Magnetoresistance of Mg, Cu, Sb, and Al at Liquid Helium Temperatures*†

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(Received July 9, 1952)

The resistance of pure samples of magnesium, copper, antimony, and aluminum was measured at temperatures between 1.1°K and 4.22°K in transverse magnetic fields ranging from zero to 22 kg. In a magnesium specimen the dependence of the magnetoresistance on the resistance in zero field was in strict agreement with the Kohler rule, even though the temperature coefficient of the resistance in zero field was negative. The copper samples also showed negative temperature coefficient of resistance, and the temperature dependence of the magnetoresistance was qualitatively in accord with the Kohler rule. The second derivative with respect to temperature of the resistance of the copper samples in zero field was negative in the liquid helium range.

I. INTRODUCTION

THE effect of a magnetic field on the electrical resistance of pure metals becomes very large at low temperatures. The pioneering work by Kapitza,[1] who made measurements with very high fields on samples at the temperature of liquid nitrogen, and the subsequent work at lower temperatures by many experimenters have shown that the magnitude and form of the variation of the resistance with magnetic field strength varies widely among the pure metals. Extensive references may be found in articles by Justi, Kramer, and Schulze[2] and by Mendoza and Thomas.[3]

Attempts to find theoretical relations between the magnetoresistances of different metals have been limited in success, even in the case of the alkalies.[4,5] However, a rule derived by Kohler[6] is often found to describe the variation with temperature of the magnetoresistance of a particular sample, and it likewise often applies to the comparison between magnetoresistances of two samples of the same element. Kohler's rule may be written

$$\frac{\Delta R}{R_{H=0,T}}=f\left(H\times\frac{R_{0°C}}{R_{H=0,T}}\right),$$

where ΔR is the increment to the resistance at temperature T resulting from the application of the field, $R_{H=0,T}$ is the resistance in zero field, and $R_{0°C}$ is the resistance at the ice point. The deduction of this rule is based on a rather general model of the conduction process, and as Justi points out,[4] involves assumptions of (1) Ohm's law, (2) additive scattering mechanisms, (3) an isotropic mean free time of flight of the electrons, and (4) no variation in the number of conduction electrons.

Some of the samples used in the work here reported showed a negative temperature coefficient of resistance in the liquid helium range. References to the many reports of similar behavior in several elements may be found in reference 3. Giauque *et al.*[7] using impure gold found a minimum in the resistance as a function of temperature and also found negative magnetoresistance. In accord with the suggestion[7] that there is a connection between the two anomalies, Gerritsen and Linde[8] produced both effects by addition of a little manganese to silver; and MacDonald suggests that, under certain assumptions, both effects might arise from scattering by internal boundaries. However, lacking theoretical predictions of the magnitude of the negative magnetoresistance and of the temperature range in which it should occur, it is difficult to conclude from experiment whether it is necessarily connected with a minimum in the resistance-temperature curve.

II. EXPERIMENTAL TECHNIQUE

Magnetic fields up to 22 kilogauss were obtained with a large Weiss electromagnet, whose current was regulated through the field excitation of the dc generator, and stabilized by degenerative feedback from the generator output voltage. Throughout the space occupied by the sample in which the resistance was measured the field strength was always within one percent of that at the center of the magnet gap, being calibrated in terms of magnet current by means of a fluxmeter which had been standardized against the proton resonance frequency. In this standardization the mean deviation of the fluxmeter readings from the field strength indicated by the proton resonance was 5 gauss.

The samples were immersed in liquid helium in a Dewar flask, in turn surrounded by liquid nitrogen. The temperature was determined from the vapor

* Assisted by the U. S. Office of Naval Research.
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[1] P. Kapitza, Proc. Roy. Soc. (London) **A123**, 292 (1929).
[2] Justi, Kramer, and Schulze, Physik. Z. **41**, 308 (1940).
[3] E. Mendoza and J. G. Thomas, Phil. Mag. **42**, 291 (1951).
[4] E. Justi, Physik. Z. **41**, 563 (1940).
[5] D. K. C. MacDonald, Proc. Phys. Soc. (London) **A63**, 290 (1950).
[6] M. Kohler, Ann. Physik **32**, 211 (1938).
[7] Giauque, Stout, and Clark, Phys. Rev. **51**, 1108 (1937); W. F. Giauque and J. W. Stout, J. Am. Chem Soc. **60**, 388 (1938); and J. W. Stout and R. E. Barieau, J. Am. Chem. Soc. **61**, 238 (1939).
[8] A. N. Gerritsen and J. O. Linde, Physica **17**, 473, 584 (1951).

