THERMAL CONDUCTIVITY AT HIGH TEMPERATURES.

By M. F. Angell.

Introduction.

WITH the growth of the electron theory and its application to the flow of heat in metals the measurement of thermal conductivity becomes of greater interest. The determinations, up to the present time, have been confined within narrow limits of temperature and the object of this investigation was to determine the thermal conductivity of a few metals over a wide range. The first measurements at high temperatures were made by Forbes,[1] using the well-known "Forbes bar method," on wrought iron at temperatures of 0°, 100°, 200° and 275° C.; giving a decrease in thermal conductivity from .207 at 0° C. to .124 at 275° C. Tait[2] and Mitchell[3] used the same method, but found an increase in conductivity with temperature, which is undoubtedly in error, as shown by the later work of Jäger and Diesselhorst.[4] Lorenz[5] heated a rod at one end by contact with a large slab and determined the temperature gradient by means of thermocouples inserted in holes along the rod; the source of heat was then removed and the temperature gradient determined when the rod was cooling. Between 0° C. and 100° C. he found an increase in conductivity with temperature for aluminum, brass, copper and german silver; a decrease for antimony, bismuth, cadmium, iron, lead and zinc; and a constant for magnesium. Baillie,[6] with the Forbes method, determined the thermal conductivity of nickel between 0° C. and 100° C. to be .132 and found this value to be changed only in the third decimal place at a temperature of 200° C. Jäger and Diesselhorst[4] used a method suggested by Kohlrausch,[7] which consisted in heating a rod with a constant electric current; the ends of the rods being in contact with large baths, a steady flow of heat was maintained from the center to the ends. The temperature was measured at three points along the rod by means of thermocouples inserted in holes. Determinations were made

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[1] J. D. Forbes, Athenäum, p. 1012, 1852.

[2] P. G. Tait, Trans. Roy. Soc. Edinb., p. 717, 1880; Phil. Mag. (5), 12, p. 147, 1881.

[3] A. C. Mitchell, Trans. Roy. Soc. Edinb., p. 435, 1887.

[4] W. Jäger u. H. Diesselhorst, Abh. d. Phys.-Techn. Reichsanstalt, 3, 269, 1900.

[5] L. Lorenz, Wied. Ann., 13, p. 422, 1881.

[6] T. C. Baillie, Trans. Roy. Soc. Edinb., 39, p. 361, 1897–98.

[7] F. Kohlrausch, Ztschr. f. Instruementk., 18, 139, 1898; Drude's Ann., 1, 145, 1900.

on a large number of materials at 18° C. and 100° C.; an increase in thermal conductivity with temperature was shown by aluminum, constantin, gold, manganin, palladium, platinum and tombac; and a decrease by bismuth, cadmium, iron, copper, lead, nickel, silver, steel and zinc.

A New Method for the Determination of Thermal Conductivity.

In this investigation a new method, suggested by Professor C. E. Mendenhall, was used for the determination of thermal conductivity of metals at high temperatures. If a long cylindrical rod is heated electrically the temperature over a short distance *l*, symmetrically situated with respect to the ends, is approximately uniform and this approximation may be made as close as we please by increasing the length of the rod. In this central section, *l*, Fig. 1, the energy flow is then radial, *i. e.*, from the center to the circumference, and the quantity passing through any concentric cylindrical surface, of radius r and length l, is given by $-2\pi rl\lambda dT/dr$; where λ is the thermal conductivity and dT/dr the temperature gradient at r. When a steady state is reached we have

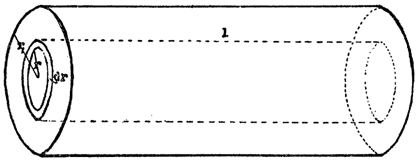

Fig. 1.

$$\pi r^2 lEI = -2\pi rl\lambda dT/dr;$$

integrating

$$\frac{EI}{2}\int_0^{r_1} rdr = -\lambda\int_{T_2}^{T_1} dT,$$

or

$$\lambda = \frac{EIr_1^2}{4(T_2 - T_1)}, \tag{1}$$

where r_1 is the radius of the rod, E the fall of potential along one centimeter, I the current density, which is assumed constant over the cross-section and T_2 and T_1 are the temperatures at the center and circumference of the rod respectively. If the measurement of the fall of potential along l is difficult, as with alternating current, a separate determination of resistance at different temperatures may be made and IR substituted for E in the equation, R being the specific resistance.

