to that for Cu(Mn). The low-temperature resistivity of the Cu(Co) alloys increases with decreasing temperature and no maximum occurs down to 1.6°K. The magnetization of the Cu(Co) alloys shows neither remanence nor hysteresis but is nonlinear with field and with concentration. Comparison of results on these systems with existing theories delineates the areas of agreement and of disagreement.

1. INTRODUCTION

DILUTE alloys of transition metals in noble metals show interesting electrical and magnetic properties at low temperatures. The most extensive experimental work has been done on Cu(Mn).[1] This alloy—as well as Au(Mn) and Ag(Mn)—has an anomalous temperature-dependent resistivity and a negative magnetoresistance at low temperatures.[2,3] The magnetic behavior at liquid helium temperatures reveals evidence of a cooperative magnetic transition.[3,4] The relation between the electrical and magnetic behavior of Cu(Mn) has also been studied.[3]

Other properties of Cu(Mn) have been measured: electron[4] and nuclear resonance,[4–7] specific heat,[8,9] thermoelectric power,[5,10] Hall coefficient,[6,10] and thermal conductivity.[5,6] In addition, several theoretical papers have attacked the problem of magnetic or electrical behavior of this alloy.[11–17] In spite of this concerted attack on Cu(Mn) there remain several important problems that have not been solved. One of these is the origin of the "parasitic ferromagnetism"; i.e., the hysteresis and remanent magnetization.

We report here experiments on the remanence in a 1.8 atom percent Mn in Cu alloy at 4.2°K. The isothermal remanence saturates, after application of a field of about 14 kilo-oersteds, at a value equal to the saturation thermoremanence obtained by cooling in fields $\geq$1.5 kilo-oersteds. Moreover, both remanences reverse in relatively low fields ($\sim$2 koe).

The extensive work on Cu(Mn) has not been duplicated for other dilute alloys of transition metals in noble metals, although many alloys have been looked at in one way or another. There is a need to examine both the electrical and magnetic properties of such systems in order to codify the types of behavior observed, to see if the ideas developed for Cu(Mn) have wider applicability, and to see if the behavior of other systems give hints about those problems not yet understood for Cu(Mn).

We also report low-temperature resistance, magnetoresistance, and magnetization measurements on Cu(Co) solid solutions. These alloys show a resistance minimum at low temperatures, as reported earlier by Linde,[18] and

† An abstract of this work was presented at the Kamerlingh Onnes Conference, Leiden, June, 1958 [I.S. Jacobs and R. W. Schmitt, Suppl. Physica **24**, S174 (1958)].

[1] We shall designate dilute alloys by the notation $X(Y)$, X being the solvent and Y the solute.

[2] A. N. Gerritsen and J. O. Linde, Physica **17**, 573, 584 (1951); **18**, 877 (1952); A. N. Gerritsen, Physica **19**, 61 (1953).

[3] R. W. Schmitt and I. S. Jacobs, Can. J. Phys. **34**, 1285 (1956); J. Phys. Chem. Solids **3**, 324 (1957).

[4] Owen, Browne, and Kip, Phys. Rev. **100**, 965(A) (1955), Owen, Browne, Knight, and Kittel, Phys. Rev. **102**, 1501 (1956), Owen, Browne, Arp, and Kip, J. Phys. Chem. Solids **2**, 85 (1957).

[5] Gorter, van den Berg, and de Nobel, Can. J. Phys. **34**, 1281 (1956).

[6] G. J. van den Berg, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, August, 1957* (University of Wisconsin Press, Madison, 1958), Paper 44-1.

[7] Van der Lugt, Poulis, Hardeman, and Hass, Physica **23**, 797 (1957); W. van der Lugt and N. J. Poulis, Kamerlingh Onnes Conference, Leiden, June, 1958 [Suppl. Physica **24**, S158 (1958)].

[8] F. E. Hoare and J. E. Zimmerman, Bull. Am. Phys. Soc. Ser. II, **3**, 124 (1958).

[9] J. de Nobel and F. J. du Chatenier, Kamerlingh Onnes Conference, Leiden, June, 1958 [Suppl. Physica **24**, S175 (1958)].

[10] Shibuya, Tawara, Tanuma, Saito, Muto, and Fukuroi, Kamerlingh Onnes Conference, Leiden, June, 1958 [Suppl. Physica **24**, S175 (1958)].

