Electrical Resistivity and Hall Effect of Noble Metals at Very Low Temperatures

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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	8
page range	205-212
year	1956
URL	http://hdl.handle.net/10097/26767

Electrical Resistivity and Hall Effect of Noble Metals at Very Low Temperatures*

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(Received March 14, 1956)

Synopsis

The electrical resistivity and the Hall effect of gold, silver and copper were measured at low temperatures. The Hall effect of gold which showed the minimum at 6°K in the resistivity-temperature curve was found to be dependent on temperature below 6°K. Since the electron mobility deduced from the resistivity and the Hall coefficient was nearly constant at temperatures below 6°K, it was suggested that the origin of the resistance minimum might be ascribed to the change in the concentration of current carrier. On the other hand, the silver and copper specimens showed the normal behaviour of electrical resistivity and the temperature-independent Hall effect. In general, the Hall coefficients of these noble metals were found to be constant at low temperatures, the values being about 20 per cent larger than those at room temperatures, which fact indicates that the Hall effect is temperature-dependent at intermediate temperatures (20∼300°K).

I. Introduction

It is well known that the noble metals and magnesium show the minimum in the resistance-temperature curve at low temperatures owing to the presence of very small amount of specific impurities. Many workers(1)∼(5) ascribed this anomaly to the anomalous electron scattering in metals due to chemical or physical impurities. On the other hand, Slater(6) explained this phenomenon as being a result of splitting of Brillouin zone; according to his idea, the resistance minimum should not be ascribed to the anomalous scattering but to the change in the concentration of current carrier. Slater's model, however, had not been based on the experimental evidence, and so it is necessary to examine which is the cause of the anomalous resistivity, the anomalous electron scattering or the anomalous change in the electron concentration. The present investigation was undertaken to clarify this point from measurements of the electrical resistance and the Hall effect of the metals in question. Of three specimens of the noble metals, gold showed the minimum in the resistance-temperature curve at about 6°K, below which the Hall effect was found to be temperature-dependent. In silver and copper which showed the normal behaviour of electrical resistance down to the lowest temperature, the

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* The 836th report of the Research Institute for Iron, Steel and Other Metals.

(1) K. Korringa and A. N. Gerritsen, Physica, **19** (1953), 457.

(2) T. Inoue, Busseiron-Kenkyu (in Japanese), **68** (1953), 21.

(3) J. S. Koehler, Phys. Rev., **94** (1954), 1071.

(4) W. B. Pearson, Phil. Mag., **45** (1954), 1081.

(5) M. Tsuji, Busseiron-Kenkyu (in Japanese), **87** (1955), 40.

(6) J. C. Slater, Phys. Rev., **84** (1951), 179.

Hall effect also remained nearly constant between 1 and 20°K. The electron mobility in gold was deduced from the specific resistance and the Hall coefficient, by assuming the one band conduction of electrons, and was found to show the normal behaviour in the temperature range in question. In contrast to the usual conceptions for this phenomenon, this result implies that the anomalous change of resistivity of gold would be caused rather by the change in the concentration of current carrier than by the anomalous scattering.

Apart from the problem of resistance minimum of gold, it was observed that the Hall coefficients of these noble metals were, generally speaking, temperature-dependent at intermediate temperatures (20~300°K), but remained constant at very low temperatures, the absolute values being about 20 per cent larger than those at room temperature. Such a behaviour suggests that the usual simple relationship $-1/ne$ in e. m. u. for the Hall coefficient of the monovalent metals does not hold at low temperatures. But considering the difference in the absolute values of the coefficients between ambient and low temperatures, it should be assumed that the Hall coefficient of the noble metals at low temperatures is larger in the absolute value by a certain constant factor than that deduced from the said simple relation at high temperatures.

II. Specimens and experimental procedure

The specimens of gold, silver and copper were the rolled foils suitable for measuring the electrical resistance and the Hall effect. The dimensions of the specimens are as follows:

gold: $22.0 \times 5.0 \times 0.0220$ mm^3,
silver: $21.5 \times 5.0 \times 0.0307$ mm^3,
copper: $21.7 \times 4.2 \times 0.0307$ mm^3.

The gold specimen was a leaf prepared by the manufacturer. The silver specimen was made from Kahlbaum's sample. It was cast in the form of a plate and then rolled to the thickness of 0.031 mm. The copper specimen was prepared from the electrolytic one rolled in the form of a thin plate. All of these specimens were not annealed.