The above discussion is on the assumption that the variation of specific resistance, due to the variation of temperature from inside to outside of the rod, may be neglected. As a closer approximation we may assume the radial variation of resistance to be proportional to r^2, as would follow to a first approximation from equation (1); substituting E/R for I we may write

$$R = R_2 - \alpha r^2,$$

where R_2 is the resistance at the center of the rod. Then

$$\int_0^r \frac{E^2}{R_2 - \alpha r^2} 2\pi r l dr = -2\pi r l \lambda dT/dr .$$

and

$$\frac{E^2}{2\alpha} \log \frac{R_2 - \alpha r^2}{R_2} = r\lambda dT/dr .$$

Dividing the equation by $E^2 r/2\alpha$ and integrating we obtain

$$\int_0^{r_1} \log\left(1 - \frac{\alpha}{R_2} r^2\right)\frac{dr}{r} = \int_{T_1}^{T_2} \frac{2\alpha}{E^2} \lambda dT$$

or

$$\lambda = \frac{E^2 r_1^2}{R_2 4(T_2 - T_1)}\left[1 - \frac{\alpha r_1^2}{4R_2} + \frac{\alpha^2 r_1^4}{9R_2^2}\cdots\right]. \qquad (2)$$

In this case the term outside the bracket is the value of λ obtained above. By substituting the values of α and R_2 as approximately known for any metal, the terms containing these quantities are seen to be negligible for rods less than 2 cm. in diameter.

For a hollow cylinder, where r_2 and r_1 are the inside and outside radii respectively, we have

$$\pi(r^2 - r_2^2) l E I = -2\pi r l \lambda dT/dr.$$

Integrating

$$-\lambda \int_{T_2}^{T_1} dT = \frac{EI}{2} \int_{r_2}^{r_1} (r^2 - r_2^2)\frac{dr}{r}$$

and

$$\lambda = \frac{EI}{2(T_2 - T_1)}\left[\frac{r_1^2 - r_2^2}{2} - r_2^2 \log\frac{r_1}{r_2}\right]. \qquad (3)$$

This is the formula used in the present investigation. As the energy is measured in watts, λ must be multiplied by .239 to reduce it to cal./cm. sec. degree.

When alternating current is used, these formulæ will not apply to magnetic substances as the "skin effect" must be considered in expressing the distribution of current inside the rod. The problem of determining thermal conductivity under these conditions was found too complicated for the present investigation and determinations on these substances were limited to temperatures such that the magnetic properties, as indicated by the presence of an appreciable skin effect, had disappeared.

EXPERIMENTAL DETAILS.

The determination of thermal conductivity requires the measurement of three quantities: the dimensions of the rod, energy flow and temperature difference between the inside and outside of the rod.

1. *Dimensions of the Rod.*—Preliminary experiments showed that on heating a hollow rod six inches long the temperature was quite uniform over a length of one centimeter at the center. In order to decrease the heat flow to the ends of the rod the central hole was made larger at the ends and to within 1½ centimeters of the center; this increased the heat generated each side of the center by increasing the resistance and made the temperature uniform over a greater length. Determinations of temperature inside the rod at about 1000° C. showed a variation of approximately two per cent. over a length of two centimeters and less than one tenth of one per cent. over one centimeter. The measurement of temperature gradient did not require a uniform temperature over so great a length, but in the resistance determinations a uniform temperature was assumed over a length of one centimeter. The inside hole, .168 cm. in diameter, was drilled from each end and carefully reamed. In order to correct for any eccentricity, which might be present, temperature measurements were made at the ends of several radii in the central section. The outside diameter was approximately 1.2 cm., but varied slightly in the different determinations, due to polishing the surface. In order to eliminate oxidation the rod was enclosed symmetrically in a large, water-cooled cylinder from which the air could be exhausted.