[11] J. Korringa and A. N. Gerritsen, Physica **19**, 457 (1953); J. Korringa, Can. J. Phys. **34**, 1290 (1956).

[12] R. W. Schmitt, National Science Foundation Conference on Low-Temperature Physics and Chemistry, Baton Rouge, December, 1955 (unpublished), Paper D-2; Phys. Rev. **103**, 83 (1956).

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

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

[15] G. W. Pratt, Jr., Phys. Rev. **106**, 53 (1957); **108**, 1233 (1957).

[16] A. Blandin and J. Friedel, Colloque International de Magnétisme, Grenoble, July, 1958 (unpublished), Paper 50; J. phys. radium (to be published).

[17] H. Hasegawa and R. Kubo, International Conference on Electronic Properties of Metals at Low Temperatures, Geneva, New York, August, 1958 (unpublished).

[18] J. O. Linde, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, August, 1957* (University of Wisconsin Press, Madison, 1958), Paper 41-1.

a negative magnetoresistance. However, no maximum in resistivity occurs down to 1.2°K. The magnetic behavior shows no evidence for a cooperative magnetic transition, although the magnetization is nonlinear in field. The magnetoresistance and magnetization are related by $\Delta\rho = -b\sigma^2$, where b is temperature independent in contrast to Cu(Mn).

In the last section of this paper we will discuss the contrasting behavior of Cu(Mn) and Cu(Co).

2. MAGNETIC REMANENCE IN A Cu(Mn) ALLOY

(a) Experimental Methods

Very high magnetic fields are needed for an adequate study of the isothermal remanent magnetization (IRM) in our 1.8 atom percent alloy at 4.2°K. A pulsed-field coil magnet[19] delivering unidirectional field pulses up to 140 koe is used. The field pulses are shaped like half a sine wave. The time elapsing between zeros of the field is 28 milliseconds at high fields, and substantially longer for low fields.

The IRM of the 1.8% Cu(Mn) alloy decreases with increasing temperature [see Fig. 5 of the second reference 3] so it is important to avoid eddy current heating of the sample. For this reason the solid cylinder used for static magnetization measurements was rejected in favor of an annealed bundle of wire of the same 1.8 atom percent Cu(Mn) used for electrical measurements. Eddy current heating is proportional to the square of the sample radius, and these wires were small enough to avoid such heating.

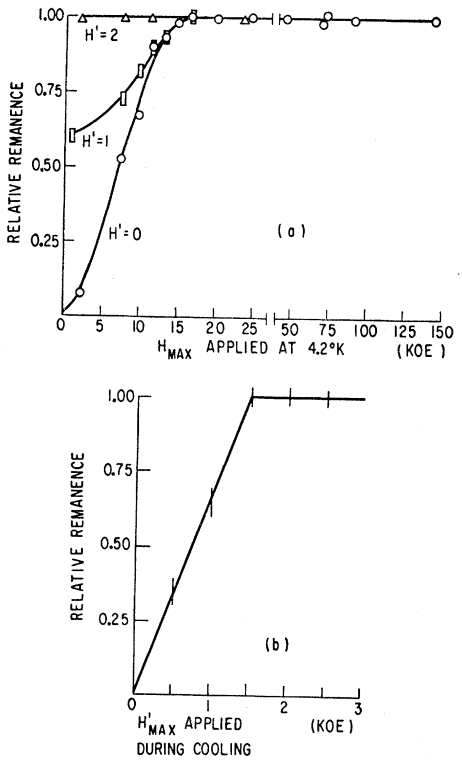

FIG. 1. Behavior of isothermal remanence and thermoremanence of 1.8 atom percent Mn in Cu at 4.2°K. Scale: $1.0 \approx 3\times10^{-2}$ μ_B/Mn atom $\approx 0.75\%$ alignment of Mn atoms. (a) Saturation of isothermal remanence from various initial states; field H' (koe) applied during cooling. (b) Saturation of thermoremanence.

[19] I. S. Jacobs and P. E. Lawrence, Rev. Sci. Instr. **29**, 713 (1958).