The impurities in these specimens were spectrographically tested along with the measurements of residual resistance, of which results are summarized in Table 1.

Table 1. Spectrographic analyses of the specimens

Intensity of lines / Sample	+ +	+	(+)	$R_{4.2°K}/R_{273°K}$
Gold	Cu	Pb, Fe	Mg, Si, Al, Ca	2.6×10^{-2}
Silver	Cu		Mg, Si, Al, Ca, Pb, Fe	5.6×10^{-2}
Copper		Mg, Si	Fe, Al	3.8×10^{-2}

+ + …… Raies ultimes can be recognized clearly,
+ …… ″ ″ weakly,
(+) …… ″ ″ faintly.

The electrical resistance and the Hall effect were measured by an ordinary direct current method. The sample current was about 1 Amp. and the magnetic field applied was about 20 kilo-oersteds. The potential drop in the specimens and the Hall potential were measured to 10^{-8} V by the Wolff's Disselhorst type potentiometer. Since the measured Hall potential was, at the most, of the order of a few μV, it was very difficult to know the exact value, provided there is the thermoelectric force in the measuring circuit. In order to remove this disturbance as much as possible, the wires of the same kind as the specimen were used for the potential leads which were attached to both sides of the specimen by spot-welding, and thus the error could be reduced to less than 1 per cent.

The specimen was immersed in the liquid helium bath and the temperatures from 1 to 4.2°K were controlled by regulating the vapour pressure above the liquid helium. In order to attain 1°K, the oil rotary vacuum pump, 3000 litres per minute in capacity, was used. The temperatures above 4.2°K were obtained by keeping the specimen in a styrofoam cover and holding it above the level of liquid helium.

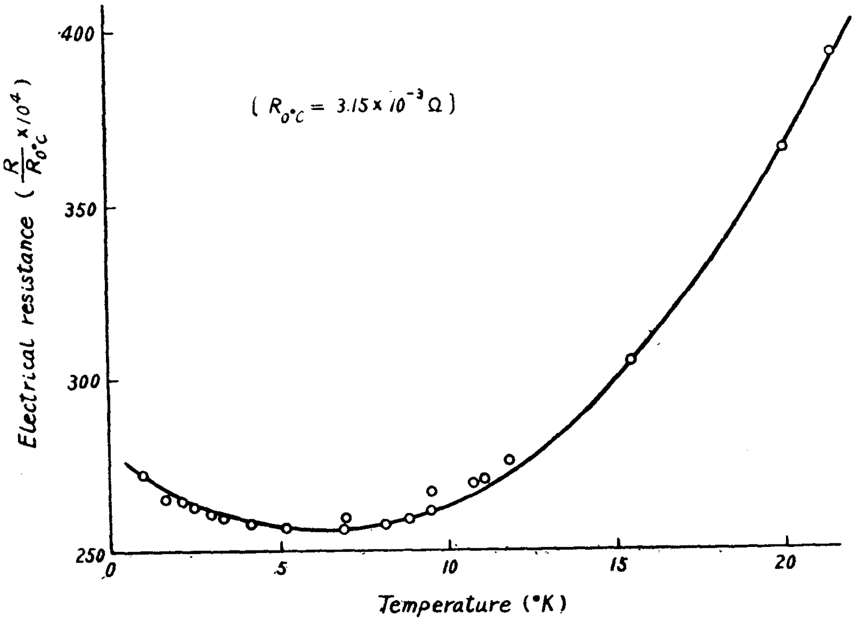

Fig. 1. Electrical resistance of gold as a function of temperatures.

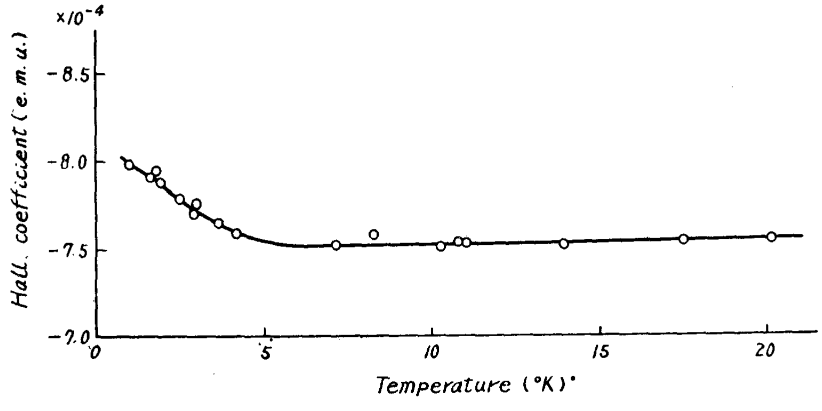

Fig. 2. Hall coefficient of gold as a function of temperatures.