2. *Energy Flow Measurements.*—As sufficient direct current was not available a welding transformer was used, capable of furnishing 1700 amperes at 2½ volts. The current was measured by means of a Weston ammeter accurate within one per cent. and a current transformer designed by Professor E. Bennett, of the engineering department of the university, accurate within one per cent. The measurement of low voltages with alternating current being unreliable a separate determination of the resistance at different temperatures was made, using direct current, and the resistance-temperature curve was plotted. For the resistance measurements the same rods were used as for thermal conductivity, with the outer diameter greatly reduced. The temperature for the resistance measurements was determined by a thermocouple in-

side the rod midway between the ends. The ammeter and voltmeter were calibrated in terms of laboratory standards. In order to eliminate the peltier effect at the point of contact of the potential terminals with the hot rod the terminals were made of fine wires of the same material as the rod; these being held parallel to each other and against the rod by brass frames. The distance between the terminals, approximately one centimeter, was measured by means of a micrometer gauge.

3. *Temperature Measurements.*—The temperatures were determined by two thermocouples, of No. 40 platinum and platinum-rhodium wire, standardized by using the boiling point of sulphur, the freezing point of antimony and the melting points of silver and gold. The electromotive forces of the thermocouples were measured on a potentiometer made for this work, the slide wire being one meter in length with six additional resistances each equal to that of the wire. One millimeter indicated 2 microvolts or about .2 degree and estimates were made to one tenth of this quantity. For small temperature differences the galvanometer deflections were also calibrated and could be estimated to one fifth of a microvolt or approximately .02 degree centigrade.

Measurement of Temperature Inside the Rod.—For the measurement of temperature inside the rod, the fine wires leading to the thermocouple were enclosed in small quartz tubes running longitudinally through the inside of the rod, with the junction itself midway between the ends. Breaking the quartz tube at the center appeared to make no difference in the temperature determinations.

Measurement of the Temperature of the Surface.—The greatest difficulty was to insure that the outer couple indicated the actual temperature of the surface; for this reason fine wires were used and, drawn diagonally

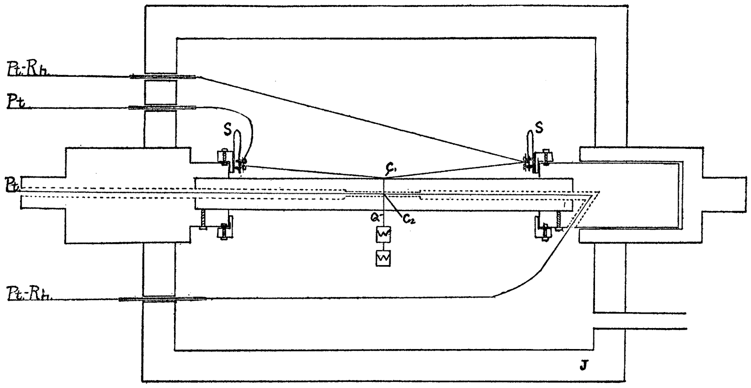

Fig. 2.

SS, springs; *CC*, thermocouples; *WW*, weights; *Q*, quartz fiber; *J*, water-jacket. Springs were rotated from position shown across the rod by two springs, were held close to the surface along its entire length (Fig. 2). The thermal junction was rolled in steel rolls to a thickness of .01 mm. and forced into contact with the highly polished surface by the small springs and by small weights hung over the rod by means of quartz fibers. A uniformly radiating surface in the neighborhood of the couple was found to be most important, so that either the rod must be platinum plated or the thermal junction covered with a layer of the same material as the rod. On account of the difficulty of platinum plating the second method was adopted; a piece of the same material as the rod was rolled in the form of a ribbon to a thickness of .01 mm. A short piece of this was then placed over the couple and held in contact with the rod by the quartz fibers and small weights, producing a uniform surface over the entire rod. Under these conditions the difference in temperature between the inside and outside of the rod was determined differentially at different temperatures and the curve plotted (Fig. 3, *A*); this curve could be repeated after rotating the outer couple around the rod, shifting slightly the inner couple or replacing the original couples by new ones from the same wire. The formation of a