pressure of the helium bath, using either a mercury or an oil manometer and the Mond vapor pressure tables.[9]

All the samples were between 1.0 mm and 0.9 mm in diameter. For mechanical protection they were mounted, in various ways, inside thin-walled cylindrical metal holders. These fitted inside a narrow section at the bottom of the helium Dewar, so that the samples were held between the magnet poles in a transverse field. The holder used with the copper samples was of brass, and those used with the other samples were of stainless steel. The distortion of the magnetic field by the slightly paramagnetic stainless steel was judged to be negligible, especially in view of the circular symmetry of the holders. All the holders were designed so that, once mounted, the samples were safe from mechanical abuse and could not be strained by differential contraction with the holders on cooling. Current leads were soldered to the copper and antimony samples with Rose metal while potential contacts were made by spot welding. On one of the magnesium samples all electrical contacts were made with a conducting silver paste; to the other, leads were held by small U-shaped phosphor-bronze clips. The aluminum samples were mounted before the final anneal, the potential leads being held against them by manganin springs and asbestos being used for insulation; after the annealing, current leads were soldered with Rose metal to the sample ends, which had previously been plated with copper.

Each sample, except for some of the copper samples as will be mentioned, was cleaned by etching about 0.02 mm off its diameter before each anneal. With the exception of the same copper samples, the copper, magnesium, and antimony were annealed in a vacuum of better than 10^{-5} mm of Hg. The aluminum was annealed in a vacuum maintained by a fore pump at about 50 microns of Hg.

Resistance was measured by the change in the potential drop between two points on the sample when a current through it of known magnitude was reversed. In order to check for drift in the thermal emf's in the potential measuring circuit between the times of the two potential readings, the current was reversed a second time and the potential read again. If the drift was small between the first and third readings, their average was used in the calculation of the change due to the reversal of the measuring current. As a precaution against the production by the Hall effect of spurious increments to the observed resistance, a resistance measurement was made at least once on each sample with the direction of the magnetic field reversed.[10] No significant discrepancy was detected in this way.

The potential to be measured was amplified with a dc amplifier manufactured by the Perkin-Elmer Corporation of Norwalk, Connecticut. Following MacDonald,[11] the input impedance of the amplifier was increased by degenerative feedback to about 3000 ohms so that variations of the resistance in leads and contacts would be insignificant. The output voltage from the circuit consisting of amplifier and feedback network was measured with a Leeds and Northrup Type K potentiometer and a galvanometer. The period of the latter, about two seconds, limited the effective "noise" in the amplifier to a narrow frequency band, with the result that the "noise" level was equivalent to about 10^{-9} volt of input signal. The current through the sample was supplied by a storage battery and regulated by suitable variable resistors and was measured with a set of standard resistors and a potentiometer.

In most of the measurements the scatter of the data was much greater than any of the expected systematic errors. This scatter was caused by changes in the thermal emf's between potential readings and by electromagnetic pickup in the loop formed by the sample and potential leads. This pickup was especially severe at fields greater than 20 kg, so that the measurements at these highest fields are less reliable than the others. Uncertainty in the measuring current, uncertainty in the resistance of the potential leads, and uncertainty in the amplifier gain total one part in 2000 in each resistance measurement. In the helium II range the temperature difference between the sample and the bath could be calculated[12] and was negligible. That convection was adequate in the helium I range is indicated by the absence of anomalies in the resistance-temperature curves at the lambda point and by the fact that the resistances were ohmic for all currents up to a value at which the potential readings became unstable, presumably due to large bubbles in the helium I. In the measurements of the ice point resistance the error due to uncertainty in the temperature of the sample was not greater than 1 part in 1000.

III. SAMPLES AND RESULTS

(a) *Magnesium.*—This was Johnson Matthey and Company magnesium in the form of rods, Lab. No. 1848. They report the following impurities measurable chemically: Fe, 0.013 percent, Mn, 0.0023 percent; Pb, 0.0013 percent. Detected spectrographically were: Mn, Fe, Si, Cu, Ag, Pb, Al, Ca, and Na. Baker and Company of Newark, New Jersey, drew the material cold through clean diamond dies to 0.0395-inch diameter. In an attempt to obtain random crystal orientation sample No. 2 was annealed for one hour at 350°C, work-hardened by flexing, and annealed again for an hour at 365°C. Sample No. 5 was annealed only once, for one hour at 365°C. Microscopic examination of samples prepared in the same way as No. 2 and No. 5

[9] H. van Dijk and D. Shoenberg, Nature **164**, 151 (1949).
[10] C. J. Milner, Proc. Roy. Soc. (London) **A160**, 207 (1937).
[11] D. K. C. MacDonald, J. Sci. Instr. **24**, 232 (1947); and B. Frankenhaeuser and D. K. C. MacDonald, J. Sci. Instr. **26**, 145 (1949).
[12] P. L. Kapitza, J. Phys. (U.S.S.R.) **4**, 181 (1941).