The styrofoam cover was used in order to suppress the fluctuation of temperature due to the unstable vaporization of helium⁽⁷⁾. In this way, the temperature was slowly raised as the helium level went down, but because of the heat of conduction from the lead wires, the temperature of specimen was somewhat uncertain (~0.5°K) in the range from 4.2 to about 10°K. The temperatures were determined by the vapour pressure of helium (1949 scale) from 1 to 4.2°K and by the resistance of a carbon composition resistor from 4.2 to about 20°K.

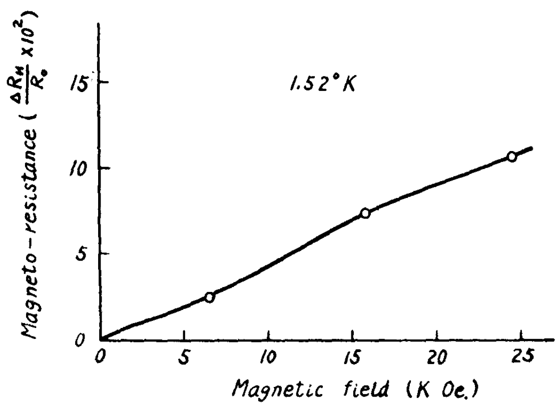

Fig. 3. Magneto-resistance of gold as a function of the intensity of magnetic field.

III. Experimental results

In Figs. 1 and 2 the electrical resistance and the Hall coefficient of gold are plotted against temperatures. It will be seen that the increase of resistance below the resistance minimum temperature, from about 6° to 1°K, is about 5.8 per cent and

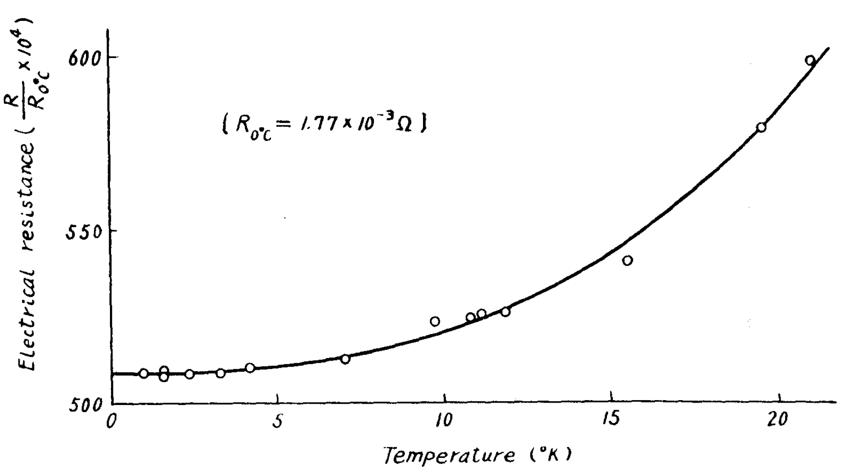

Fig. 4. Electrical resistance of silver as a function of temperatures.

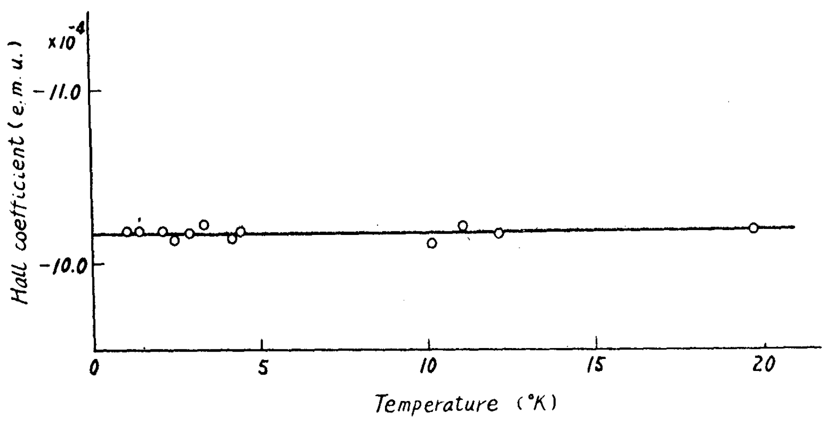

Fig. 5. Hall coefficient of silver as a function of temperatures.