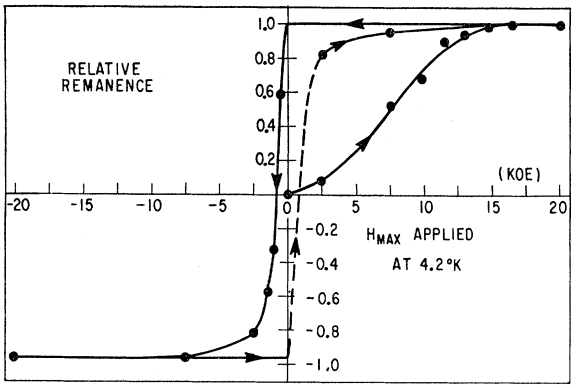

FIG. 2. Remanence hysteresis behavior of 1.8 atom percent Mn in Cu at 4.2°K: cooled in zero field. Scale as in Fig. 1.

For studying the thermoremanent magnetization (TRM) after cooling in fields of 2500 oersteds or less, a dc solenoid was used. This solenoid was external to and concentric with the pulsed field coil and double Dewar arrangement.

Remanent magnetizations were detected by the flux change on withdrawing the sample from a coil. The flux change was measured with a Grassot type fluxmeter after amplification by a 75-cps chopper amplifier.

(b) Experimental Results

Previous experiments showed that isothermal remanences occurred in Cu(Mn) samples with 0.4 atom percent or more Mn.[3,4] The isothermal remanence in our 1.8 atom percent sample at 4.2°K increased with field up to 7 koe which was the highest field used in our earlier measurements. The thermoremanent magnetization (TRM), acquired by cooling to 4.2°K in a field, was several times larger that the IRM attained at 7 koe.[3]

The new results of studying the 1.8 atom percent sample at 4.2°K are shown in Figs. 1 and 2. The main feature of Fig. 1(a) is that the IRM rises with maximum applied field until a saturation value is reached at about 14 koe. Similar results have recently been obtained by Lutes.[20] No further increase in IRM occurs despite the application of field pulses up to 140 koe. This saturation IRM equals the TRM obtained after cooling to 4.2°K in fields equal to or greater than 1.5 koe as shown in Fig. 1(b). The field dependence of the TRM is also shown in Fig. 1(b).

[20] O. S. Lutes, International Conference on Electronic Properties of Metals at Low Temperatures, Geneva, New York, August, 1958 (unpublished).

These results indicate that the sample (at 4.2°K) has a characteristic saturation remanence. To further test this result we established the same saturation remanence by producing part of it as a thermoremanence and the rest of it isothermally. This is also shown in Fig. 1(a)—the curve marked $H'=1$ represents results on a sample cooled in 1 koe and then subjected to isothermal field pulses. Moreover, if the full saturation remanence is produced as a TRM, then no further increase in it can be produced by isothermal field pulses. This is shown by the curve marked $H'=2$ in Fig. 1(a). This behavior accords with the simple theory of IRM and TRM described by Néel.[21]

The hysteretic behavior of the saturation remanence is shown in Fig. 2. The isothermal saturation remanence, so difficult to establish, reverses easily with a remanence coercivity near 1 koe. This behavior does not accord with the simplest model of IRM-TRM behavior. The remanence coercivity for the saturated TRM is only slightly larger than 1 koe.

The value of the saturation remanence in Cu (1.8 atom percent Mn) at 4.2°K is about 0.03 Bohr magnetons (μ_B) per Mn atom, or about 0.75% alignment of Mn atoms assuming $4\mu_B$ per Mn atom. This is comparable with a TRM value of $0.025\mu_B$ per Mn atom reported by Owen *et al.*[4] in a 1.4 atom percent Mn alloy after cooling in 5 koe. This is surely a saturation TRM and its value is in good accord with our value.

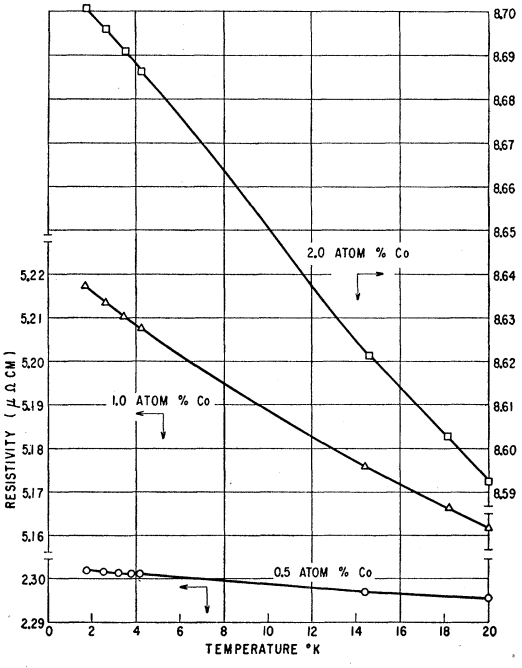

FIG. 3. Resistivity behavior at low temperature of dilute solid solutions of Co in Cu.