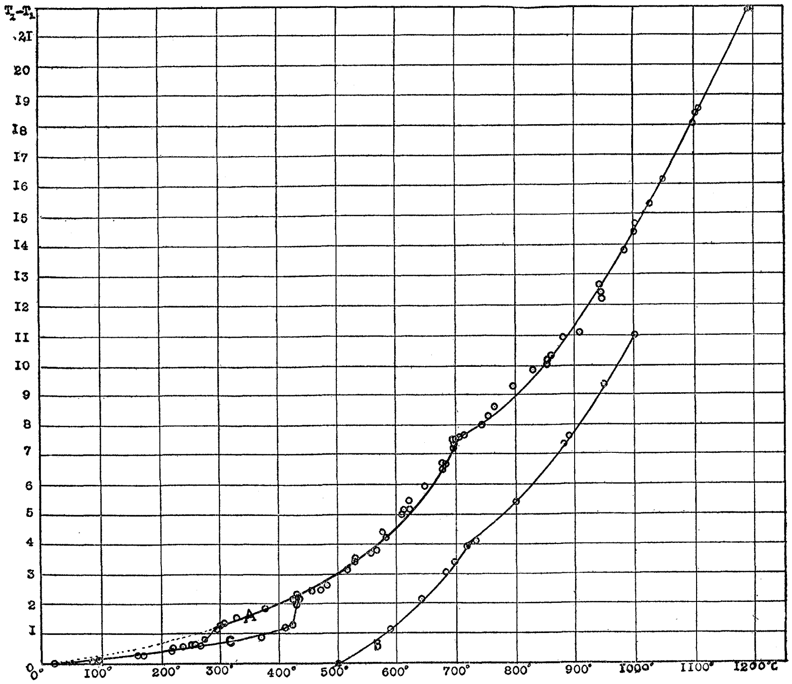

Fig. 3.

Variation of temperature-difference with temperature.

thin layer of oxide produced but small effect. The curve *B*, Fig. 3, of no value in the determination of thermal conductivity, was obtained when the nickel foil covering the couple was removed and the couple exposed. The platinum, being a poorer radiator than the nickel, acted as a shield at this point and the temperature was raised; below 500° C. the outer couple indicated a higher temperature than the inner. Poor contact between the outer ribbon and the rod was quickly indicated by the unsteady readings of the couple. In the work with nickel the dissociation temperature of nickel oxide was reached, due to the low pressure, at about 900° and the protecting ribbon was so completely welded to the rod that the two could not be distinguished. With the couple welded to the rod and imbedded under the surface to a depth of .01 mm. the quartz fibers were removed and the thermal conductivity curve determined with the rod rotated 120 degrees and 240 degrees from its original position. The agreement of curves indicated a symmetrical radiation from the surface of the rod in all directions. The rod was also heated when exposed to the air and a thick layer of oxide formed; under these conditions the temperature gradient was increased as the radiation from the surface was greater than before and temperature differences, for given inside temperatures, were greater than indicated by the curve (Fig. 3, *A*). There was, however, a corresponding increase in the energy required to maintain this temperature and the computed thermal conductivity curve coincided with that found when a bright surface was used. As criteria for deciding that the true value of thermal conductivity is obtained by this method we have, with a bright surface, the repetition of the temperature difference curve, on rotating the rod, rotating the thermocouple around the rod, displacing slightly the inner couple or on replacing the original couples by new ones from the same wire and the repetition of the thermal conductivity curve with a different radiating surface and therefore a different temperature gradient. Considering all the errors in measuring the dimensions of the rod, temperature, resistance and current, even when alternating current is used the error should be less than two per cent. above 300° C., while with direct current the error should not be over one per cent.

RESULTS. NICKEL.