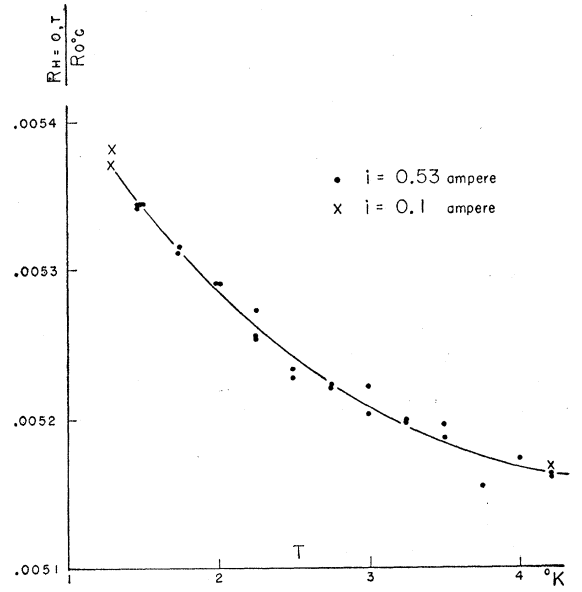

FIG. 1. Resistance of magnesium sample No. 2 at liquid helium temperatures in zero magnetic field.

showed equiaxed grains, those in the sample corresponding to No. 2 being roughly 1/15 the wire diameter in width, those in the sample corresponding to No. 5 being about 1/30 the wire diameter.

The variation of the zero field resistance of sample No. 2 with temperature is shown in Fig. 1. Sample No. 5 had slightly larger residual resistance than sample No. 2 but the same variation with temperature in the helium range. This variation is in accord with the results of previous workers.[13–15] The increase of resistance in magnetic field is shown in a Kohler plot, Fig. 2, where measurements of resistance in the magnetic field were made with a current of 0.1 ampere. In each sample the variation of magnetoresistance with temperature was closely in accord with the Kohler rule. In order to display this on a sufficiently large scale, the following artifice was used. Figure 3 plots differences between the ordinates of the arbitrarily selected line drawn dotted in Fig. 2 and the ordinates of the points for sample No. 2.

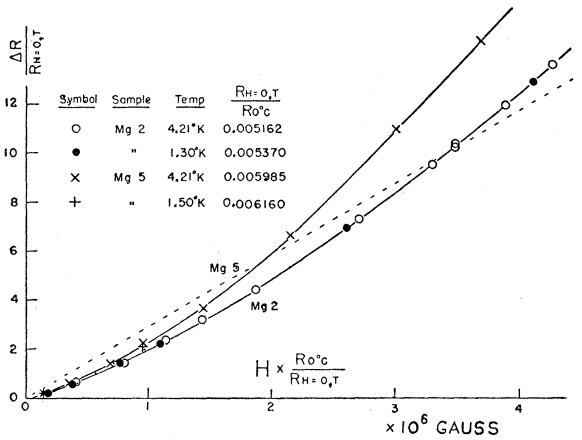

FIG. 2. Kohler plot of magnetoresistance of magnesium samples at liquid helium temperatures. Measuring current 0.1 ampere.

The magnetoresistance was positive even in very small fields, as shown in Fig. 4.

(b) *Copper.*—The copper also was supplied by Johnson Matthey and Company in the form of rods, Lab. No. 1562. They report the following impurities determined spectrographically: Ag, 0.0003 percent; Ni, 0.0005 percent; Pb, 0.0004 percent; Fe, less than 0.0005 percent; Ca, Si, and Mg all faintly detectable. They further report no sign of embrittlement on heating in hydrogen, indicating an absence of oxygen. Baker and

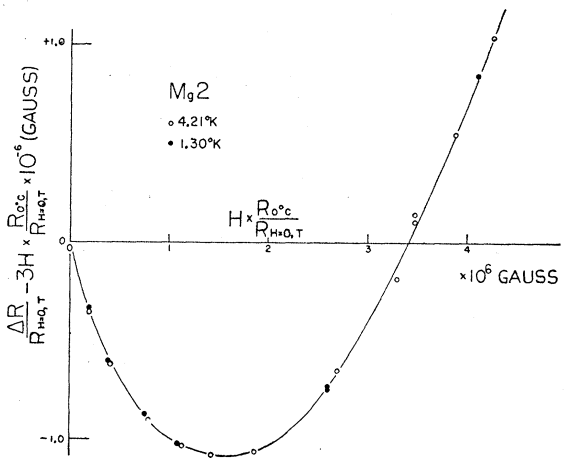

FIG. 3. Magnetoresistance of magnesium sample No. 2 plotted on an expanded scale to show agreement with the Kohler rule. The ordinate of this graph is the difference between the ordinate of Fig. 2 and an arbitrarily chosen term, indicated by the dotted line in Fig. 2, proportional to the abscissa.