[21] L. Néel, Ann. Géophys. 5, 99 (1949); *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 191.

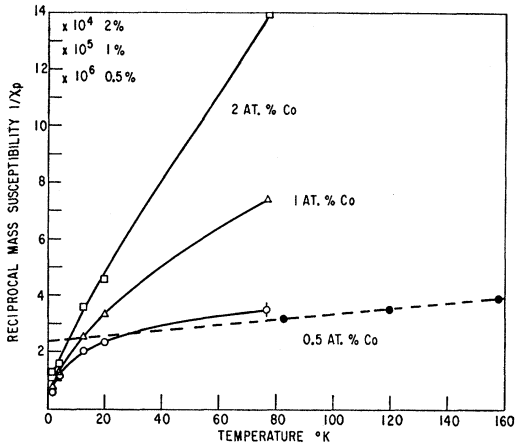

FIG. 4. Temperature dependence of initial magnetic susceptibility of dilute solid solutions of Co in Cu. Solid line: this work. Broken line: Hildebrand, reference 24.

(c) Discussion

Our results indicate that the saturation remanence is independent of the way it is established and, once established, is relatively easy to reverse. Thus the saturation remanence is a parameter that is meaningful to study as a function of temperature and concentration. Lutes[20] is making such a study and his results should give a valuable clue about the origin of the remanence.

3. RESISTIVITY, MAGNETORESISTANCE, AND MAGNETIZATION OF Cu(Co) ALLOYS

(a) Experimental Methods

Nominal compositions of the alloys studied were 0.5, 1.0, and 2.0 atom percent Co in copper. They were made by the methods described in our previous paper.[3] Chemical analyses were made of parts of the ingots adjacent to the portions used for magnetic measurements and for electrical measurements. These analyses indicated compositions of 0.48 ± 0.05; 0.99 ± 0.10, and 1.98 ± 0.21 atom percent cobalt.

The solubility of Co in Cu is limited, the phase boundary between the homogeneous solid solution and the two-phase region occurring at 830°C for 2.0 atom percent, 750°C for 1.0 atom percent, and at 640°C for 0.5 atom percent cobalt.[22] Consequently all samples, both electrical and magnetic, were solution heat-treated at about 900°C for one-half hour and quenched in ice water. This prevents precipitation of the ferromagnetic cobalt-rich phase which has been the subject of much study.[23]

The techniques of measurement were those used and described in our previous work on Cu(Mn).[3]

[22] *Metals Handbook* (American Society for Metals, Cleveland, 1948); J. Livingston (private communication).

[23] See list of references in Bean, Livingston, and Rodbell, J. phys. radium (to be published).

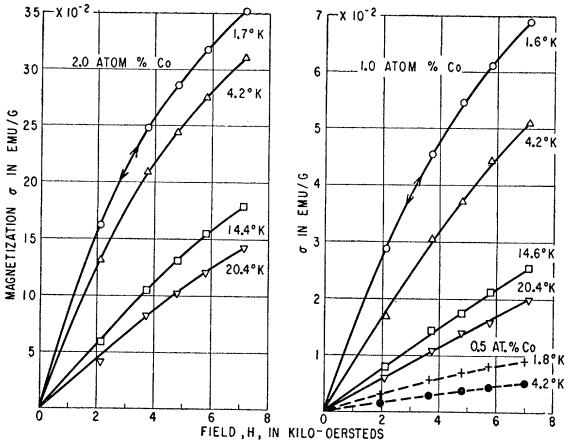

FIG. 5. Low-temperature magnetization behavior of dilute solid solutions of Co in Cu.

(b) Resistivity and Magnetization

Room temperature resistivities of the alloys are 4.02 μohm cm, 6.70 μohm cm, and 9.93 μohm cm for the nominal 0.5, 1.0, and 2.0 atom percent cobalt, respectively. The resistive behavior between 1.6°K and 20°K is shown in Fig. 3. Each alloy shows a resistance minimum somewhere above 20°K. Such minima in Cu(Co) alloys have been reported by Linde[18] and he observed no maximum in resistivity down to 1.2°K.