Two rods of nickel from the same piece were used. This was obtained from H. Boker, New York, as the best available and no analysis has yet been made; probably however, it contains from two to three per cent of cobalt. The first rod was not heated above 700° C., and, within experimental error, gave the same temperature difference between the inside and outside, at a given inside temperature, for different positions of the couple around the rod and with the first couples replaced by new ones of the same wire. The second rod was of the same dimensions as the first and the curve showing temperature difference between the inside and outside of the rod for different temperatures coincided with that for the first rod and is shown in Fig. 3, *A*. The sharp rise in the curve at about 300° C. indicates the temperature at which nickel loses its magnetic properties; a change in the slope of the curve is also seen at about 700° C. From the electrical resistance at different temperatures, as shown in Fig. 4, the thermal conductivity at different temperatures was computed and the curve drawn (Fig. 5). If this curve is prolonged to zero it will pass very nearly through the values of thermal conductivity given by Jäger and Diesselhorst, viz., .1420 at 18° C. and .1374 at 100° C. A prolongation of the curve may also be obtained by extending the temperature difference curve, shown by the dotted line in Fig. 3, *A*, as if undisturbed by skin effect and computing the thermal conductivity, at any temperature, from the current required to produce this temperature and the temperature difference determined from the curve. The second method is less reliable, however, as it does not allow for the fact that a greater amount of energy is required to produce a given inside temperature than if there were no skin effect. If the values of thermal conductivity found by Jäger and Diesselhorst at 18° C. and 100° C. are

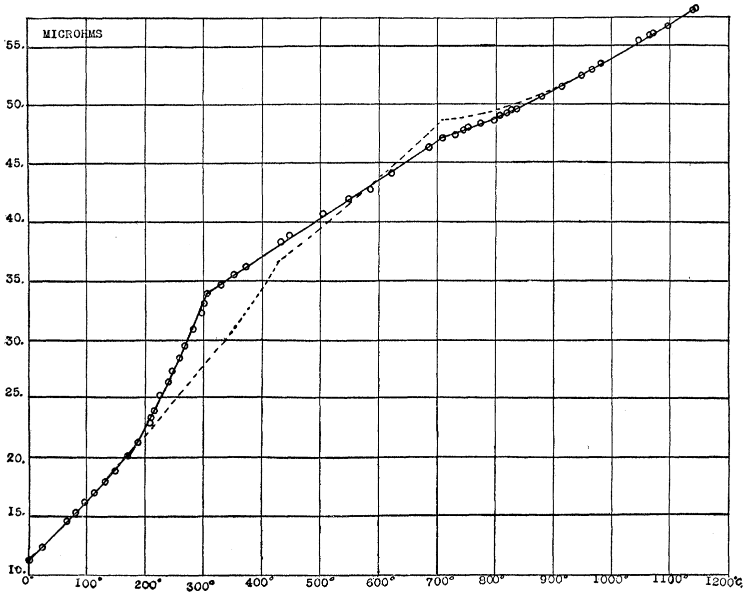

Fig. 4.

Resistance of nickel between 0° and 1200° C. The dotted line shows the resistance after sudden cooling; the full line, the resistance on first heating.

assumed for this specimen there is no change in the slope of the thermal conductivity curve at the temperature where nickel loses its magnetic properties, where, however, the change in the electrical conductivity is very marked. The thermal conductivity decreases more rapidly as the temperature increases up to 700° C., where its value is .069. At this point there is a most decided change in slope and the thermal conductivity decreases very slowly to 1225° C., with a value of .058 at this temperature. From the abrupt change in the slope of the curve one would conclude that an allotropic form of nickel is formed at about 700° C.

The temperature difference curve (Fig. 3, *A*) was repeated many times, and it was found that the readings did not check with the original curve between 300° C. and 420° C. after the rod had been suddenly cooled from high temperatures; the form of the new curve is shown by *C*, Fig. 3. Due to the sudden cooling the magnetic transformation point, as indicated by the sudden rise in the temperature difference curve, was changed from 310° C. to about 420° C. After annealing at about 900° C. and cooling very clowly to room temperature the transformation point was found at about 290° C., lower than at first. With this treatment it was possible to shift the transformation point at will between these limiting temperatures, 290° C. and 420° C.