Company drew the material cold through clean diamond dies to 0.0394-inch diameter. Sample No. 11 was not annealed but was etched. Samples Nos. 12, 22, and 23 were annealed, each for one hour, at 750°C, 430°C, and 1000°C, respectively. In samples Nos. 5, 6, and 8 the attempt was made to randomize the orientations of the crystal axes by a second recrystalization. They were annealed for one hour at 600°C, worked by bending until hard, and annealed again for one hour, No. 5 at 550°C, No. 6 at 680°C, and No. 8 at 820°C under a vacuum of about 50 microns. These three samples were not etched. Microscopic examination of pieces prepared in the same manner showed that the grain size increased strongly with annealing temperature. Samples Nos. 13 and 14 were prepared in order to investigate further whether the grain size affected the resistance at liquid helium temperatures. They were annealed for one hour at 750°C, bent until hardened

[13] W. Meissner and B. Voigt, Ann. Physik **7**, 761 (1930).
[14] Garfunkel, Dunnington, and Serin, Phys. Rev. **79**, 211 (1950).
[15] D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A202**, 523 (1950).

and annealed for one hour at 720°C. Then they were cold worked again, No. 13 being worked lightly, and No. 14 heavily. They were given a final anneal at 550°C. Microscopic examination of pieces prepared in similar fashion showed that the grain size of sample No. 13 was 3 or 4 times that of sample No. 14.

Figure 5 shows the resistance of the copper samples at liquid helium temperatures. They all had a negative temperature coefficient, similar to the spectroscopically pure copper samples of MacDonald,[16] and the "commercial" wire samples of Mendoza and Thomas.[3] Figure 6 is an expanded plot of the resistance of sample No. 12 as a function of temperature; and such plots for the other samples all show the same negative curvature. The slopes of the curves for No. 5, No. 8, No. 11, and No. 22 are the same as for No. 12; that for No. 13 is

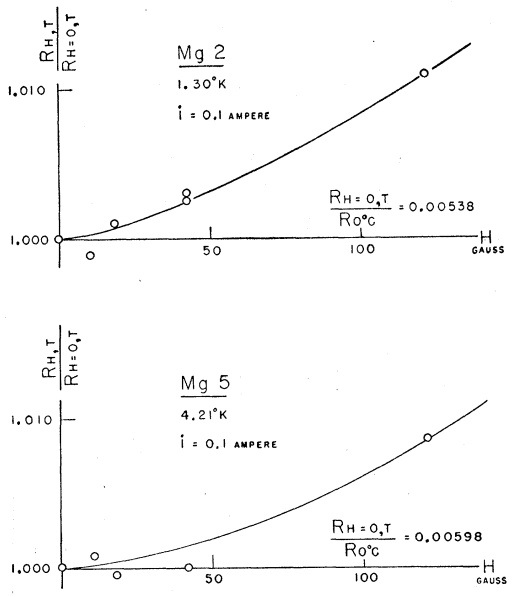

FIG. 4. Magnetoresistance of magnesium samples in low fields. Upper graph, sample No. 2 at 1.30°K. Lower graph, sample No. 5 at 4.21°K. Measuring current 0.1 ampere.

less steep by 0.00002 per degree K. In Fig. 7 is displayed graphically the heat treatment of the samples, and the resistance in liquid helium of each sample in its final form. The resistance appears to depend in a regular fashion only on the temperature of the final anneal. The increase of the resistance with annealing temperature between 550°C and 820°C is similar to the behavior noted in gold samples by de Haas and van den Berg,[17] who found that the value of the minimum resistance increased with the duration of the anneal.