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(7) N. S. Rasor, Rev. Sci. Instr., **25** (1954), 315.

the corresponding increase of the absolute value of the Hall coefficient is about 5.3 per cent. Above 6°K the Hall coefficient remains nearly constant. Fig. 3 shows the magneto-resistance effect of gold at 1.52°K, at which no anomalous change is observable. Figs. 4, 5, 6 and 7 show the results for silver and copper. They show the normal behaviour of resistances and the temperature-independent Hall effects.

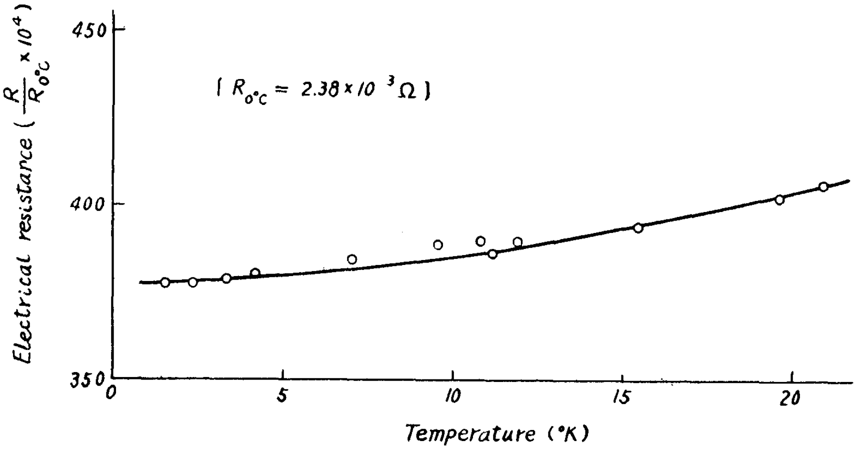

Fig. 6. Electrical resistance of copper as a function of temperatures.

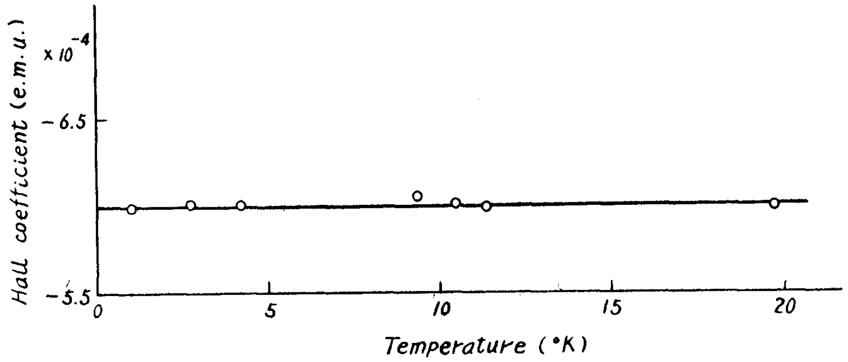

Fig. 7. Hall coefficient of copper as a function of temperatures.

As shown above, the Hall coefficients of the noble metals remain constant at low temperatures, at least, below 20°K, except the coefficient of gold corresponding to its anomalous resistance changes. But they are about 20 per cent larger in their absolute values than those at room temperature, from which it can be inferred that at intermediate temperatures they are temperature-dependent. This temperature-dependence of the Hall effects is given in Fig. 8.

IV. Discussion

1. Temperature-dependence of Hall effect

In general, the Hall coefficients of the noble metals are denoted by $A_H = -\frac{1}{ne}$ in e.m.u., on an assumption that the free electron model is valid. Here, n is the concentration of conduction electron and $-e$ the charge of an electron. The same relationship is also obtained quantum-mechanically by solving the Boltzmann equation on the assumptions that the relaxation time can be defined and that the constant energy surface of electrons in k-space has the shape of an ellipsoid. But