As there is a decided change of slope in the electrical resistance curve at the magnetic transformation point the change in this curve was investigated when the transformation point was shifted; it had already been noticed that a smooth resistance curve could be passed through the points determined on the first heating of the rod, while those determined on cooling were not on this curve. The form of the curve as first determined and after sudden cooling is shown in Fig. 4, the transformation point being at 310° C. in the first case and approximately 420° C. in the second. With the transformation point between these limits the temperature-resistance curves were determined and when the transformation point was between 350° C. and 400° C., as assumed by Harrison[1] and Marvin,[2] the resistance between 0° C. and 350° C. could be approximately represented by a parabola. For a lower transformation point the form of the curve was shown by Knott[3] and is nearly a straight line up to 200° C. where the slope increases and continues nearly constant to the transformation point. Investigations of the magnetic properties of nickel by different observers have shown the transformation point to vary between 270° C. and 400° C.;[4] the lower values were commonly

[1] E. P. Harrison, Phil. Mag., June, 1904.

[2] C. F. Marvin, Phys. Rev., 30, p. 522, 1910.

[3] C. G. Knott, Trans. Roy. Soc. Edinb., p. 33, 1888.

[4] Honda and Shimizu, Phil. Mag., Oct., 1903.

supposed to be due to impurities, but from this work appear to depend more upon the treatment of the specimen. The probable explanation of the fact that different observers have not obtained more nearly the same magnetic transformation point is the lack of annealing at a sufficiently high temperature.

It is customary to associate a change in the properties of a substance with a change in molecular structure and metallurgists have found an alpha, beta, gamma and even a delta state for iron and an alpha and beta state for nickel, but I believe this is the first indication of a third allotropic form, "gamma," for nickel, which appears at about 700° C. The change in the thermal conductivity curve at this temperature is very decided, as is shown in Fig. 5; the change in the resistance curve is not marked when the transformation point is in the neighborhood of 300° C., but with the transformation point at 420° C. a decided change of slope is observed. In the resistance curve given by Sommerville,[1] this change of slope is not apparent, but in a later paper[2] where the slope of the curve is given the change is plainly shown. Apparently there is a molecular rearrangement at about 700° C., producing an allotropic form of nickel, which is carried down by quenching and causes a change in the resistance and magnetic properties.

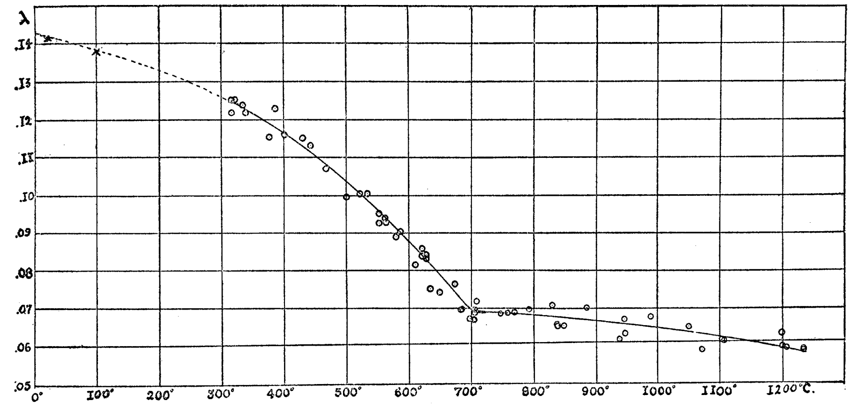

Fig. 5.

Thermal conductivity of nickel, 300°–1200° C. ×× , values of Jäger and Diesselhorst.

In order to compare the elasticity under different conditions a test was made with a Shore scleroscope, by measuring the rebound of a small hammer dropped upon the specimen; using the same rod as for the electrical and thermal conductivity experiments, the rebound was found to be much less after quenching, in the ratio of 7.2 to 14.

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[1] A. A. Sommerville, Phys. Rev., 30, p. 532, 1910.

[2] A. A. Sommerville, Phys. Rev., 31, p. 261, 1910.

ALUMINUM.