The magnetoresistances of the copper samples at 4.2°K are shown in the Kohler plot, Fig. 8. Measurements with magnetic fields at more than one temperature were made on samples No. 11, 12, and 22, and in each of these the magnetoresistance was smaller at the lower temperature. The data on sample No. 12 are shown in Fig. 9. Figure 10, which is a Kohler plot of

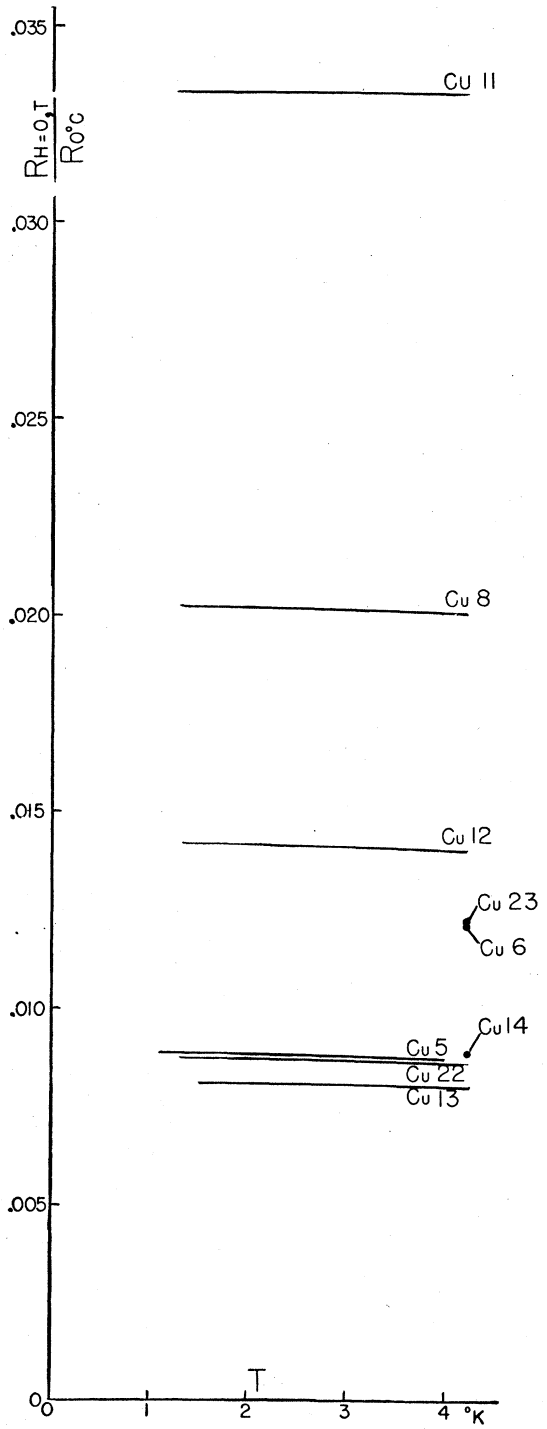

FIG. 5. Resistance of copper samples at liquid helium temperatures in zero magnetic field.

[16] D. K. C. MacDonald, Proceedings of the International Conference on Low-Temperature Physics, Oxford, August (1951).

[17] W. J. de Haas and G. J. van den Berg, Comm. Leiden No. 241d; Physica 3, 440 (1936); and W. J. de Haas and G. J. van den Berg, Comm. Leiden No. 249b; Physica 4, 683 (1937).

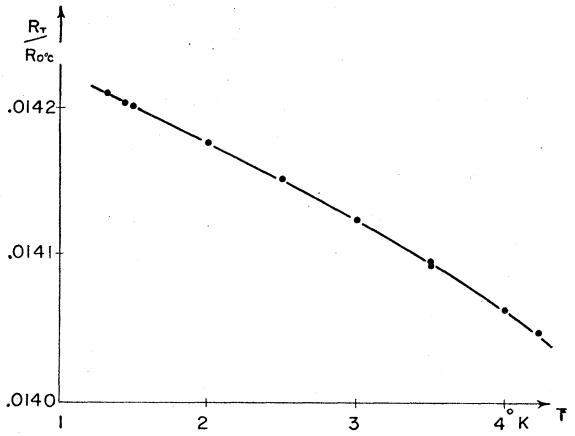

FIG. 6. Resistance of copper sample No. 12 at liquid helium temperatures in zero magnetic field, plotted on expanded scale. Measuring current 2.14 ampere.

the same data, suggests that the temperature dependence of the magnetoresistance is slightly stronger than would be predicted by the Kohler rule, although the discrepancy is not great enough to be conclusive. Samples Nos. 11 and 22 showed better agreement with the rule.

The magnetoresistance at small field strengths was investigated in sample No. 12, and no decrease in resistance could be detected, as is shown in Fig. 11.

Ohm's law was found to hold within the accuracy of measurement for all zero field resistances up to the maximum currents used, which were from 1 to 5 amperes depending on the sample. In sample No. 8 the magnetoresistance at the maximum field was investigated as a function of current and found to be proportional to the latter for currents of 0.1 and 0.05 ampere.