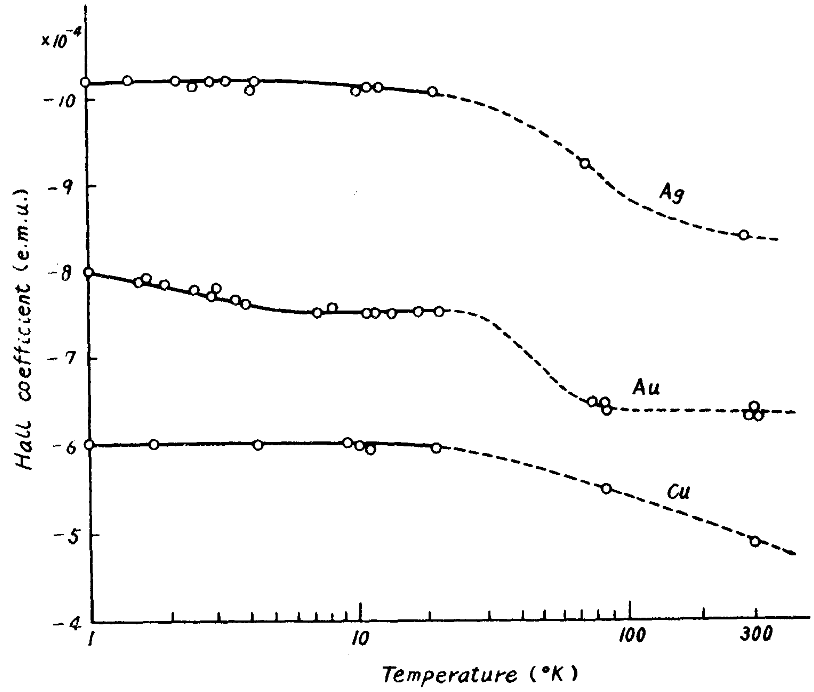

Fig. 8. Hall coefficients of silver, gold and copper as functions of temperatures.

the relaxation time is defined rigorously only at high temperatures ($T \gg \Theta$, Θ the Debye's characteristic temperature) but not at low ($T \ll \Theta$) and intermediate temperatures ($T \simeq \Theta$). Kohler(8) calculated the Hall coefficient of the monovalent metals at low temperatures on the next three assumptions:

1° Fermi surface is spherical;

2° Electron gas and phonon are always in equilibrium;

3° Quantization of electron orbit by magnetic field is neglible.

Then, it is concluded that the same relation $-1/ne$ is valid as at high temperatures. But as shown above, the Hall coefficients of the noble metals are about 20 per cent (more precisely 19 per cent in the case of gold) larger at low temperatures than at room temperatures in defiance of this calculation. Therefore, it will be assumed that they can be expressed by the relation $A_H = -\frac{A}{ne}$, in which A is a constant factor larger than unity corresponding to the difference between the calculation and experiments, which difference would be due to the inadequacy of the above assumptions. At intermediate temperatures, the Hall coefficient has not been calculated exactly, but it is seen from the present experiments that it is temperature-dependent in this range. It was also found that this temperature-dependence has a bearing on the respective Debye's temperatures Θ, for in gold which has the lower value of Θ (175°K) than silver (223°K) or copper (315°K), the temperature-dependent range is lower than the latter two.

Since the mean free path together with the mean collision time of the conduction electrons will increase at very low temperatures, there will arise in the conduction

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(8) M. Kohler, Ann. Phys., [6] **34** (1939), 23.

mechanism some questions which deserves a close examination. First, since the thickness of the specimens is very thin to be suitable for measuring the Hall effect, the size effect is expected, and so comparisons were made of the mean free path of the electrons, which was calculated from the specific resistance, with the thickness of the specimens. For example, in gold the mean free path is about 2μ at 6°K and the thickness is about 20μ. Consequently, it can be concluded that the size effect will be negligible in our gold specimen. The same conclusion is also valid for the silver and copper specimens. Second, it is expected that the orbital rotation of the conduction electrons will be induced by the transverse magnetic field. In this case, it is necessary to take into account the quantization of the electron orbits due to the magnetic field. Therefore, the orbital rotation time was also compared with the mean collision time. For example, the orbital rotation time of gold was estimated to be 2.1×10^{-11} sec and the collision time to be 8.9×10^{-13} sec at 6°K. Thus, it can also be concluded that this effect will be negligible in gold. A similar conclusion can be obtained also for silver and copper.