A single aluminum rod, of the best commerical grade, 99 per cent. pure, was tested. The determination of thermal conductivity, shown in Fig. 6, was less satisfactory than with nickel, on account of the low electrical resistance and high thermal conductivity, which increases with temperature; both of these properties tending to decrease the temperature difference between the inside and outside of the rod. The determinations near 100° C. agree well, however, with the value .492, which was found by Jäger and Diesselhorst at this temperature and their values were used to prolong the curve to zero. Their values may be assumed for this specimen as the purity of the aluminum was about the same in both cases. The thermal conductivity of aluminum increases more rapidly at high temperatures than between 18° C. and 100° C., increasing from .49 at 100° C. to 1.0 at about 600° C.

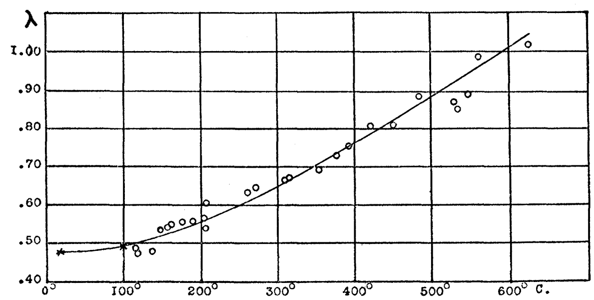

Fig. 6.

Thermal conductivity of aluminum. × ×, values of Jäger and Diesselhorst.

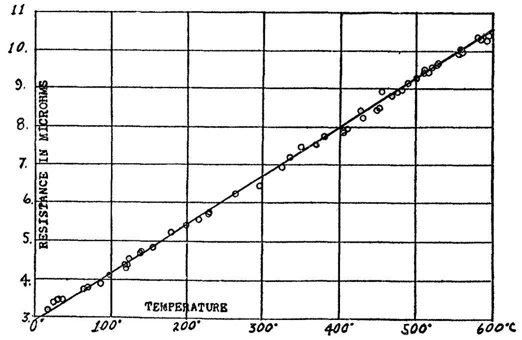

Fig. 7.

Resistance of aluminum.

In order to insure good contact with aluminum, where the protecting strip could not be welded to the rod, a small weight with a very sharp point was dropped repeatedly upon this outer strip and very fine holes made into the rod, then with a small hammer the strip was pounded down tight and smooth over the surface. By this method very many small portions of the outer strip were forced into the holes in the rod and the strip held in close contact.

The electrical resistance curve (Fig. 7) coincides very closely with that given by Sommerville[1] for a good grade of commercial aluminum.

Summary.

1. A new method of determining thermal conductivity has been tried and shown practicable with metals at high temperatures.

2. The thermal conductivity of nickel, between 300° C. and 1200° C. and of aluminum between 100° C. and 600° C. has been determined.

3. There is no constant ratio between electrical and thermal conductivities for these metals at high temperatures. At high temperatures the thermal conductivity of aluminum increases, and of nickel up to 700° C. decreases, more rapidly than from 0° C. to 100° C.; above 700° C. the thermal conductivity of nickel decreases very slowly up to 1225° C.

4. A third allotropic state for nickel has been found at about 700° C., with a change in the form of the electrical and thermal conductivity curves at this point.

5. The magnetic critical temperature of nickel has been shown to be shifted through a range of one hundred and thirty degrees by heat treatment; annealing from high temperatures giving a low value and sudden cooling producing values as high as 420° C.

6. The electrical resistance of nickel between 0° C. and 1200° C. and of aluminum between 0° C. and 600° C. has been found and, for nickel, the change in the form of the curve which accompanies a change in the magnetic critical temperature due to heat treatment has been determined. It was found that the temperature-resistance curve could be approximated by a parabola only when the critical temperature was in the neighborhood of 370° C.

7. The elasticity of nickel was greatly reduced by quenching, but could be increased to its original value by annealing at high temperatures.

In conclusion I wish to express my most sincere thanks to Professor Snow for placing the necessary apparatus at my disposal and to Professors Mendenhall and Mason for their kindly interest and helpful suggestions throughout this investigation.

Physical Laboratory,
University of Wisconsin,
July, 1911.

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[1] A. A. Sommerville, Phys. Rev., 31, p. 261, 1910.