(c) *Antimony.*—This was supplied by Johnson Matthey and Company in the form of ingots, Lab. No. 2696. The manufacturers report impurities totaling 0.0887 percent, including As, Cu, Fe, Ni, S, Pb, Bi, Al, and Si. Baker and Company extruded the metal through iron

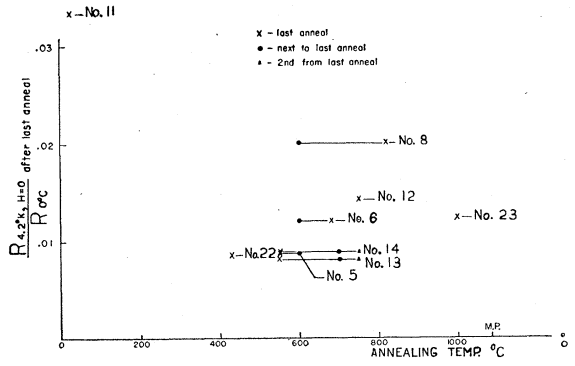

FIG. 7. Heat treatment of copper samples, displayed *vs* resistance of samples in final form at 4.2°K in zero magnetic field. Samples which were annealed more than once were cold worked between anneals. Sample No. 11 was cold drawn wire, unannealed.

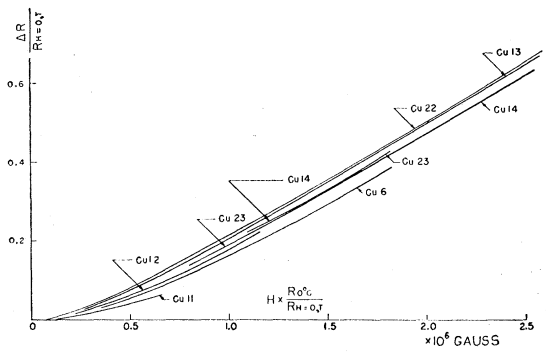

FIG. 8. Kohler plot of magnetoresistance of copper samples at 4.2°K.

dies at approximately 400°C, forming wire 0.0394 inch in diameter. Two samples, Nos. 2 and 3, from this wire were annealed for one hour at 365°C. Sample No. 5 was not annealed but was etched. In microscopic examination of a piece of the unannealed wire individual grains could not be seen, but there were fine striations parallel to the wire axis. Samples annealed like Nos. 2 and 3 showed large grains, of which some were equiaxed and others were longer in the direction of the wire axis than in the direction of its radius.

The variation of the resistance of sample No. 2 with temperature is shown in Fig. 12. A similar plot for sample No. 5 would have an average slope steeper by 0.0003 per °K. The value of $R_{H=0,T}/R_{0°C}$ for sample No. 5 was 0.0353 at 4.19°K and 0.0350 at 1.26°K and

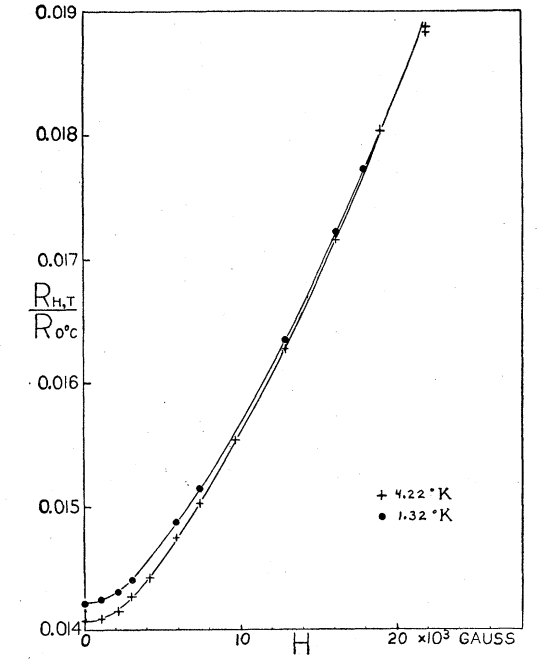

FIG. 9. Magnetoresistance of copper sample No. 12, plotted on expanded scale. Crosses represent measurements at 4.22°K; circles, at 1.32°K. Measuring current 2.14 ampere.