2. Resistance minimum in gold

Assuming that the Hall coefficient can be expressed by $A_H = -\frac{A}{ne}(A>1)$, the increase of the electrical resistance and the Hall coefficient in the absolute value in gold at temperatures below 6°K will be explained by the decrease of n, the concentration of conduction electron. Seeing that the electrical resistance is proportional to the product of the concentration and the mobility of current carrier, the decrease of conduction electron is further understood well by referring to the normal behaviour of the electron mobility as illustrated in Fig. 9. Here, the electron mobility μ is calculated by $\mu = \frac{1}{1.19} \cdot \frac{|A_H|}{\rho}$, by applying the values of the specific resistance $\rho\,(=\frac{1}{ne\mu})$ and the Hall coefficient A_H, and by assuming that the Hall coefficient of gold at low temperatures is expressed by $A_H = 1.19 \times \frac{1}{ne}$,

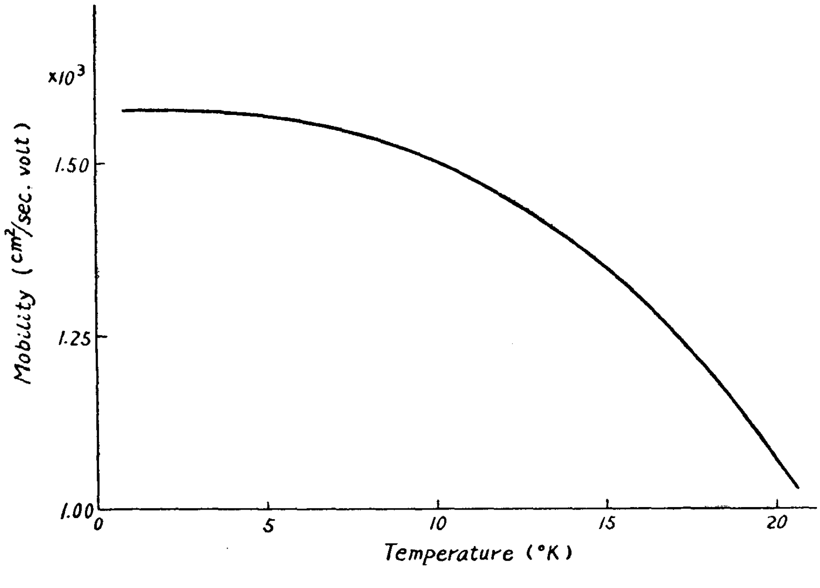

Fig. 9. Mobility of electrons in gold as a function of temperatures

in which an allowance is made for the difference of 19 per cent in the absolute value from the one at high temperatures.

It is well known that the resistance minimum has to do with the presence of a certain kind of impurities. In silver and copper as well as in gold this anomalous phenomenon has been observed(9)(10) under an appropriate condition of impurities in kind and quantity. On the other hand, though gold is the metal which is liable to show this anomaly, it is also observed(11) that the very pure gold specimens show the normal behaviour in the resistance-temperature curve. Consequently, the change in the concentration of conduction electron should be discussed in relation to the impurity which may be either chemical or physical. Inasmuch as this anomalous change cannot be easily understood from the usual simple band theory, it will be necessary to consider a new machanism in the electron conduction. For example, it may be, as Slater has suggested, the splitting of the Brillouin zone which gives the metal the property akin to a semiconductor or impurities form the trapping centres of conduction electrons.

It is frequently observed that the magneto-resistance effect of the noble metals, which are known to give evidence for the resistance minimum, also shows the anomalous negative effect(12)(13)(14) (the decrease of resistance due to the magnetic field), and it has been considered that this behaviour is due to the presence of the small quantity of transition elements. However, in our gold specimen which showed the resistance minimum, the anomalous magneto-resistance effect was not observed as illustrated in Fig. 3.

Summary

The appearance of the resistance minimum at very low temperatures in the specimens of gold and others has usually been considered to be due to the anomaly in the mobility of conduction electrons. This phenomenon, however, may also be caused by the change in the number of conduction electrons. Therefore, the measurement of the Hall effect was carried out in the temperature range in question. And it was found that the temperature change of the Hall effect was almost proportional to that of resistance below that temperature at which the said anomaly appears.

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(9) A. N. Gerritsen and J. O. Linde, Physica, **17** (1951), 573.
(10) W. B. Pearson, Phil. Mag., **46** (1955), 920.
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(12) W. F. Giauque, J. W. Stout and C. W. Clark, Phys. Rev., **51** (1937), 1108.
(13) N. M. Nakhimovich, J. Phys. U. S. S. R., **5** (1941), 141.
(14) A. N. Gerritsen, Physica, **19** (1953), 61.