The reciprocal initial susceptibility (corrected for Cu diamagnetism in the conventional way) is plotted *versus* temperature in Fig. 4. Data for the 0.5% sample are in rough agreement with earlier work of Hildebrand.[24] This composition was the highest cobalt concentration studied by Hildebrand and it behaved differently from his other samples of lower concentration: the temperature dependence of $1/\chi$ above 80°K was larger. The magnetic behavior illustrated in Fig. 4 is not simple.

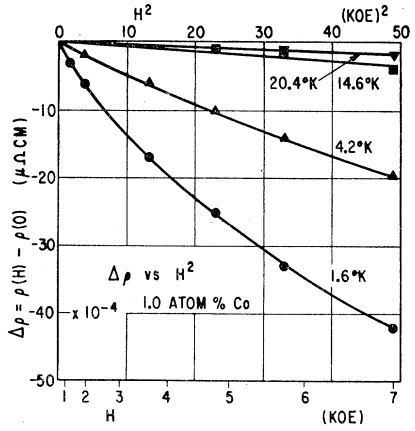

FIG. 6. Magnetoresistive behavior of 1.0 atom percent Co in Cu solid solution. $\Delta\rho=\rho(H)-\rho(0)$ *versus* H^2.

[24] E. Hildebrand, Ann. Physik **30**, 593 (1936).

The separate ordinate scales for different concentrations denote a very nonlinear dependence on concentration. Moreover, the $1/\chi$ curves are nonlinear in temperature —a Curie-Weiss law does not hold in the temperature range of measurement.

Magnetization isotherms to 7 koe at helium and hydrogen temperatures are plotted in Fig. 5. The nonlinear concentration dependence is evident in these graphs. The magnetization is also nonlinear in field at lower temperatures, but neither hysteresis nor significant remanence is observed.

The two-phase region is close to the solution heat-treating temperature for the 2.0 atom percent sample. It is necessary to consider the possiblity that small Co-rich precipitates form during the quench and are responsible for the magnetic behavior. Such precipitate particles would be ferromagnetic, but the direction of their magnetization would fluctuate thermally[25] in the way termed superparamagnetic.[26] The magnetization of an assembly of such particles follows a Langevin curve and would be difficult to distinguish from the paramagnetism of the solid solution. However, the size of the assumed precipitate particles can be estimated from the initial susceptibility at 4.2°K.[26] This size turns out to be one containing 5±3 cobalt atoms. Therefore, if clusters of cobalt atoms do play a role in the magnetization process one probably should not view them as a second phase precipitate.

(c) Magnetoresistance and Its Correlation with Magnetization

The resistance of these alloys decreases in a magnetic field, although the decrease of the 0.5 atom percent

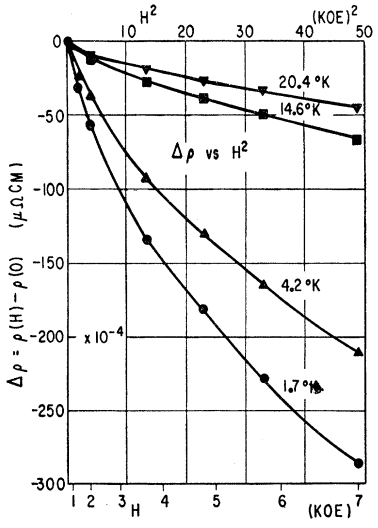

FIG. 7. Magnetoresistive behavior of 2.0 atom percent Co in Cu solid solution. $\Delta\rho$ *versus* H^2.

[25] L. Néel, reference 21; Compt. rend. **228**, 664 (1949); Revs. Modern Phys. **25**, 293 (1953).

[26] C. P. Bean, J. Appl. Phys. **26**, 1381 (1955); C. P. Bean and I. S. Jacobs, J. Appl. Phys. **27**, 1448 (1956); J. J. Becker, Trans. Am. Inst. Mining Met. Engrs. **209**, 59 (1957).

sample was just measurable at the lowest temperature. The size of the transverse and longitudinal effects is the same. Results are shown in Figs. 6 and 7 where $\Delta\rho=\rho(H)-\rho(0)$ is plotted *versus* H^2 for the 1.0 and 2.0 atom percent samples. The quantity $\Delta\rho$ is nonlinear in H^2, but no hysteresis is observable within the accuracy of measurement.