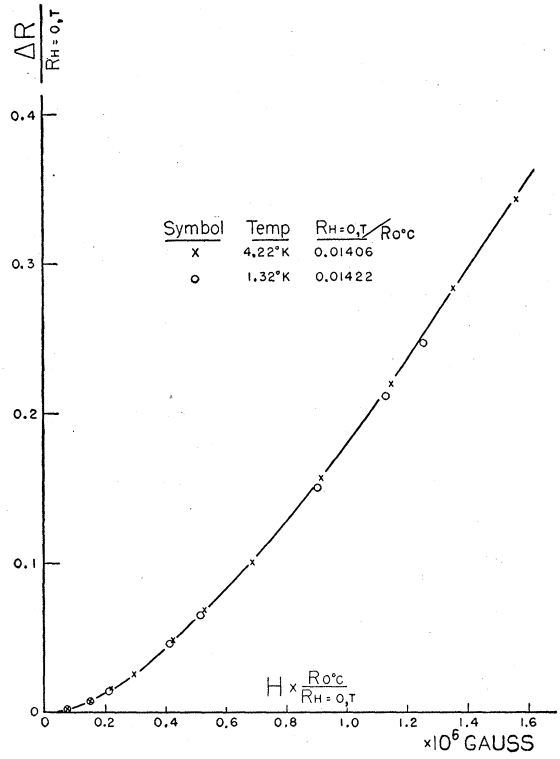

FIG. 10. Kohler plot of magnetoresistance of copper sample No. 12. Crosses represent measurements at 4.22°K; circles, at 1.32°K.

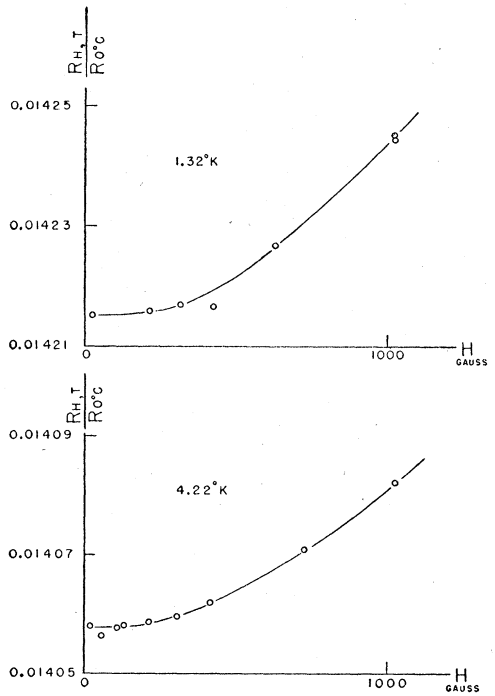

FIG. 11. Magnetoresistance of copper sample No. 12 in small fields. Upper graph, at 1.32°K. Lower graph, at 4.22°K. Measuring current 2.14 ampere.

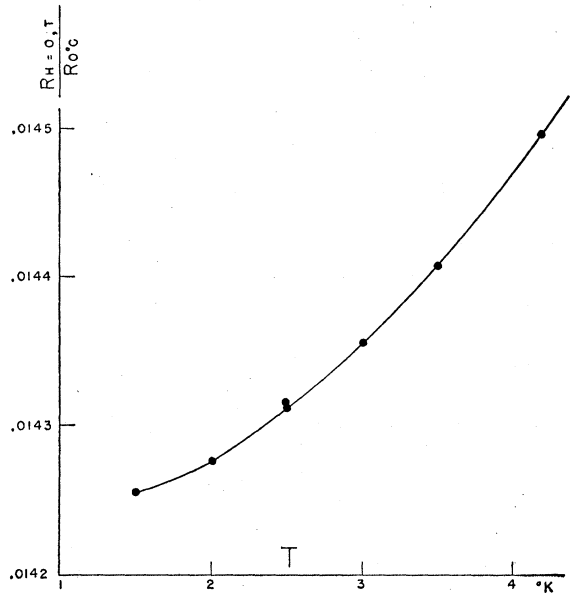

FIG. 12. Resistance of antimony sample No. 2 at liquid helium temperatures in zero magnetic field. Measuring current 0.1 ampere.

for sample No. 3, 0.0142 at 4.19°K. The magnetoresistance of samples Nos. 2 and 5 is shown in a Kohler plot, Fig. 13. Points for No. 3 would lie on the curve for No. 2 in this figure. The resistance in zero field was ohmic for currents from 0.001 to 0.1 ampere. The dependence of magnetoresistance on current was not investigated. The currents used in the magnetoresistance measurements were 0.001 ampere for samples No. 2 and No. 3, and 0.005 ampere for sample No. 5.