Correlation of the magnetoresistance with magnetization is striking and is shown in Figs. 8 and 9, including data for the 0.5 atom percent sample at 1.8°K. The magnetoresistance, $\Delta\rho$, is proportional to the square of the magnetization, σ^2. This result is the same one found for Cu(Mn) with one important difference. The coefficient of proportionality between $\Delta\rho$ and σ^2 is independent of temperature for Cu(Co) between 1.6°K and 20.4°K, whereas this coefficient is a strong function of temperature for Cu(Mn) in the same temperature range.[3] Observed values of the coefficient $b=\partial(-\Delta\rho)/\partial\sigma^2$ are 2.1±0.1, 0.87±0.02, and 0.23±0.002 for the 0.5, 1.0, and 2.0% samples, respectively. Thus the coefficient, b, although temperature independent for a given sample, is still concentration dependent.

4. COMPARISON OF Cu(Co) AND Cu(Mn)

Both Cu(Co) and Cu(Mn) have a resistance minimum at low temperatures, and the origin of this minimum remains an unsolved problem.

Only Cu(Mn) has a resistance maximum, and only it shows evidence for a cooperative magnetic transition at low temperatures. These facts are consistent with our previous suggestion[3,12] that the decrease in resistance at temperatures below the resistance maximum is due to the onset of a cooperative magnetic transition.

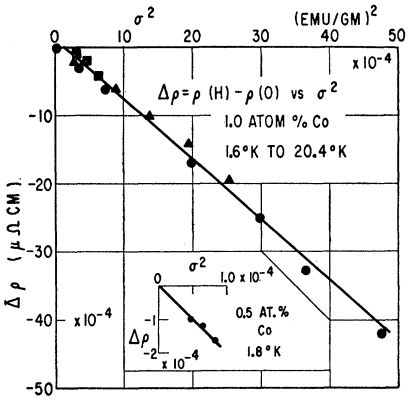

FIG. 8. Correlation of magnetoresistance with magnetization for 1.0 and 0.5 atom percent Co in Cu solid solutions. $\Delta\rho$ *versus* σ^2.

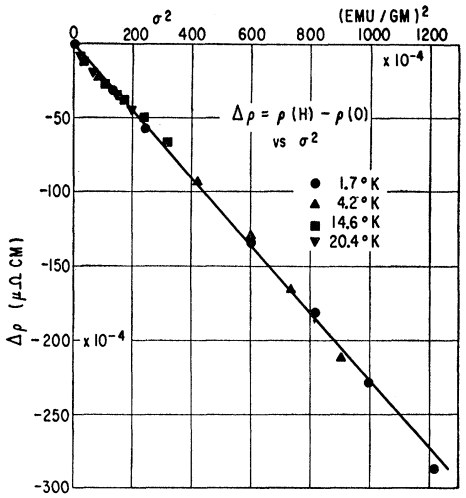

FIG. 9. Correlation of magnetoresistance with magnetization for 2.0 atom percent Co in Cu solid solution. $\Delta\rho$ *versus* σ^2.

The alloy Cu(Co), exhibiting no such transition, does not show a resistance maximum.

Although Cu(Co) is "paramagnetic," its magnetic behavior is not simple. This is shown by the failure of the initial susceptibility to obey a Curie-Weiss law and by the nonlinear dependence of magnetization on field and on concentration. The initial susceptibility of Cu(Mn) alloys also deviates from a Curie-Weiss law, but these deviations can be reconciled with the onset of the cooperative transition.[4]

Previous derivations[3,14] of the relation $\Delta\rho=-b\sigma^2$ are applicable to any alloy in which the net magnetization of the virgin sample is zero within any volume of dimensions comparable to the electron free path.[3] Either an "antiferromagnetic" or paramagnetic alloy would be expected to obey the relation so it is not surprising that both Cu(Mn) and Cu(Co) do so. However, the theories predict the coefficient, b, to be temperature independent; this is true only for the Cu(Co) alloys.

The major problems that remain to be solved about Cu(Co) seem to be explanations of (1) the magnetic behavior and (2) the resistance minimum. For Cu(Mn) the major problems seem to be explanations of (1) the hysteresis and remanence, (2) the resistance minimum, and (3) the temperature dependence of the coefficient, b.

5. ACKNOWLEDGMENT

We are indebted to Mr. David Greene, Mr. Philip Lawrence, and Mrs. Ethel Fontanella for making many of the measurements.