(d) *Aluminum.*—Hilger aluminum from Johnson Matthey and Company was supplied in the form of rods, Lab. No. 1011. The manufacturers report impurities totaling a 0.0045 percent, consisting of Mg, Si, Cu, and Fe. The material was cold-drawn through clean diamond dies by Baker and Company to 0.0394-in. diameter. In an

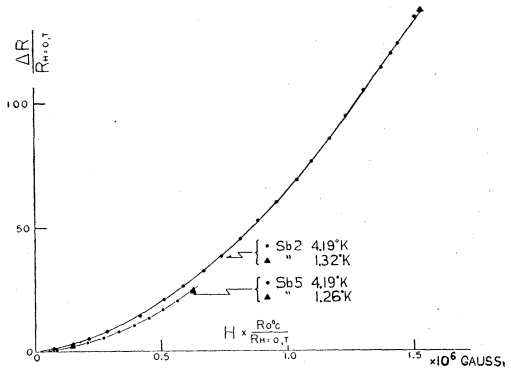

FIG. 13. Kohler plot of magnetoresistance of antimony samples. Upper curve: sample No. 2, measuring current 0.001 ampere, dots for measurements at 4.19°K, triangle for measurement at 1.32°K. Lower curve sample No. 5, measuring current 0.005 ampere, dots at 4.19°K, triangles at 1.26°K.

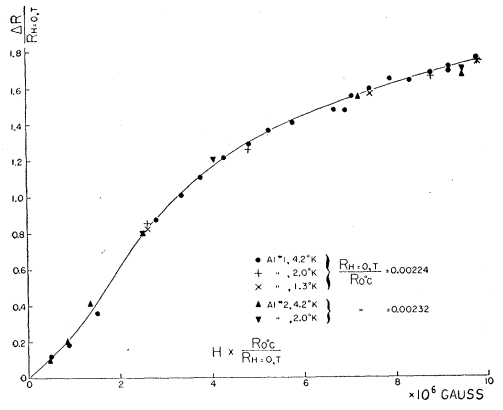

FIG. 14. Kohler plot of magnetoresistance of aluminum samples at liquid helium temperatures.

attempt to make the crystal orientations random the two samples used were annealed for one hour at 320°C, cold worked by bending until hard, and annealed again for an hour at 360°C. Then, in order to find whether grain size was important, they were worked again—sample No. 1 heavily, and sample No. 2 lightly—and annealed for the last time for three hours at 340°C. A piece prepared like sample No. 1 had equiaxed grains of width ranging up to one-tenth the wire diameter; one like sample No. 2 had equiaxed grains about one-fourth the wire diameter in width.

The resistance measurements were made with a current of 0.1 ampere. Within the accuracy of measurement (±0.5 percent), the resistance in zero field was constant throughout the liquid helium temperature range. The results of magnetoresistance measurements are shown in a Kohler plot, Fig. 14. The shape of the curve, with the change in sign of the curvature, is in agreement with the curve compounded by Justi *et al.*[18] from their data at various temperatures.

[18] E. Justi and H. Scheffers, Physik. Z. **39**, 105 (1938); Foroud, Justi, and Kramer, Physik. Z. **41**, 113 (1940).

IV. DISCUSSION

Previous reports of the temperature variation of magnetoresistance as being qualitatively in agreement with the Kohler rule, in cases where the zero field resistance showed negative temperature coefficient, have been made by Nakhimovich[19] on gold samples and by Gerritsen and Linde[8] on silver samples. These reports, together with the present results on samples of copper and magnesium, are of interest in attempting to account for a negative temperature coefficient. For these data would support the hypothesis of a mechanism of scattering which becomes increasingly effective with decreasing temperature, since the assumptions implicit in the Kohler rule would apply to such a case. On the other hand, an explanation of the resistance minimum based on a change in the density of effective conduction electrons or on some sort of change in their acceleration by the electric field would not lead to the observed decrease in magnetoresistance with decrease in temperature.

MacDonald's hypothesis[20] that scattering by impurities in the grain boundaries increases in effectiveness with decreasing temperature could permit a plausible explanation of the effect of annealing observed in the present work on copper and in the work of de Haas and van den Berg on gold.[17] For impurities would presumably collect at the grain boundaries in increasing concentration with increasing time and, within limits, with increasing temperature of annealing.

It is a pleasure to express my appreciation to the members of the Yale low-temperature group, who assisted in the taking of data, to Professor W. D. Robertson and Mr. W. E. Tragert, who gave advice and suggestions regarding the metallurgical aspects of the work, and especially to Professor C. T. Lane, who suggested and directed the research.

[19] N. M. Nakhimovich, J. Phys. (U.S.S.R.) **5**, 141 (1941).
[20] D. K. C. MacDonald, Phil. Mag. **42**, 756 (1951); D. K. C. MacDonald, Phil. Mag. **43**, 124 (1952).